tion equivalents for several of the samples and found to be within the range to be expected of normal acid mixtures having similar iodine values. Also, the fatty acids were completely soluble in Skellysolve-F which is a very poor solvent for oxidized fats, and sample number six, which was the most highly oxidized of those examined, gave fatty acids of the highest iodine values.

One practical application of the principles developed in this study would be in the purification of deodorizer catch basin sludge, either for analysis in the laboratory or for commercial recovery of by-products therein. As a preliminary to analysis, it would be sufficient to dissolve the sludge, just as it forms, without heating to remove water, in a volume of Skellysolve-F equivalent to 50 ml. per gram of fat present and centrifuge the solution. This would rid the sludge oil of water and the bulk of its mineral content at the same time, without subjecting the complex organic compounds present to the violent chemical action of heat and mineral acids. A somewhat similar treatment should also be suitable for commercial application.

Summary

A method of determining and recovering the metallic soaps present in deodorizer catch basin sludges has been described. It is based on the apparent low solubility of calcium and iron soaps in a commercial solvent known as Skellysolve-F. Using the method evolved, six samples representing material from four refineries were examined. It was found that the metallic soaps varied all the way from 0.51% to 28.02%. The recovered soaps were analyzed for both mineral and fatty acid content. In five of the six soaps examined above 90% of the metal present was found to be calcium, but in one sample about 27% of the metal was iron. In all cases, less than the theoretical amount of fatty acid was obtained from the soaps and the loss was attributed to solubility of some of the acids in water. The fatty acids obtained by hydrolysis of the soaps were all much more saturated than would be predicted from the iodine values of the sludge oils from which they were formed. It is postulated that the free fatty acids found in deodorizer distillates are disproportionally more saturated than are the combined fatty acids. In the course of other work the free fatty acid contents of the various sludges examined were determined. They were found to run usually from 9.5% to 19.9% although one sample ran 53.7%.

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The Determination of the Rate of Extraction of Crude Lipids From Oil Seeds With Solvents*

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THE rate of extraction of oil is an important consideration in the design of equipment for the solvent processing of oil seeds and the operation of that equipment. It has been found that rapid, convenient laboratory methods of study are needed to precede and supplement large scale studies of extraction.

Two basic methods have been developed in the Blaw-Knox laboratories for the determination of the rate of extraction of "oil," or more precisely crude lipids, from oil-bearing materials. A familiar example of such an extraction is the extraction of soybean flakes with commercial hexane. These methods have been found to be useful in making equipment design and operating studies, in making theoretical studies of the variables influencing extraction rate, and as an aid in making a quick evaluation of the suitability of various materials for extraction in existing types of plants and equipment. The methods have been used successfully both as presented and with some modification for special studies.

The literature contains a meager amount of material dealing with the subject of determining extraction rates. An extensive series of studies has been conducted at the University of Michigan employing a method of extraction rate determination in which individual samples of soybean flakes were placed in wire baskets and suspended in a very large quantity of circulating trichlorethylene or trichlorethylene miscella for varying lengths of time. Each sample was then analyzed for oil after centrifuging (1, 5, 6). Collins and Kroher (3), in a study of the prevailing American Oil Chemists' Society method for total extractibles, determined rates by running indi-

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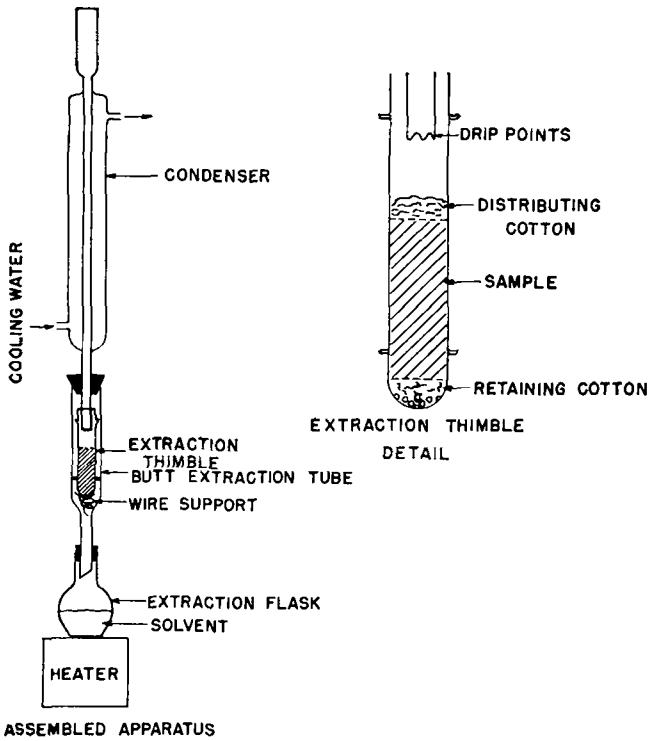


FIG. 1. Apparatus for Percolation Method.

vidual samples for varying lengths of time. Another method, used in a theoretical study, involved the extraction of a series of individual samples, and the loss in weight of a subsequent batch extraction on each sample was used for obtaining total lipids (4).

In addition to the usual mechanical difficulties of precise determination of a rate the problem is complicated by the variable nature of the extractibles. The material extracted is not "oil" but a mixture of lipids whose composition depends on the solvent, the temperature of the extraction, and the history of the sample (7). In recognition of this, the American Oil Chemists' Society Method Ba 3-38 states that the material determined is the petroleum ether extractibles under the conditions of the test. In addition, the composition of the extracted lipids changes as the extraction progresses (2, 7).

In view of these complications it was necessary to make an arbitrary definition of the material on which the rate was to be determined. Accordingly, extractibles were accepted as the material extracted by commercial hexane under set conditions. This solvent was chosen because of its importance in commercial operation, and the conditions were chosen for convenience in conducting the test. Although this definition served for most of the studies made by this method, modifications have been made to extend the usefulness of the method to other solvents.

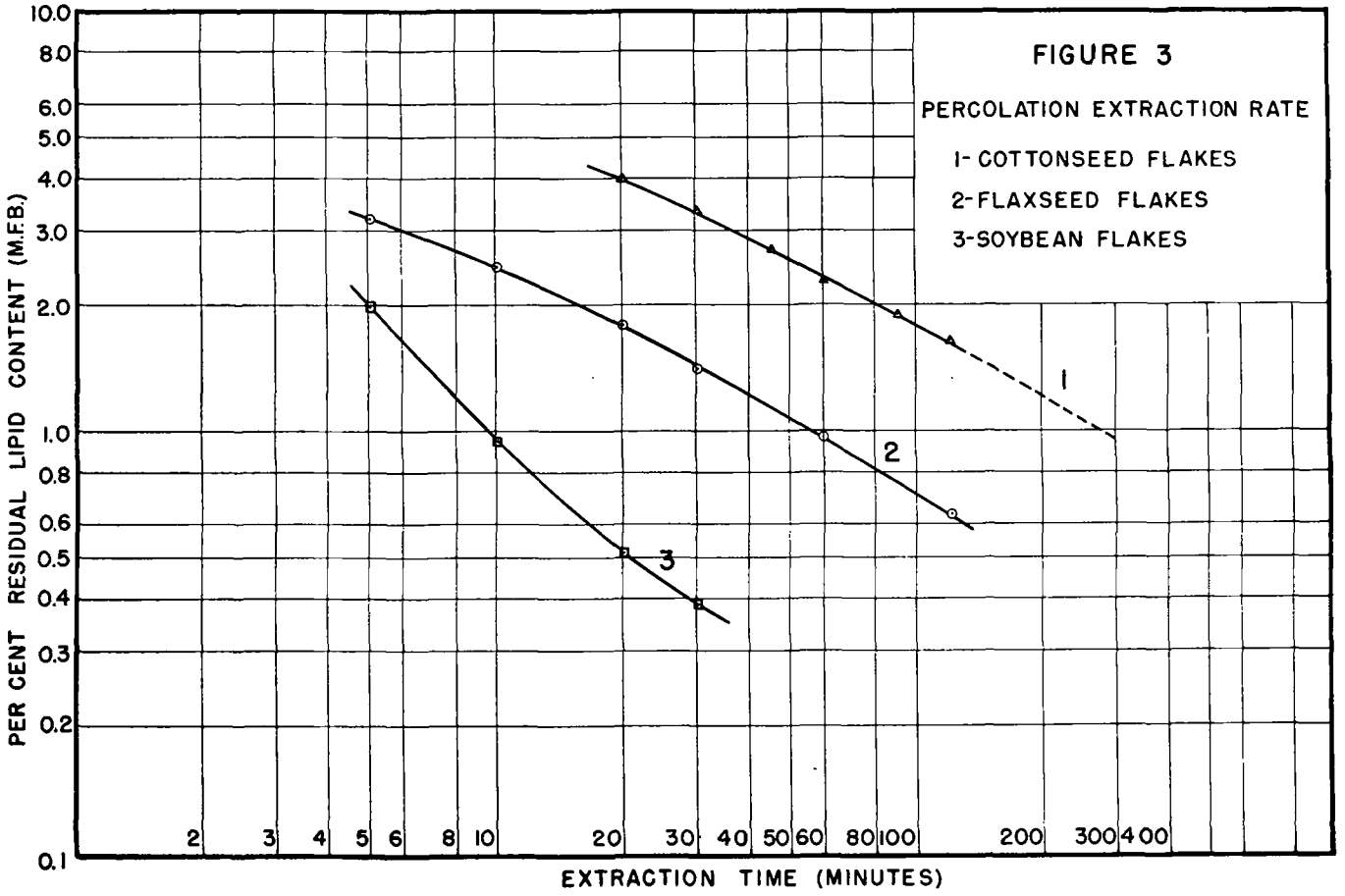
The Percolation Method

The simpler of the two basic methods has been termed "Percolation method" because of its mode of operation. It is adapted from The American Oil Chemists' Society method for total extractibles employing a Butt-type extraction apparatus. This method determines the amount of oil removed from a single sample of oil-bearing material by fresh solvent percolating through the bed of sample by gravity. This manner of making the determination dictates that the material be of such a nature that it will pass solvent.

The apparatus is essentially that set forth in Method No. Ba 3-38 in the Official and Tentative Methods of the American Oil Chemists' Society, 2nd Edition. The following minor changes were made: Instead of the usual filter paper for retaining the sample, a pyrex glass thimble, 21 mm. I. D. by 100 mm. in length and perforated on the bottom with 13 holes of 2-3-mm. diameter, is used in order to insure that all the solvent passes through the bed of material being extracted. The reflux condenser was also modified by drawing out numerous drip points to aid in distributing the solvent. The apparatus is shown in Fig. 1.

The extraction thimble is prepared by placing a thin layer of fat-free cotton wool in the bottom to prevent the loss of fine particles of meal, weighing into the thimble eight grams of sample to 0.1 milligram, and placing a thin layer of fat-free cotton on top of the sample to aid in solvent distribution. The thimble is then placed in the Butt tube, 50 ml. of solvent are added to the extraction flask and the apparatus assembled as shown in Fig. 1. The flask is heated with an electric heater which has previously been adjusted to produce a reflux rate of 18 ml. per minute. Timing is begun when the easily visible band of condensing vapor moves up to the condenser through the Butt tube. At the end of the first desired time interval a pressed asbestos fiber block is inserted between the heater and the flask, the flask containing the extract is removed and replaced with another containing 50 ml. of fresh solvent, and the heat reapplied. A series of consecutive extractions is so made on that sample over a period of two hours, after which the sample is removed from the thimble, allowed to desolventize somewhat in air, and placed in a mortar and reground with a pestle using 200 vigorous strokes. This reground material plus the cotton wool from the extraction thimble is then transferred to a molded paper thimble and extracted for two additional hours. The "oil" determined is added to that determined in the series of consecutive extractions and the total arbitrarily designated as total extractibles. All extracts are filtered and washed through a fritted glass filter funnel and transferred to tared flasks. The bulk of the solvent is removed on a steam bath and the crude lipid residues are brought to constant weight by removing the last traces of solvent and water with vacuum on a water bath. The residues are weighed to 0.1 milligram.

During the development of the method certain limitations became evident. One of these was the tendency of the solvent to channel through a bed of flaked material. When this occurred, diverse results in the early stages of the extraction were obtained on duplicate runs. It was found that if the flakes were broken lightly by hand to pass U. S. S. Sieve No. 10, the channeling was eliminated. This was determined by running a series of screened fractions of flakes. The effect of rate of solvent flow through the bed was studied also and from the results obtained, the high 18 ml./minute rate was selected because variation in that range had no effect on results. The primary limitation of this method as presented is the inability to



operate on materials which will not pass 18 ml./minute of solvent.

COTTONSEED FLAKES
THICKNESS ..... .017"
MESH FRACTION 10-25
HULL-FREE
TOTAL OIL CONTENT--(M.F.B.) 37.92%
MOISTURE CONTENT--(AS IS) 11.6%
GRAMS OF SAMPLE 8.00
SOLVENT ..... COMMERCIAL HEXANE
TEMPERATURE ..... 150°F.

TIME OF EXTRACTION (MINUTES)	OIL EXTRACTED (GRAMS)	%RESIDUAL "OIL" IN FLAKES (M.F.B.)
20	2.4992	4.00
30	2.5327	3.37
45	2.5596	2.71
60	2.5791	2.29
90	2.5974	1.89
120	2.6088	1.64
TOTAL OIL	2.6821	0.00

FIG. 2. Typical data, percolation extraction rate.

Moisture content is determined on a representative sample of the material to be run and the data are presented on a moisture-free basis as per cent residual "oil" content at the stated time of extraction. The data are usually plotted on log-log paper to relate extraction time in minutes to per cent residual "oil" content on a moisture-free basis. The log-log plot was chosen for convenience because it was observed that the curves obtained by this plot are approximately straight lines, and interpolation and extrapolation are facilitated. The criterion of extraction rate has been chosen as the extraction time required for 1.0% residual lipid content. Inasmuch as the primary purpose of the commercial extraction is to reduce the "oil" content to this range, it was decided that this type of reference point would be the most useful from a practical viewpoint. Duplication of the time to 1.0% for duplicate runs has always been found to be less than 5% of the total time required. The manner of presentation of a typical set of data is shown in Fig. 2. Three typical extraction rate curves obtained using this method are shown in Fig. 3.

The Batch Co-Current Method

In the second of the two basic extraction rate determination methods, an agitated batch extraction is carried out as is indicated by the name. This method was developed for materials which, because of their small particle size, could not be run by the Percolation Method. This method has been useful in carrying out extractions with varied oil content miscellas rather than fresh solvent and the data applied directly to a stagewise extraction operation. This method requires more attention and more precise work done than does the Percolation Method and accordingly is reserved for special studies where the Percolation Method will not suffice.

Fig. 4 shows the apparatus assembled for operation. A more detailed description of the important parts is as follows:

Extraction Flask — A 3,000-ml. round bottom flask, fitted with two sidenecks set at angles to the neck.

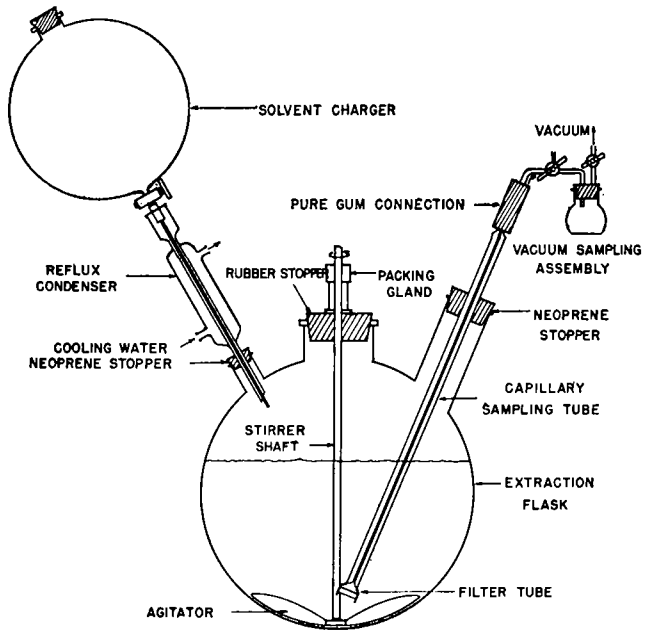


FIG. 4. Batch co-current extraction rate assembly.

1. Sampling Sideneck— 130 mm. in length by 30 mm. I. D.
2. Condenser Sideneck—95 mm. in length by 18 mm. I. D.

Sampling Filter—A Allihn filter tube, 20-mm. diameter disc of medium frit glass, sealed to a 2-mm. bore capillary. The overall length is 380 mm.

Solvent Charger — A 2,000-ml. round bottom flask with a short piece of 10-mm. tubing sealed in the bottom.

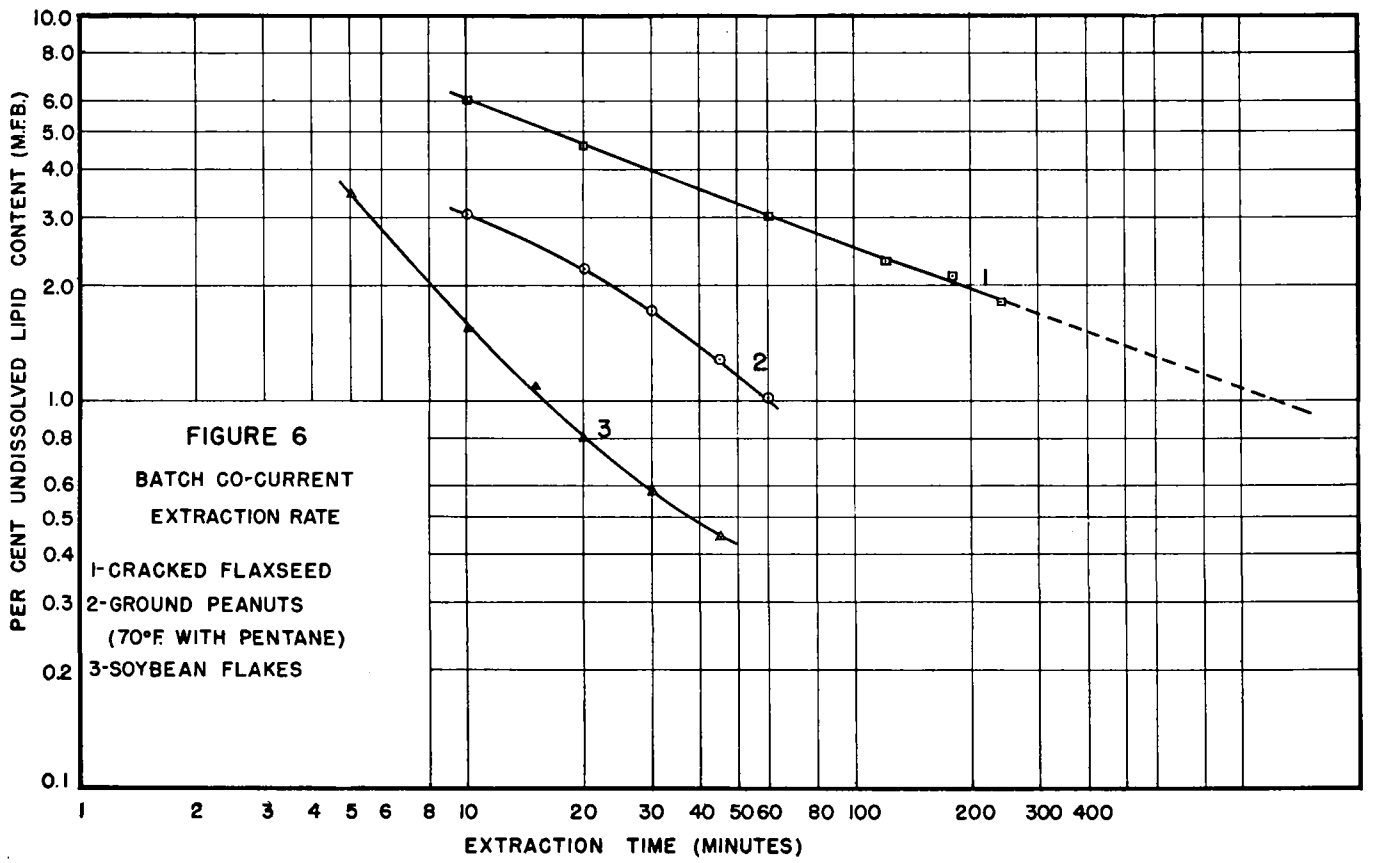
Agitator Assembly — A motor-driven hinged propeller-type stirrer fitted with a packing gland or other vapor seal. Agitation is at 125 r.p.m.

Vacuum Sampling Assembly — 150-ml. sample flask fitted with a 3-position and a 2-position stopcock.

Moisture and total lipid contents are determined on representative samples of the material to be run. The total lipid is determined by extracting for two hours with commercial hexane in the Butt extractor, regrinding, and extracting for two additional hours with hexane.

With the agitator assembly in place and the bulb of the extraction flask immersed in a constant temperature bath maintained at 125°F., a weight of oil-bearing material, which will yield approximately a 2% miscella if all the available crude lipid were taken into solution by the solvent added, is charged to the flask through the sampling sideneck. The sampling filter is then placed in position. Fifteen hundred (1500) grams of solvent preheated to 125-130°F. is charged through the condenser from the tared solvent charger, using an extension tube to keep the hot solvent from coming in contact with the water-cooled condenser. Timing is started when one-half the solvent has been added and the agitator started at that time. The charge is weighed back to 0.1 gram to obtain the exact weight of solvent charged.

Samples of miscella are withdrawn at the desired time intervals in the following manner: The vacuum sampling assembly, which has been previously evacuated to 1-mm. pressure and weighed to 0.01 gram, is connected flush to the sampling filter with a short piece of heavy wall pure gum tubing. Just before sampling the sampling filter is purged of miscella by blowing air through the 3-position stop-cock. Connection is made with the evacuated sample flask 30 seconds before the desired time and sampling is con-



tinued for 60 seconds.* The amount of sample taken is controlled by the degree of opening the stopcock. Miscella retained in the open end of the sampling assembly is blown back and washed with 1-2 drops of solvent. The assembly is disconnected and weighed to 0.01 gram to obtain the sample weight. Miscella retained in the internal capillary of the sampling assembly is washed into the sample flask by drawing in fresh solvent. The residual vacuum is then broken with air, and the procedure from this point is identical to the treatment of extracts obtained in the percolation method. This operation is repeated at each desired time interval. Where samples are to be taken in rapid succession, several vacuum sampling assemblies are prepared.

SOYBEAN FLAKES

TOTAL OIL CONTENT--(AS IS) 20.34%

(M.F.B.) 21.9%

MOISTURE CONTENT--(AS IS) 8.00%

SAMPLE WEIGHT 150.0 GRAMS

SOLVENT--COMMERCIAL HEXANE 1497 GRAMS

TEMPERATURE 125°F

TIME MINUTES	EXPERIMENTAL MISCELLA CONCN.	MISCELLA SAMPLE WEIGHT	WT% UNDISSOLVED OIL IN THE MEAL
5	1.757%	30.65 GRAMS	3.47
10	1.891%	29.41 GRAMS	1.53
15	1.924%	33.57 GRAMS	1.10
20	1.946%	27.28 GRAMS	0.08
30	1.963%	44.33 GRAMS	0.58
45	1.976%	29.75 GRAMS	0.44

FIG. 5. Typical data, batch co-current extraction rate.

The mathematical treatment of the data in this method is more involved than that in the percolation method. The per cent "undissolved" lipid content is calculated by material balances on lipid, on solvent, and on moisture-free solids. The term "undissolved" oil is applied to the difference between the total oil content of the sample used and the oil that is calculated to be in the miscella from the analysis of the miscella sample and the amount of solvent present. The residual lipid content of an extracted meal will include this "undissolved" lipid plus the oil contributed by desolventizing any entrained miscella. The usual method of reporting the data lists "undissolved" oil for various times of extraction as shown in Fig. 5. The data are again plotted on log-log paper in the same manner as the data for the Percolation Method. Typical data are shown in Fig. 6.

The method, depending as it does on measurement of small differences in relatively large quantities, demands extreme care in experimental manipulation, precision of weighing, and mathematical treatment of the results. Care must be taken also to obtain a representative sample of the material for analysis for total lipids.

The method as presented has been found to be reliable and gives good duplication. Any modification for special studies requires a careful evaluation of the effects that such changes may involve. For example, in one modification that used a small sized sample, the solvent in the vapor space became a factor which had to be taken into account in the calculations.

Summary

Two basic methods have been presented for measuring the rate of extraction of crude lipids from "oil"-bearing materials with solvent. In the Percolation Method the extraction is carried out by percolating fresh solvent through the sample and measuring the "oil" recovered at succeeding time intervals. In the Batch Co-current Method samples of miscella are withdrawn periodically from an agitated batch of known quantities of oil-seed and solvent and analyzed for lipids to check the progress of the extraction.

These methods have been used successfully in the Blaw-Knox laboratories over the last four years in making studies of factors influencing equipment design and plant operation as well as fundamental studies contributing to a general understanding of extraction. Some of the "oil"-bearing materials which have been studied using these methods include: soybeans, cottonseed, peanuts, flaxseed, corn germ, castor beans, wheat germ, rice bran, mowrah seeds, tung nuts, grain sorghum, and various expeller and press cakes. Special studies include methods of preparation, temperature effect, moisture content, nature of solvent, varieties of seed, and particle size.

* NOTE: Fig. 4 may tend to give a false impression about the sampling technique. The 2-way stopcock, through which the sampling assembly is evacuated, is closed when the pressure reaches 1 mm. and no further vacuum is pulled on the assembly during sampling.

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