b) Of the above soap/solvent mixtures which are dispersible hot, there results, on cooling and aging for one week at room temperature, a two-phase system (consisting of swollen soap and solvent) in about 80% of the cases and a homogeneous system in about 20% of the cases.

c) In the case of the two-phase swollen-soap/solvent system a) the swollen soap appears to have a limited swelling ability, in that, beyond a critical soap concentration (a limiting swelling concentration), no further soap swelling occurs and b) the solubility of the soap in the solvent is generally very slight (on the order of less than 1%).

d) In the case of the homogeneous one-phase system there occurs a gradual increase in the consistency or body of the solvent as soap is added to it, with no intermediate stage where liquid separation takes place (at least up to the 60% maximum soap concentration employed in this study).

e) Magnesium ricinoleate is the most soluble of the six metallic soaps, eight solvents dissolving this soap up to a 40% soap concentration and beyond to give clear, thin, soap solutions. Calcium ricinoleate is the next most soluble soap.

f) Aluminum (tri) and magnesium ricinoleates tend to give clear soap/solvent mixtures whereas the other four soaps tend to give mostly translucent mixtures. Aluminum (tri) ricinoleate, with only few exceptions, swells to give clear, hard gel structures with limited swelling, whereas magnesium ricinoleate tends to give clear, thin to viscous, solutions.

g) Whereas the metallic stearates as a class, with the exception of aluminum tristearate, show a pattern of general inertness in solvents, the metallic ricinoleates show a wide pattern of solubility and swelling behavior, ranging from clear thin solutions to hard gels. In comparison with aluminum (tri) stearate, the metallic ricinoleates generally show either an equal or more extensive solubility or swelling action, and definitely a more varied behavior.

h) As anticipated, the metallic ricinoleates as a class exhibit marked solubility or swelling action in alcohols, ether-alcohols, and glycols as opposed to the marked insolubility and non-swelling of the metallic stearates, including aluminum (tri) stearate, in these hydroxy-type solvents.

i) One fact of practical significance is that a) fatty-oil type vehicles and b) hydroxy-containing liquids can generally be bodied to produce clear liquids of any viscosity by the proper use of a suitable metallic ricinoleate.

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[Received March 3, 1953]

# Determination of Moisture in Peanut Butter

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THE moisture content of peanut butter is relatively low (6) as a result of the roasting operation. It is important to know the moisture contents of roasted peanuts and of peanut butter in order to calculate a materials balance during the processing of peanut butter, or to determine the amount of shrinkage that occurs from loss of moisture. Moisture content is particularly important in the calculation of uniformity of incorporation of stabilizers in peanut butter, in consideration of the fact that peanut butter is often stabilized by the addition of as little as 0.8% of hydrogenated peanut oil, an amount smaller than the amount of moisture present in the peanut butter. It also is important to know the moisture content of stored peanut butter because of the undesirable effect of high moisture on product quality.

At the present time there is no official method for the quantitative determination of the moisture content of peanut butter. The Official and Tentative Methods of Analysis of the American Oil Chemists' Society describe two oven weight-loss techniques (1a, b) for the determination of moisture and volatile matter in peanut kernels. Original moisture and volatile matter on the sample as received is determined by the loss in weight on heating a 40-50-g. whole kernel sample for three hours at 130°C. (designated Ab 2-49). The second method (designated Ab 3-49) is used in the determination of oil and ammonia. It consists of heating a 40-50-g. whole kernel sample 20 minutes at 130°C., followed by slicing the complete sample and then heating a 5-g. portion for two hours at 130°C. The two methods are designed to lower both materials, the whole kernel sample and the sliced, partially dried sample, to the same state of dehydration. Inasmuch as peanut butter and roasted peanuts are partially dried, the second method was considered more appropriate for the determination of moisture and volatile matter in these materials.

During an investigation of the manufacture of peanut butter at the Southern Regional Research Laboratory, Morris, *et al.*,[3] found differences in moisture content of 0.2-0.6% as determined by the forced-draft oven method for "second" moisture between the blanched, roasted peanuts and peanut butter made from such peanuts. Since the product was heated little in passage through the grinder, it was considered doubtful that the lower moisture content of the peanut butter indicated a real loss of moisture but rather that the method used was inadequate for peanut butter.

Hoffpauir (4) has pointed out that the determination of moisture content of biological materials by loss-in-weight on heating is an entirely empirical procedure, governed by temperature of heating, time of exposure, surface area of the sample, pressure, and nature of the material. It is a matter of common experience that different moisture contents are obtained for the same material on use of different methods. Without doubt such results are produced by differences in methods which impose more or less drastic conditions and hence result in greater or less loss of volatile matter from the sample. Hoffpauir's results (4) indicate that a more drastic set of conditions produces a higher apparent moisture content.

The methods of Bidwell and Sterling (2), Dean and Stark (3), and various refinements of these methods for the determination of moisture by toluene distillation have been used frequently. The improved apparatus of Tryon (5) for use with this type of method appeared to offer advantages in the determination of moisture in peanut butter, particularly in consideration of its applicability to materials of low moisture

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[3] Unpublished data.

content. Hence the purpose of the present work was to ascertain whether Tryon's refinement of the toluene distillation procedure is satisfactory for the determination of moisture in peanut butter. Results obtained using Tryon's apparatus and A.O.C.S. Official Methods are compared in order to ascertain whether these methods lower peanuts and peanut butter to the same degree of dehydration.

## Materials

*Raw Peanuts.* The raw peanuts used in this investigation were shelled, white Spanish peanuts (33.4 g./100 kernels), Pearl variety of white skin peanuts (38.5 g./100 kernels), Runner peanuts (44.7 g./100 kernels), and Virginia peanuts (91.5 g./100 kernels). All of the materials were allowed to attain a moisture content at equilibrium with that of the air of the laboratory. The sample materials were then stored in hermetically-sealed containers, which were opened only to remove samples. The sliced sample material was prepared by passing the peanuts through a laboratory Henry Slicer.[4] The sliced material was immediately resealed in the moisture-tight jars.

*Peanut Butter.* Peanut butter samples used varied in color from very light to very dark.

## Methods of Analysis

*Raw Peanuts.* A.O.C.S. Official Method Ab 2-49 (1a) and the toluene distillation procedure as modified by Tryon (5) were used in the determinations on raw peanuts.

*Peanut Butter.* A.O.C.S. Official Method Ab 3-49 (for "second" moisture) (1b) and the toluene distillation procedure (5) were used in the determinations on peanut butter. Also four samples of peanut butter were analyzed for moisture by heating in a vacuum oven maintained at 130°C. and less than 5 mm. of mercury for 2 hours, for comparison with results by the "second" moisture method.

## Toluene Distillation Procedure

Essentially the toluene distillation method involves the formation of an azeotrope of an immiscible organic liquid with water, distillation of the azeotrope, and separation of the water as a separate phase. The water is then measured volumetrically.

The improved apparatus of Tryon (5) for determining moisture by distillation with toluene was used. In this apparatus the water is measured in a graduated capillary tube, which allows more precise measurement than apparatus formerly used. The interior of the trap and condenser was coated with "GE 9977 Drifilm,"[4] a water-repellent silicone polymer, to prevent water droplets from adhering to the walls.

A slurry was made of 50 g. of peanut butter and 100 ml. of toluene (reagent grade) which had been dried over anhydrous sodium sulphate for 24 hours.

During distillation the temperature of the slurry within the flask was not allowed to exceed 130°C. Uniform heating was accomplished by enveloping the boiling flask in a "Glas-Col" mantle[4] provided with a voltage control. A 60-minute distillation period was found to be sufficient to remove all moisture.

## Results and Discussion

*Raw Peanuts.* In Table I results obtained for raw peanuts with the toluene distillation method and with A.O.C.S. Official Method Ab 2-49 are compared. The moisture content as determined by the toluene distillation method is only slightly higher than that determined by the oven method for all except the whole Virginia kernels. This exception indicates that the toluene method is not suitable for use with whole peanut kernels. The average difference between the two methods for the peanut samples is 0.41%, and the moisture content obtained by the oven method is 94% of that obtained by the toluene distillation method.

TABLE I

Moisture in Raw Peanuts

| Sample No. | Variety | Toluene Method[a] | A.O.C.S. Official Method Ab 2-49 | Difference in methods |
|---|---|---|---|---|
| | | % | % | % |
| 1 | Virginia (sliced) | 6.86 | 6.42 | 0.44 |
| 2[b] | Virginia (sliced) | 6.86 | 6.49 | 0.37 |
| 3 | Virginia (whole) | 5.19[c] | 6.41[c] | ..... |
| 4 | Spanish (sliced) | 6.56 | 6.15 | 0.41 |
| 5 | Runner (sliced) | 7.14 | 6.54 | 0.60 |
| 6 | Pearl variety or white skin (sliced) | 8.07 | 7.81 | 0.26 |
| Av. | | 7.10 | 6.68 | 0.41 |

[a] Sample wt. approximately 20 g.
[b] Same material as No. 1.
[c] Omitted from averages.

*Peanut Butter.* Table II shows results obtained by the toluene distillation method and A.O.C.S. Official Method Ab 3-49 on eight peanut butter samples ranging in color from very light to very dark. Results by the distillation method are again slightly higher than those obtained by the forced draft oven method. The average difference in results obtained by the two methods is 0.28%. The moisture contents by the oven-method average 84% of those by the distillation method.

TABLE II

Moisture in Peanut Butter

| Sample No. | Toluene Method[a] | A.O.C.S. Official Method Ab 3-49 | Difference in methods |
|---|---|---|---|
| | % | % | % |
| 1 | 2.41 | 1.97 | 0.44 |
| 2 | 1.98 | 1.73 | 0.25 |
| 3 | 1.92 | 1.67 | 0.25 |
| 4 | 1.79 | 1.52 | 0.27 |
| 5 | 1.73 | 1.41 | 0.32 |
| 6[b] | 1.74 | 1.42 | 0.32 |
| 7 | 1.34 | 1.14 | 0.20 |
| 8 | 1.24 | 1.09 | 0.15 |
| Av. | 1.77 | 1.49 | 0.28 |

[a] Sample wt. approximately 50.0 g.
[b] Same material as No. 5.

A comparison of results on peanut butter obtained by A.O.C.S. Official Method Ab 3-49 with those obtained using a vacuum oven is given in Table III. The results by both methods are considered to be the same.

These results indicate that the toluene distillation method and A.O.C.S. Official Method Ab 2-49 bring raw peanuts practically to the same state of dehydration. However, in the case of peanut butter, use of A.O.C.S. Official Method Ab 3-49 resulted in only 84% of the moisture indicated by the toluene distillation method. These results indicate that the toluene distillation method and A.O.C.S. Official Method Ab 3-49 do not lower peanut butter to the same state of

[4] The use of trade names in this article is for identification and implies no endorsement of the manufacturer or the product.

TABLE III

Moisture in Peanut Butter

| Sample No. | A.O.C.S. Official Method Ab 3-49 | Vacuum-Oven Method [a] |
|---|---|---|
| | % | % |
| 1 | 2.43 | 2.31 |
| 2 | 1.45 | 1.37 |
| 3 | 1.30 | 1.22 |
| 4 | 1.15 | 0.96 |

[a] Sample wt. 5.0 g.; heating period 2 hours at 130°C.; pressure less than 5 mm. of mercury.

dehydration. These differences may be explained by the fact that the whole peanut kernel has a relatively porous structure which permits moisture to escape with comparative ease during oven heating. However this structure is destroyed on grinding, and moisture cannot escape as readily from the resulting viscous compact mass.

The determination of moisture and volatile matter on four samples of peanut butter by heating in a forced-draft oven and in a vacuum oven were performed to ascertain whether peanut butter heated in air increases in weight from oxidation hence appears to have a lower moisture content. The conditions for both determinations corresponded to those of A.O.C.S. Official Method Ab 3-49 except that the pressure in the vacuum oven was reduced to less than 5 mm. of mercury. The slightly lower moisture values for the samples heated in the vacuum oven are not considered significant and probably result from less efficient transfer of heat in the vacuum oven than in the forced draft oven.

## Summary and Conclusion

The moisture and volatile content of whole peanuts has been determined by A.O.C.S. Official Method Ab 2-49 and has been compared with the moisture content of the sliced peanuts determined by a toluene distillation procedure described by Tryon (5). For practical purposes the results obtained by these methods are in agreement.

Moisture of peanut butter has been determined by an oven loss-in-weight technique corresponding to the conditions of A.O.C.S. Official Method Ab 3-49 for "second" moisture, and by the toluene distillation method. The results indicate that less dehydration was attained by A.O.C.S. Official Method Ab 3-49 than by the toluene distillation procedure.

Losses in weight of peanut butter samples have been determined in vacuum and forced-draft ovens at 130° C. No differences were observed which would indicate that the conditions of A.O.C.S. Official Method Ab 3-49 produce low results because of oxidation.

It can be concluded that the toluene distillation procedure, using apparatus described by Tryon (5), is suitable for determining the relatively small amounts of moisture present in peanut butter. The unique features of this apparatus seem to make the method particularly adaptable to peanut butter. This information is presented to provide the peanut butter industry with an additional method for use in problems involving determination of small amounts of moisture and for comparison with other prevailing methods.

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[Received March 16, 1953]

# The Chemical Utilization of Fats and Oils. I. Preparation of Aralkyl Ketones and Hydrocarbons

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CERTAIN studies have been made in these laboratories over the past few years in an effort to utilize fats and oils through chemical modification. One of these studies was on the production of straight chain alkylbenzenes as detergent intermediates.

A detergent intermediate produced in volume is that prepared from benzene and propylene tetramer. The resultant detergent thus contains a branched alkyl chain. It was thought that different and desirable properties might be obtained from a straight alkyl chain. It was also felt that mixtures of alkylaryl sulfonates having alkyl chains of from 14 to 18 carbon atoms might possess desirable detergent and solubility properties even though the individual compounds might not be entirely satisfactory. The use of mixtures would also have economic advantages.

## Experimental

A satisfactory general laboratory synthesis of the desired aralkyl compounds consisted in the preparation of the acyl chloride from the fatty acid with phosphorous trichloride, condensation of the acyl chloride with the aromatic compound using aluminum chloride, and hydrogenation of the ketone over nickel on kieselguhr.

Myristic acid was condensed with benzene in the presence of aluminum chloride in the manner described for shorter chain acids (4, 9, 10, 13, 14).

The use of hydrogen fluoride (3, 4, 5, 6, 7, 11, 12, 15) as a condensing agent for the direct acylation of benzene with myristic acid was also studied. Experiments at atmospheric pressure were carried out by introducing hydrogen fluoride through a cooled copper coil into the reactants contained in a copper beaker immersed in an ice bath. The beaker was fitted with a vented copper lid. After the desired time interval the hydrogen fluoride was allowed to evaporate at room temperature from the open beaker. To study reactions under autogenous pressure the reactants were placed in a rocking autoclave, which was cooled in an ice bath, and the hydrogen fluoride was introduced through a cooled copper coil. The