ple dissolved and made up to volume with distilled water. The pH of this solution must be checked to pH 6.2 (methyl red indicator) and any samples taken for analysis must be brought to this pH, by the addition of the necessary 1/10 normal acid or alkali in order not to interfere with the formic acid determination.

A pipetted 50-ml. aliquot of the solution to be oxidized is mixed with exactly 50 mls. of oxidant (b) in a 600-ml. beaker. The covered beaker is stirred by swirling and allowed to stand for one hour. At the end of this time 5 mls. of 50% ethylene glycol-water solution is pipetted in, mixed, and allowed to stand for an additional 20 minutes. Dilute the reaction mixture to 300 mls. and titrate with 0.1N KOH using the 100-ml. chamber burette to pH 7.60, employing a pH-meter or 12 drops Brom-thymol blue indicator. Stir continuously and add alkali slowly toward the end-point. Record the volume of KOH used to the nearest 0.01 ml. (The Brom-thymol indicator end-point is a sharp green to blue transition.)

Run a blank similarly with 50 mls. of water and 50 ml. of oxidant (b) and titrate in the same manner. Calculate the per cent of glycerol as given in equation (1) under calculations.

II. *Determination of "Total Oxidizable as % Glycerol" Value*

Pipette a 25-ml. aliquot of the solution used for the determination of free glycerol into a 500-ml. Erlenmeyer iodine flask. Pipette in 50 mls. of oxidant (a). Stir by gentle swirling and let stand for one hour. After the reaction period is complete add 18-20 mls. of 25% KI solution and titrate the liberated iodine with 0.2N sodium thiosulphate to a starch-iodine end-point, employing a 100-ml. chamber burette. Record this reading to the nearest 0.01 ml.

Run a blank and record the value. The difference between the sample and blank titrations must indicate the necessary excess for complete oxidation (equation 3). Where this difference indicates less than the 5:1 ratio required, a smaller aliquot or sample must be taken.

Equation (2) gives the "total oxidizable value as % glycerol."

III. *Determination of Water Content*

The water content of the sample should be known so that corrections necessary in equation (4) can be calculated. The Karl Fischer method for water content is very well suited. Using the appropriate sized sample determine water according to method in reference (7).

Results and Comments

The proposed method described has been used to analyze a large number of commercial samples of "diglycerol" and the data is shown in Table IV. Careful Claisen vacuum distillations of the same samples are compared with this new method.

The glycerine analysis described herein has certain unique advantages compared with other methods and is simple and easy to use. The application of the glycerine method to different problems such as glycerine crudes, etc., where large amounts of various impurities are present, may be feasible.

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Pilot-Plant Manufacture of Peanut Protein[1]

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MANY industrial uses of peanut protein and meal have been reported by this Laboratory in the fields of synthetic fibers (9) and adhesives (1, 3, 4, 5, 6). These specialized industrial uses for peanut protein require proteins such as those found in solvent-extracted meals, which are more soluble and less modified than those isolated from hydraulic-press or screw-press meals (5). This is one of the reasons that the development of the solvent-extraction process for the removal of the oil from peanuts is a prerequisite to the commercial development of peanut meal and protein as industrial raw materials. A process for the isolation of peanut protein from solvent-extracted meals has been previously reported (2). An improved process is reported in this paper in which the yield of protein has been greatly increased and operations simplified.

[1] Presented at the 39th Annual Meeting of the American Oil Chemists' Society, New Orleans, Louisiana, May 4 to May 6, 1948.
[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Production of Solvent Extracted Meal

Peanuts were dried at 140° to 150°F. until the skins could be removed by aeration. The peanut kernels were flaked, and the oil was extracted in a batch extractor by means of n-hexane at room temperature as described in a previous publication (10). The bulk of the solvent was removed by aeration at room temperature, and the meal was further dried at 125° to 130°F. The dried meal contained about 1% lipids and 10% nitrogen.

Protein Manufacture

An outline of the various steps required in processing peanut meal for protein and by-products is shown in Fig. 1. Peanut meal is suspended in water (80 parts per million hardness and 150 parts per million solids) in the weight ratio of 10 parts of water to 1 part of meal and wetted by agitation in the protein peptizing tank (Fig. 2). Sodium hydroxide (aqueous, 30%) is added to the meal suspension

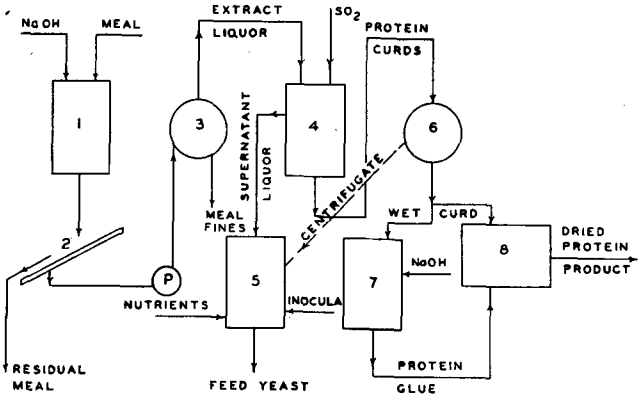

FIG. 1. Flow sheet for the pilot-plant production of peanut protein.

1—Peptization tank; 2—Vibrating screens; 3 and 6—Solid basket centrifuge; 4—Precipitation tank; 5—Yeast propagation tank; 7—Neutralization tank; 8—Drying oven.

until the pH of the suspension is adjusted from the initial value of 6.2 to the final value of 7.5, which is the optimum pH of peptization of the peanut protein (7). About one-half pound of sodium hydroxide is required per 100 pounds of meal. The meal suspension is then stirred for about 30 minutes.

The protein extract liquor is clarified by passing the water-meal suspension over vibrating 40- and 150-mesh screens at which time the meal is washed by sprays of water. A total of one-half of the original extracting water volume is used in the sprays thereby increasing the water-meal ratio to 15 to 1.

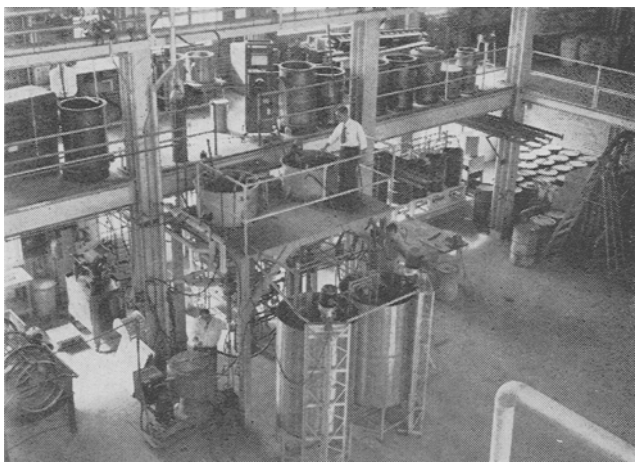

FIG. 2. Peanut protein pilot plant.

The liquor is further clarified through the removal of fines by centrifugation at 1,000 times gravity in a solid basket centrifuge and is pumped into the steam-jacketed protein precipitation tank (Fig. 2). The temperature of the liquor is adjusted to the desired value, and gaseous sulfur dioxide is introduced at a measured rate through the diffusion manifold into the protein extract liquor until the pH is decreased to 4.5, the point of minimum protein solubility (7).

The curd is allowed to settle after which the percentage of moisture in the curd is reduced to about 50% by centrifugation in a solid basket centrifuge. The isolated curd is dried to less than 7% moisture in a forced-draft oven at 120°F.

The clear supernatant liquor containing soluble protein, non-protein nitrogen, minerals, carbohydrates, and other materials has been used as a media for feed yeast propagation (8).

Effect of rate of addition of sulfur dioxide on protein curds. The rate of addition of gaseous sulfur dioxide to the protein extract liquor affects the type of protein curd formed. In Fig. 3 this effect is shown as a function of the rate of settling of the curd. The sulfur dioxide was introduced at the indicated rates until the isoelectric point of the dispersed protein, pH 4.5, was attained. (About one pound of sulfur dioxide was required per 100 pounds of meal.) The

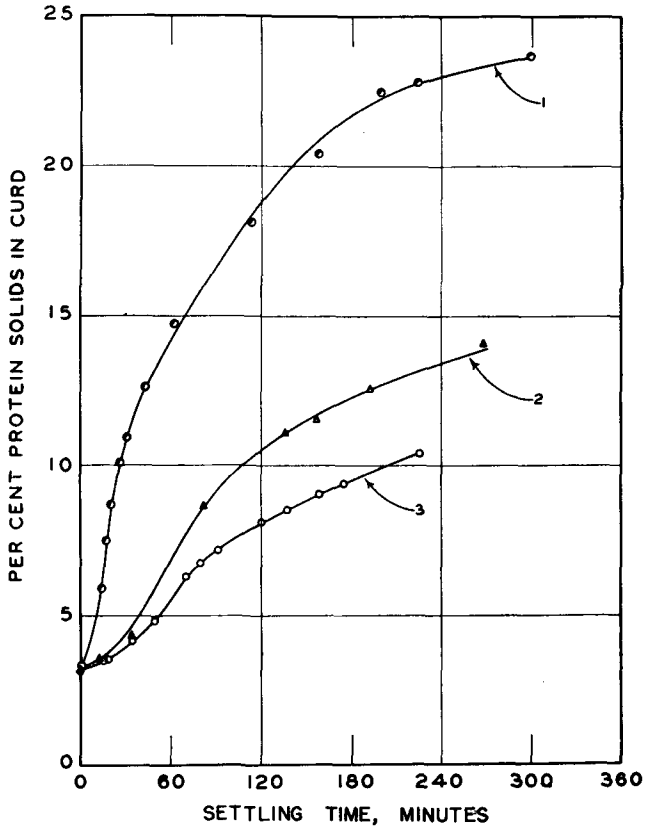

FIG. 3. The effect of rate of addition of sulfur dioxide on protein curds at 90°F.

1—0.230; 2—0.157; 3—0.0729 lb. SO_2/min./100 lb. meal.

zero time for observing the rate of settling of the precipitated protein was taken after addition of the sulfur dioxide. The data demonstrate that the rate of addition of sulfur dioxide determines the rate of settling of the curd. At high rates of addition of sulfur dioxide the total protein solids in the "protein curd" mother liquor increased at a greater rate. At a higher rate of addition of sulfur dioxide then 0.230 lb. SO_2/min./100 lb. meal the gas was not completely dissolved by the liquor and was lost to the atmosphere.

Effect of temperature on protein curds. The temperature of the extract liquor, during precipitation of the protein, also affects the density of the protein curd and the rate of settling, as shown in Figs. 4 and 5. In Fig. 4 it is shown that at 150°F. the protein curd formed had a lower density than curds formed at lower temperatures. With increasing temperature of extract liquor the density of the curd decreased. In Fig. 5 the protein solubility at the isoelectric point of the curd, pH 4.5, is shown to increase with increasing temperature. The protein remaining in solution at the isoelectric point is not

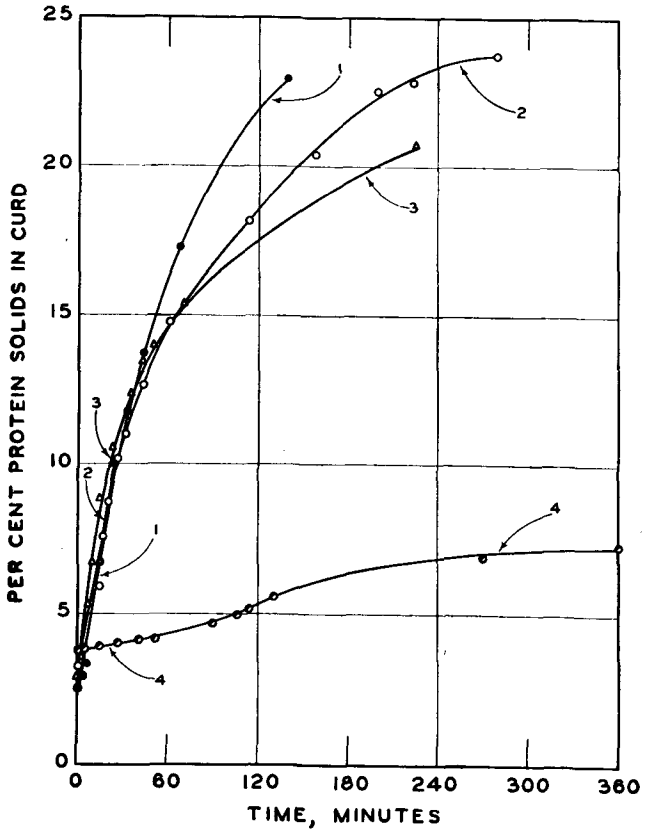

FIG. 4. The effect of temperature on protein curds at 0.230 lb. SO_2/min./100 lb. meal.
1—73°F.; 2—90°F.; 3—120°F.; 4—150°F.

recoverable as protein by this process. At temperatures less than 70° the density of the curd decreased. Therefore it may be concluded that for increased yields of protein a temperature of 75° to 90°F. of the extract liquor at the time of precipitation is desirable.

Protein Yields and Analyses

Utilizing a rate of addition of sulfur dioxide of 0.230 lb. SO_2/min./100 lb. meal at 90°F., four typical protein preparations are shown in Table I, and the average yield values are compared with those previously reported (2).

The analyses of the extracted proteins for nitrogen, phosphorus, and ash are given in Table II. No significant differences were observed in the proteins as the temperature of the extract liquor was varied or as the rate of addition of sulfur dioxide to the extract liquor was changed. All of the above-mentioned proteins had desirable characteristics for use in the manufacture of adhesives and synthetic fibers.

TABLE I

Yields of Protein Obtained by Improved Methods of Precipitation [1]

No.	Initial quantity of meal, lb.	Yield of protein, lb.	Protein [2] yield, %	Nitrogen in meal, lb.	Nitrogen in protein, lb.	Nitrogen yield, %
1	93.3	34.2	36.7	9.23	5.58	60.5
2	93.1	36.8	39.5	9.22	5.99	65.0
3	92.6	38.3	41.4	9.17	6.20	67.6
4	93.6	42.8	45.7	9.18	6.93	75.5
Average	93.2	38.0	40.8	9.20	6.18	67.2
Other published data (2)	100	33.0	33.0	9.80	5.14	52.4

[1] The conditions of precipitation were a rate of addition of sulfur dioxide of 0.230 lb./min./100 lb. meal and a temperature of protein liquor of 90°F.
[2] Yield calculated on a dry weight basis.

TABLE II

Analyses of Proteins Prepared Under Different Conditions of Precipitation

Temperature, °F.	Rate of addition of SO_2, lb./min./ 100 lb. of meal	Nitrogen, %	Phosphorus, %	Ash, %
73°	0.230	16.2	....	2.5
90°	0.230	16.6	0.6	1.7
90°	0.157	16.0	0.8	1.5
90°	0.0729	15.3	0.8	1.5
120°	0.230	16.3	0.5	1.2
150°	0.230	15.2	0.8	2.6

Summary

Pilot-plant production of peanut protein from solvent-extracted meal was investigated with respect to the effect of temperature of extract liquor during precipitation and the rate of addition of sulfur dioxide on the settling rate of the precipitated protein. As the rate of addition of sulfur dioxide was increased, and the temperature of the extract liquor was decreased the density and the settling rate of the protein curd increased. Spray washing of the extracted meal was more efficient than the previously reported dilution method of washing and resulted in a greater yield of protein.

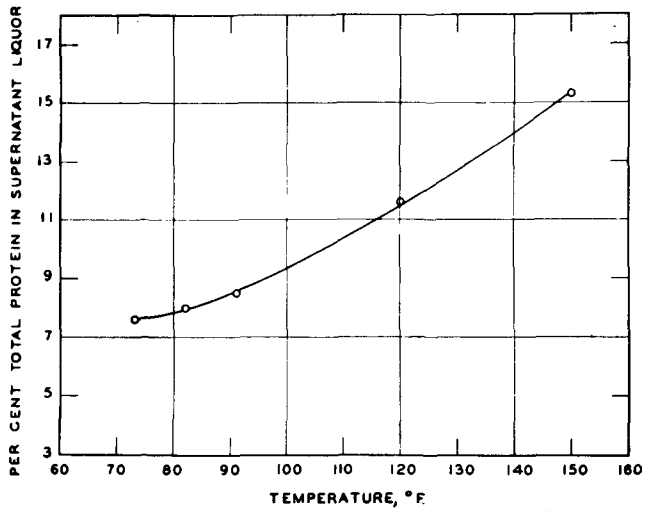

FIG. 5. The effect of temperature on protein solubility at the isoelectric point.

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