interest to note that this synergistic action was well marked when tested on the carotene-light system.

The work described in this paper was carried out in the main as part of the program of the Food Investigation Board of the Department of Scientific and Industrial Research (Great Britain) and is published by permission of the latter. The work on antioxidants in milk powder was carried out in collaboration between the Food Investigation staff of the Department of Scientific and Industrial Research and the staff of the Hannah Dairy Research Institute, Ayr, Scotland. The full results have been published in more detail in the following papers:

Some Factors Affecting the Control of Oxidative Rancidity. T. P. Hilditch. Chem. & Ind., 1944, p. 67.

A Method for Studying the Effect of Antioxidants on the Oxidation of Aqueous Suspensions of Unsaturated Fatty Acids. A. Banks. J. Soc. chem. Ind., Lond., 1944, *63*, 8.

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Oil and Meal Yields in Peanut Milling

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This paper describes a continuous processing test which was made in a commercial oil mill to determine the nature and amount of the so-called invisible oil loss which has been reported to occur in milling peanuts. Under the conditions of processing of this test run no invisible oil loss was observed.

Introduction

BEFORE the establishment of national programs for crop adjustment and soil conservation most of the domestic peanut crop was used in confectionery and food products. Under these programs there has been a marked increase in the acreage planted to peanuts throughout the Cotton Belt. These programs have, except in the later war years, resulted in the production of peanuts in excess of those which the confectionery and food industries could consume and these surplus peanuts have been diverted to crushers for the production of oil and meal. Under the pressure of wartime economy and notwithstanding extensive increases in the acreage planted in peanuts there has been a strong demand both for edible grade and oil stock peanuts.

In the past the market standards of quality for peanuts have been determined by qualities which adapt them to confectionery and food uses. Under the present wartime system of marketing (1) all peanuts are handled through the Commodity Credit Corporation and those allocated to oil mills are sold to the crushers on the basis of total kernel content, with adjustments in price made on the basis of chemical analysis (2).

Methods for analysis of whole peanuts and shelled stock were devised in 1939-40 by the Peanut Committee of the American Oil Chemists' Society (3) for the evaluation of peanuts in terms of prospective yields of oil and meal. These methods were adopted as tentative by the American Oil Chemists' Society (4) and were incorporated in the rules of the National Cottonseed Products Association (5). In the formula which is used for the calculation of crushing yields from analytical data on whole peanuts, the anticipated oil yield, calculated from the chemical analysis and an assumed oil mill efficiency, is multiplied by a factor of 97% to obtain the available yield of oil. This factor of 97% is called the invisible loss factor. Stated in another way, this means that 3% of the oil which would appear to be obtainable from a given lot of peanuts, based on the analysis of the peanuts, cannot be accounted for in the yield of oil or in the amount of extractable oil left in the meal and hulls.

A difference between the oil yield obtained on milling peanuts and that predicted on the basis of analysis has also been reported by Sethne (6) who discusses in considerable detail the various factors involved. He presented data on the analysis and oil yield of peanuts covering five years of operation on shelled stock in a mill using hydraulic presses of European construction. When the determination of the oil content of the peanuts and the cake were made using ethyl ether as a solvent for extraction, the oil yield difference over a five-year period averaged 0.70 ± 0.15 in percentage of weight of shelled peanuts milled. However, the use of petroleum ether as a solvent for the oil determinations reduced the oil yield difference to about half this value. When placed on a basis comparable with the A.O.C.S. yield calculation, this would be equivalent to an invisible oil loss of about 1% or an invisible loss factor of 99%.

This so-called invisible oil loss is of considerable importance in processing peanuts for oil and meal, and several suggestions have been made by various agencies and organizations that the factors responsible for this loss should be investigated as a service to the oilseed processing industry and to the producers or growers of peanuts. Since problems of this type form part of one of the projects of the Southern Regional Research Laboratory, such an investigation was undertaken at the first opportunity. The work involved was carried out in cooperation with a very progressive oil miller operating an eight-press cotton oil mill and peanut shelling plant. This mill employed the usual cleaning equipment, such as boll reel and shakers for separating the hay and sticks,

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the dirt and sand, and the stones. The cleaned nuts were fed to two bar hullers and the hulls were separated on shakers and by aspiration with air. The separated meats were rolled with 5-high rolls. The press room equipment consisted of a 5-high stack cooker, a cake former, 8 hydraulic presses, and a cake trimmer. The cake was fed to a cake breaker and then conveyed to the meal house for grinding.

Since the mill normally ground peanut hulls for blending with their ground cake to adjust the nitrogen content, it was possible to obtain very representative samples of all of the products entering and leaving the mill. As will become evident from the data and discussion which follows, the oil balance obtained with the existing practice in this mill failed to disclose an invisible oil loss hence no opportunity was afforded for investigating the factors thought to be responsible for the so-called invisible oil loss. However, the analytical data for the peanut stock, products, and by-products of milling, as well as the materials balance and oil and meal yields, should be of interest to those concerned with processing peanuts for oil and meal.

Methods of Sampling and Analysis

A continuous run was made on 330 tons of farmers' stock peanuts which were mainly of the Spanish type from the Southeastern area. The mill was thoroughly cleaned up prior to the start of the run. Peanuts from the seedhouse were loaded on a truck of six to seven tons capacity and were weighed on the truck before being fed to the mill. Weights were obtained on all of the materials produced from these peanuts. The hay and sticks, the dirt and sand, and the stones which were removed in the cleaning operation were sacked and weighed before being discarded.

All of the oil was weighed in tank cars except that which was not pumped from the storage tank at the end of the test. This residual oil was determined by measuring its height in the tank at the beginning and again at the end of the run after all possible oil had been pumped from the draining troughs and settling tank. The oil storage tank was calibrated in terms of pounds of oil per inch.

The hull bran was weighed in a box car after transfer from the storage bin which was adjusted to the same level at the end of the run as it had been at the start. The weight of meal was calculated from the number of 100-pound bags produced.

Each truckload of peanuts was sampled by collecting three samples of two to three pounds each from the discharge stream of the loader as the peanuts were loaded on the truck. The hull bran and the meal were sampled by taking a handful from every fifth sack. A sample was taken from each sack of hay and sticks and similar samples were taken of the dirt and sand which was collected.

These samples were accumulated in 50-pound lard cans which were kept covered in order to minimize possible changes in moisture content. The cans containing the accumulated samples were sealed and shipped to the laboratory where they were composited and quartered to appropriate size for analysis. The hay and sticks were ground in a hammer mill before being quartered and sampled. Weights which were taken before and after compositing and quartering showed that no significant changes in the moisture content had taken place during these operations.

When the whole peanuts were ground preparatory to analysis, an appreciable loss of weight was found to occur during the grinding operation. This loss in weight, which is attributed to loss of moisture, was found to be 1.52% and was included in the moisture value used in computing the materials balance. However, in calculating the oil and meal yields, the moisture value as determined by American Oil Chemists' society's tentative method (4) was used.

Moisture, oil, and ammonia were determined according to the American Oil Chemists' Society's tentative methods for the analysis of whole peanuts. A.O.C.S. methods were also used for the analysis of the meals and hulls. The percentage of ash was determined after ashing the sample for three hours in a muffle furnace at 650° C. The volumetric method of Gerritz (7) was used for the determination of potassium. Phosphorus, calcium, and magnesium were determined according to the methods recommended by the Association of Official Agricultural Chemists (8). All of the analyses reported are averages of two or more closely agreeing determinations.

Results

Analysis of peanuts and products of milling: The analysis of the peanuts fed to the mill is shown in Table 1. The analytical data for oil, ammonia, ash, and inorganic constituents which were determined on a sample of 0.88% moisture content have been calculated to an original moisture basis and to a moisture-free basis as shown in Table 1.

TABLE 1

Analysis of Peanuts to Mill. Composite of Samples From Truck Loader

	As Determined	Original Moisture Basis	Moisture-Free Basis
	per cent	*per cent*	*per cent*
Foreign matter	1.44	.....	.....
Original moisture, A.O.C.S. method	8.21	8.21	.....
Moisture, lost in grinding	1.52	.....	.....
Total moisture	9.60[1]	.....	.....
Yield of kernels on shelling	73.00	.....	.....
Second moisture	0.87, 0.89	.....	.....
Oil	38.04, 37.93	35.22	38.33
Ammonia	4.54, 4.63	4.24	4.62
Ash	4.72, 4.78	4.40	4.79
Potassium	0.60, 0.58	0.55	0.60
Phosphorus	0.29, 0.28	0.26	0.29
Calcium	0.052, 0.041	0.043	0.047
Magnesium	0.18, 0.18	0.17	0.18

[1] 1.52 + 8.21 (100.00—1.52) = 9.60%.

The analysis of the three lots of peanut meal, the hull bran, the hay and sticks, and the dirt and sand are shown in Table 2.

TABLE 2

Analysis of Products Obtained in Milling Peanuts

	Peanut Meal			Hull Bran	Hay and Sticks	Dirt and Sand
	Lot No. 1	Lot No. 2	Lot No. 3			
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Moisture	6.90	6.63	6.24	10.78	10.61	5.91
Ammonia	8.80	8.80	8.71	1.02	1.97	1.42
Oil	5.99	5.89	6.34	1.07	5.55	4.54
Ash	4.80	4.70	4.75	1.88	.....	.....
Potassium	1.12	1.11	1.10	0.45	.....	.....
Phosphorus	0.54	0.51	0.52	0.045	.....	.....
Calcium	0.092	0.099	0.102	0.106	.....	.....
Magnesium	0.28	0.27	0.29	0.09	.....	.....

Materials balance: The materials balance was made on the basis of the weights of all products entering and leaving the mill. These weights were also calculated to a moisture-free basis. The over-all materials balance is shown in Table 3.

TABLE 3

Over-All Materials Balance on Peanut Milling Test

	Weight* of Materials		Moisture	Weight (dry basis)	
	pounds	*pounds /ton*	*per cent*	*pounds*	*pounds /ton*
Peanuts to mill...	660,620	2,000.0	9.60**	597,200	2,000.0
Hay, sticks and trash.....	4,393	13.3	10.61	3,927	13.2
Dirt and sand.....	6,698	20.3	5.91	6,299	21.1
Stones.....	6,199	18.8	.....	6,199	20.8
Oil.....	208,084	630.0	<0.1	208,084	697.9
Hull bran.....	96,494	292.1	10.78	86,092	288.7
Meal, lot No. 1....	90,700	895.2	6.90	84,442	926.8
Meal, lot No. 2....	75,200		6.63	70,214	
Meal, lot No. 3....	129,800		6.24	121,700	
Total output.....	617,568	1,869.7		586,957	1,968.5
Materials loss.....	43,052	130.3		10,243	34.3
Material loss, per cent.....	6.97	6.97		1.72	1.72

* Corrected for samples taken from run.

** Includes loss of moisture of 8.21 per cent by the tentative American Oil Chemists' Society method and loss of weight on grinding of 1.52 per cent.

In calculating the weight of peanuts to a moisture-free basis, the percentage of moisture was determined by the American Oil Chemists' Society's tentative moisture method to which was added the percentage loss of weight of the sample during grinding. The food chopper used for grinding was carefully cleaned after the grinding operation to avoid any loss of material. Using the total moisture content determined in this manner, the materials loss on a moisture-free basis amounted to 1.72%. Some of this loss can be attributed to the loss of dust or material too fine to be collected. However, it is more likely to be related to the original moisture determination of the peanuts. It has been found that drying of the ground peanuts for two hours in a circulatory oven at 130° C. causes an additional loss in weight of approximately 0.8% over the one-hour drying period used in determining original moisture by the A.O.C.S. method. The various factors involved in moisture determinations of peanuts have been investigated and discussed by Hoffpauir (9).

Comparison of actual and predicted yields of oil and meal: A comparison of the actual yield of oil and meal obtained in this test run and predicted yield of oil and meal calculated on the basis of their analysis by the A.O.C.S. tentative methods is shown in Table 4. This yield calculation assumes certain milling losses and milling efficiency. It is obvious that these calculated yields are much less than the yields actually produced in the test. The following factors contribute to this difference: (a) The materials loss in the test, that is hay, sticks and trash, dirt and sand, and stones amounted to 2.62% whereas the working loss allowed in the formula is 5%. (b) The oil lost in the hulls amounted to 3.12 pounds per ton compared to 6 pounds per ton allowed in the calculation. (c) The yield calculation is based on an oil/ammonia ratio of 0.80 (Standard) whereas in the test run an oil/ammonia ratio of 0.70 was obtained.

Using the observed factors, that is a materials loss of 2.62%, 3.12 pounds of oil per ton lost in hulls, an oil/ammonia ratio of 0.70, and the available ammonia factor of 92% used in the mill efficiency formula, the predicted yields of oil and meal were recalculated and are also shown in Table 4. These data were calculated without using an invisible loss factor, and it is apparent that no invisible oil loss actually occurred during this test run since the actual and calculated oil yields are in excellent agreement. The fact that the meal yield was higher than the calculated value indicates that the available ammonia factor of 92% is slightly low for this particular test which may be due in part to more efficient separation of meats and hulls than is assumed in the formula.

TABLE 4

Comparison of Actual and Predicted Yields of Oil and Meal

	Yield obtained	Calculated yield (tentative rule)	Yield calculated on basis of analytical data from mill run without using invisible loss factor
	lbs./ton	*lbs./ton*	*lbs./ton*
Oil, crude.....	630	586	629
Meal, 45 per cent protein.....	895	846	867
Hull bran.....	292	.....	.....

Since no invisible oil loss was actually found during this test run, it was not possible to investigate the various factors responsible for this loss. However, it has been postulated that some change may occur during the cooking operation which would make the oil less extractable from the meal or cake than from the seed. In order to follow any change which might have taken place during the cooking of the rolled peanut meats, two batches of meats were followed through the cooker and sampled at each section and at the cake former. These samples were analyzed for oil, ammonia, and moisture. When calculated to a moisture-free basis, no significant change was observed in the amount of extractable oil at different stages of cooking. This observation is in accord with the fact that no invisible oil loss was found to occur under the conditions of this test run. It should be pointed out that the cooking was carried out under fairly mild conditions. Only four sections of the cooker were utilized and the total cooking time for each batch of rolled meats was about one hour. The average temperature registered by the recording thermometer on the cooker was about 235° F. Since this thermometer registered the temperature of the meats just before they were dropped from the cooker into the conveyor box, this was the maximum temperature to which the meats were subjected. During most of the cooking operation the meats were at a considerably lower temperature. Samples of oil produced from this run as taken from two tank cars after loading had a content of free fatty acids of 2.2 and 1.6% and refined with settlement losses of 5.2 and 5.4% with refined oil colors of 35 yellow, 2.2 and 2.0 red, respectively.

Summary and Conclusions

A continuous processing test was made in a commercial oil mill to determine the nature and amount of the so-called invisible oil loss which has been reported to occur in milling peanuts. In this test 330 tons of farmers' stock peanuts were crushed for oil and all products entering and leaving the mill were weighed, sampled, and analyzed. A materials balance was obtained which on a moisture-free basis accounted for all but 1.72% of the weight of peanuts entering the mill. This materials loss is believed to be due in part to the formation of dust and material too fine to be collected and in part to the moisture

content of the peanuts being somewhat higher than the moisture determined by analysis.

The yields of oil and meal which were obtained have been compared with the yields predicted on the basis of chemical analysis. Under the conditions of processing of this test run no so-called *invisible oil loss* was observed.

Acknowledgment

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Comparison of Methods for the Determination of Glycerol by Acetylation

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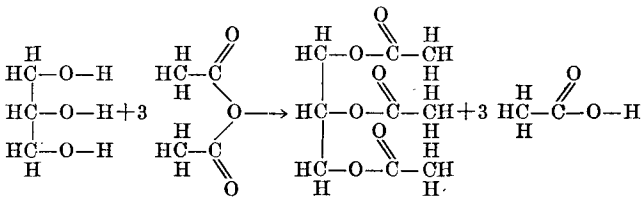
THE acetin method (3) is the accepted procedure for the determination of glycerol by acetylation although results by this method are usually considerably lower than the true value (2). In the past numerous attempts have been made to increase the accuracy of this method, but none has led to any fundamental improvement so the method remains as it was originally written.

The method to be presented in this paper was not the result of an investigation for the improvement of the acetin method but the by-product of a study of procedures for measuring the hydroxyl content of organic compounds. In the course of this investigation we found that the method of West, Hoagland, and Curtis (4) for the determination of hydroxyl groups was quantitative for glycerol. This acetylation procedure proved to be more accurate, more rapid and simpler than the conventional acetin method.

Acetic anhydride reacts with glycerol as indicated in the following equation:



One mol. of glycerol reacts with 3 mols. of acetic acid, thus the glycerol in a sample can be calculated from the amount of acetic acid combined with the glycerol. In the following procedure the acetic acid combined with the glycerol is calculated from the difference between the amount of standardized alcoholic potassium hydroxide required to titrate the acetylating reagent before and after reaction with the sample.

Experimental

The preliminary tests were made with the acetic anhydride-pyridine reagent (1 vol. acetic anhydride and 7 vol. pyridine) used by West, Hoagland and Curtis (5), but in later experiments, and in the method finally adopted the concentration of acetic anhydride was increased by changing the ratio to 1 to 6. This provided an additional excess of acetic anhydride and permitted a greater variation in the size of sample without jeopardizing the accuracy of the method.

The conditions necessary for quantitative results were determined by analysis of a C. P. glycerin that contained 95.0% glycerol. The composition of the glycerin was established from specific gravity and refractive index measurements, analysis by the periodic acid (1) method and by subtracting the moisture determined by the Fischer Volumetric Method from 100.

The time required for complete reaction between the sample and acetylating reagent was established by analyzing samples after heating for varying periods on the steam bath. The results are given in Table I.

TABLE I

Relation Between Time Allowed for Reaction on the Steam Bath and the Analyses

Time allowed for reaction on the steam bath, minutes	Glycerol found by analysis, %
15	94.8
25	95.3
30	95.1, 94.9
60	95.0, 95.0
120	94.5, 95.5
240	95.0

The reaction between the sample and acetic anhydride proceeded to completion in a very short time, and no additional reactions occurred when the heating period was extended well beyond that required for quantitative results. Thirty to forty minutes was selected as the time the sample and reagent should be heated on the steam bath in order to insure complete reaction. Since the reaction proceeded so rapidly at steam bath temperatures some tests were made at room temperature. Under these conditions the reaction was not complete even after 24 hours for the analysis indicated only 94.1% glycerol. Quantitative results can be obtained at room temperature by increasing the reaction time to two to four days,