A Laboratory Centrifugal Refining Method for Control Application

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Abstract

A control method is presented for selecting the appropriate processing conditions for alkali refining of crude vegetable oils by the centrifugal process to yield lowest losses with satisfactory color. This technique is sufficiently analogous to actual processing conditions to provide reliable information upon which plant performance can be based.

The cup method cannot be used in this manner in that it no longer approximates operating procedures as in the days of kettle refining. The chromatographic neutral oil method, on the other hand, provides an index of the amount of oil available for recovery without regard to the possibility of attaining such levels.

For these reasons the centrifugal method fills a void of long standing. Other tangible benefits that accrue from this technique are: selection of sources of oil that can be most profitably refined by establishing the relative value of competitive oils, and a means of evaluating plant efficiency.

Introduction

THE PRIMARY OBJECTIVES in alkali refining of crude vegetable oils by the centrifugal process are production of oils with a satisfactory color and, at the same time, a minimum refining loss. Although processing techniques have improved with time, the basis of trading has not kept pace. The cup refining procedure (1), a technique roughly approximating kettle refining of the past, is still the recognized method for settlement. Since the method no longer parallels the process, it is not suprising to discover that predicted losses based on cup loss are frequently unrealistic.

With these facts in mind, a method was developed which effectively represents refining in miniature by an approach which closely approximates modern processing techniques. This method serves as an excellent index of plant performance. With 100 ml of oil and a few min time, a sample of crude oil can be evaluated fully for refining characteristics, when used in conjunction with measurement of oil color (2).

Principle: A measured amount of crude oil is heated to the desired temperature, the alkali solution added, the mix shaken, transferred to centrifuge tube, centrifuged and the volume of foots read. Refining loss is calculated from the amount of alkali solution used and the volume of the foots.

A. *Apparatus*
1. Centrifuge, De Laval Precision 100 cc test tube centrifuge and special starter for controlled torque motor.
2. Centrifuge tubes, 100 ml high accuracy tip, De Laval Cat. No. 14520.
3. Stoppers for centrifuge tubes. Cat. No. 24430.
4. Special wire for cleaning centrifuge tubes. De Laval Cat. No. 25871.
5. Liners for centrifuge cups, De Laval Cat. No. 24431.
6. Water bath. Aluminum pan that will accommodate 4, 250-ml Erlenmeyer flasks with the water level slightly above the level of the oil in the flask. This may be heated with a gas burner.
7. Graduated cylinders, 100 ml.
8. Erlenmeyer flasks, 250 ml with ℱ 24/40 joint, complete with glass stopper.
9. Thermometers, 0–150C.
10. Measuring pipet, 10 ml graduated in 0.1 ml subdivisions.

B. *Reagents*
1. Glycerine, U.S.P.
2. Silicone grease.

C. *Solutions*
1. Alkali solutions 8,10,15 and 20% sodium hydroxide by wt. If Bé solutions are used, prepare as directed in the Official AOCS Method Ca 9a-52, B, 2.

D. *Operation of the Centrifuge*
1. Follow the manufacturer's instruction on operation, starting, stopping, lubricating, etc.
2. When repeated tests are made at sufficiently close intervals, there is the possibility that the motor will overheat and cut out. It will then be inoperative for several hours until it cools down.

TABLE I

Amount of Alkali and Concentration Suggested on the Basis of F.F.A. Content of the Sample

Crude Cottonseed Oil

F.F.A. in sample	Wt % of NaOH solution of				ml of NaOH solution to be pipetted for			
	15%		20%		15%		20%	
0–1.5%	2.5	3.5	2.5	3.5	2.0	2.8	1.9	2.6
1.5–2.5%	3.5	5.0	3.5	5.0	2.8	4.0	2.6	3.7
2.5–4.0%	5.0	7.0	5.0	7.0	4.0	5.5	3.7	5.2
4.0–6.0%	7.0	10.0	7.0	10.0	5.5	7.9	5.2	7.5
6.0–8.0%	10.0	13.0	10.0	13.0	7.9	10.2	7.5	9.7

Note: The use of 20% NaOH has been advantageous when difficulty is encountered in removing coloring matter. 20% NaOH may be desirable at times even though a greater loss is obtained if satisfactory colors can be obtained thus eliminating re-refining.

Crude Soybean Oil

F.F.A. in sample	wt % of NaOH solution of				ml of NaOH solution to be pipetted for			
	8%		10%		8%		10%	
Degummed Oil								
0–1.0%	1.0	2.0	1.0	2.0	0.8	1.7	0.8	1.7
Other Crudes								
0–1.0%	2.0	3.0	2.0	3.0	1.7	2.5	1.7	2.5
1.0–1.5%	2.5	3.5	2.5	3.5	2.1	2.9	2.1	2.9

Note: The authors have no experience in testing soybean oil with higher than 1.5% F.F.A. Suggest using 8% and 10% NaOH with amounts recommended for crude cottonseed oil.

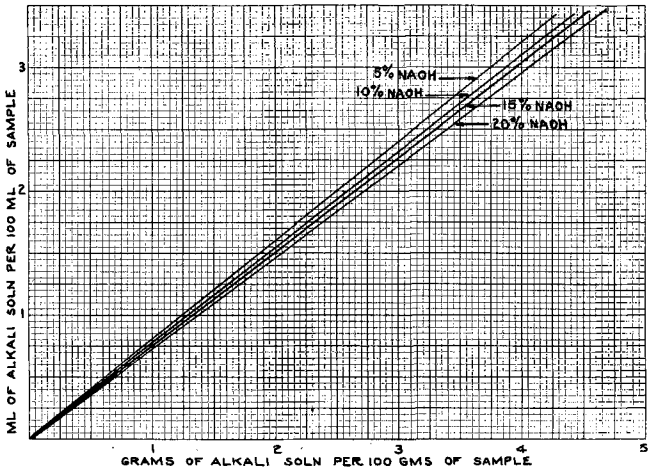

FIG. 1. Relationship between ml of alkali solution per 100 ml of sample to g of alkali solution per 100 g of sample.

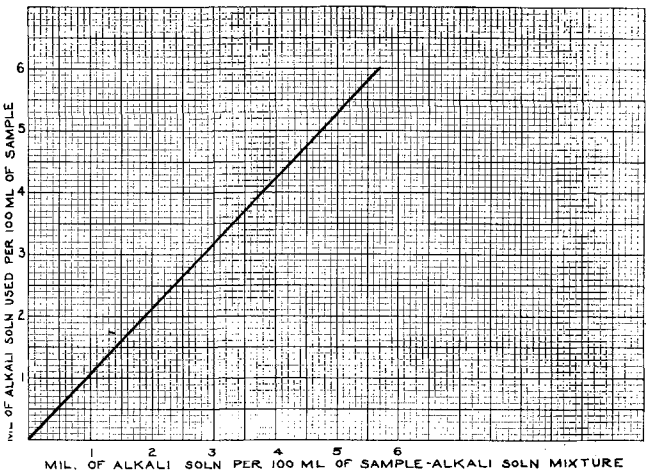

FIG. 3. Relationship between ml of alkali solution used per 100 ml of sample to ml of alkali per 100 ml of sample-alkali solution.

Operations to date indicate three series of four tubes can be centrifuged in 1 hr without overheating. When this testing rate was continued, trouble was encountered and the motor had to be cooled to protect it and permit continuous testing.

E. *Selecting Amount and Concentration of Alkali for Testing Crude Cottonseed Oils and Crude Soybean Oils*

1. When testing crude cottonseed oil samples of unknown refining characteristics, use two levels of alkali such as 15 and 20% NaOH, Table I. When testing crude soybean oils, use two levels of alkali such as 8 and 10%, Table I.

   Note: If repeated tests on crude oil from certain sources indicate one of these strengths is never suitable for refining the crude, tests may be made with only the more desirable concentration at two levels.
2. Plant refining is usually on the basis of weight, so the volumes of alkali selected for pipetting are selected to correspond to weight percentages. Figure 1 shows relationships between weight per cent, g or lb of alkali solution per 100 g or lb of oil, and ml of alkali solution per 100 ml of oil.
3. Amounts and concentrations other than those given in the table are used when experiences indicate they are more desirable.
4. Sometimes the cottonseed oil foots are too hard when low levels of alkali are used and the amount of alkali will have to be increased above the amount indicated by the centrifuge test. Figure 2 shows the average percentage by weight of 15% NaOH used when the centrifuge loss varied from 2.5–10%. The graph was extrapolated below 2.5%.

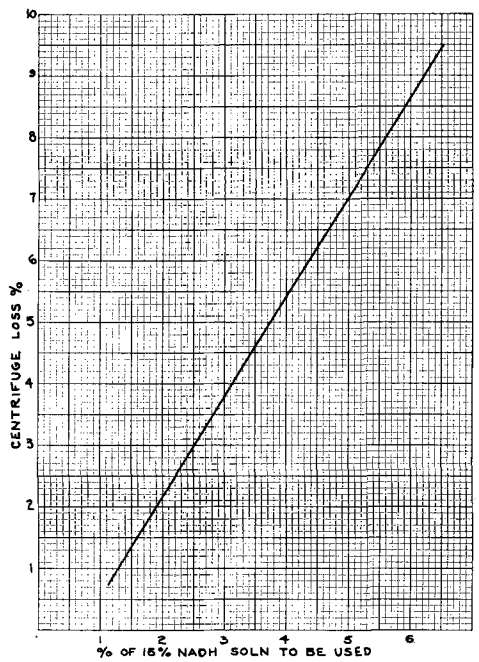

FIG. 2. Average wt percent of 15% sodium hydroxide used in a plant for different levels of centrifuge loss.

F. *Procedure*

1. Mix sample thoroughly and measure 100 ml portions into each of 2 or 4, 250-ml glass-stoppered Erlenmeyer flasks (see Note H, 1) using a graduated cylinder. Allow graduate to drain five seconds while held at a 45° angle.
2. Place a thermometer in each sample and place the flasks in a water bath maintained 65–70C and heat samples to 65 ± 2C. Shake or stir occasionally during this period.
3. Add from a measuring pipet the desired amount of alkali solution.
4. Stopper the flask, wrap in a towel and shake vigorously for 30 sec.
5. Pour 100 ml into centrifuge tube and stopper.
6. Centrifuge for 10 min at full speed. Temperature in the centrifuge should be between 120 and 150F. (See Note H, 2, 3.)
7. Read the volume of foots, calculate and record the refining loss.
8. Select for color measurement the sample that had the lowest loss. Color of refined soybean oil usually does not have to be measured.
9. If the refined C/S oil in the centrifuge is clear, pour 15–20 cc into clean, dry 19-mm round cuvette for color measurement. If the refined oil is not clear, filter and pour 15–20 cc filtered oil in clean and dry 19-mm round cuvette.
10. Measure the absorbency (optical density) at 500 mμ with a Coleman Model 6B spectrophotometer adjusted to zero transmittance when no light reaches the photocell and zero absorbency (100% transmittance) for a 19-

mm round cuvette filled with carbon tetrachloride.

11. Read and record absorbency of the refined oil. If absorbency is above that established for satisfactory bleaching, measure absorbency of the next lighter colored refined oil.

    Note: Tests at one refinery have indicated that refined oil with an absorbancy of 0.7 would bleach satisfactorily.
12. A form similar to those illustrated in Note H, 4 and 5 should be used for tabulation of data. It may be advantageous to keep data on crude oils from the same source together when frequent or regular shipments are received from the same source.
13. Suggest to the plant personnel, in regard to plant refining of cottonseed oil, the amount and concentration of alkali that gives the lowest loss and a refined oil with an absorbency of 0.7 or less. If the amount of alkali recommended is less than the average used in one refinery for a given centrifuge loss (Fig. 2) it may be necessary to increase amount of alkali to soften the foots.
14. Suggest to the plant personnel, in regard to plant refining of soybean oil, the amount and concentration of alkali that gives the lowest loss.

G. *Calculations*

$$\text{Refining Loss, \%} = \frac{D}{100 - B} \times 100$$

A = ml alkali solution, C4

B = ml alkali solution per 100 ml of sample-alkali solution mixture $= \frac{A}{100 + A} \times 100$

See Figure 3 for calculations of B for values of A between 0 and 5 ml

C = ml foots, F7.

D = ml oil lost from 100 ml of sample-alkali solution = C − B

Example: In the calculations, when 2.8 ml of 15% NaOH was used, the volume of foots was 7.2 ml.

A = 2.8

$$B = \frac{2.8}{100 \times 2.8} \times 100 = \frac{280}{102.8} = 2.7$$

C = 7.2

D = 7.2 − 2.7 = 4.5

$$\text{Refining Loss \%} = \frac{4.5}{100 \times 2.7} \times 100 = \frac{450}{97.3} = 4.6\%$$

H. *Notes*

1. The graduated cylinder will have to be filled to 2–3 ml above the 100 ml mark to deliver 100 ml. Determine amount as follows: Fill a graduate to 100 ml mark and pour into another graduated cylinder, and allow to drain 5 sec while held at a 45° angle. 100 ml minus the volume of oil in the graduate is amount that the measured 100 ml volume shall be increased to make a delivery of 100 ml.
2. Enough glycerine is poured into the centrifuge cup just before centrifuging to act as as a cushion and prevent sticking of the tube after centrifuging. If sticking occurs, wipe a thin film of silicone grease on the tube before centrifuging.
3. Cooling water is circulated through the case around the centrifuge when the temperature rises to 150F so that the temperature is maintained below 150F, preferably around 135F.
4. Suggested form for recording centrifuge refining loss data for cottonseed oil.

Centrifuge Refining Loss and Absorbancy of Refined Oil When Tested as Indicated

Sample	Date	F.F.A. 15% NaOH					
		Alk. used wt %	Ref. loss	A. at 500 mμ	Alk. used wt %	Ref. loss	A. at 500 mμ
Sample	Date	20% NaOH					
		Alk. used wt %	Ref. loss	A. at 500 mμ	Alk. used wt %	Ref. loss	A. at 500 mμ

5. Suggested form for recording centrifuge refinery loss data for soybean oil.

Centrifuge Refining Loss When Tested as Indicated

Sample	Date	8% NaOH			
		Alk. used wt %	Ref. loss	Alk. used wt %	Ref. loss
Sample	Date	10% NaOH			
		Alk. used wt %	Ref. loss	Alk. used wt %	Ref. loss

Discussion

Selection of Concentration and Amount of Alkali as Basis for Plant Control

The centrifugal refining method can be used for selecting the concentration and amount of alkali most appropriate for a given refining situation. This may be done by treating the crude oil with two concentrations of alkali at each of two levels. The selection of specific conditions for test is a function of the type of crude oil and its free fatty acid level.

Table I gives suggested amounts and concentration of alkali for the four tests, based upon the free fatty acid content of the sample. Refining loss and color are measured at each set of conditions selected. From these observations an optimum set of conditions, in regard to strength and amount of alkali, can be chosen on the basis of lowest refining loss with acceptable refined color. Table II gives examples of some tests on crude cottonseed and soybean oils. The results underlined indicate the conditions recommended for plant scale refining. Past experience has indicated that refined cottonseed oil with 0.7 color would bleach satisfactorily. When relationship between refined and bleached color has been established, this inference can be included in the selection of refining conditions.

Control of Refining Operations

As described previously, the most appropriate plant processing conditions in regard to alkali can be selected. Additional valuable information can be gained by simply filling centrifuge tube to the 100 ml mark with samples taken at various points in the plant process and centrifuging at full speed for 10 min to ascertain the following:

1. The amount of water and suspended matter in crude oil going into the process. This will detect excess sediment or dilution of the crude with water or condensed steam.
2. The amount of foots in crude-alkali mixture going to the centrifuge. This provides a check on loss being attained and operation of the proportioning equipment.
3. The amount of foots in the refined oil leaving the centrifuge. This indicates whether the centri-

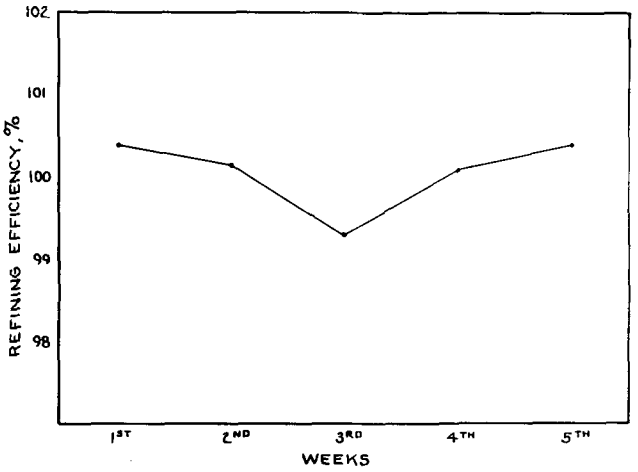

FIG. 4. Refining efficiency of plant operations based on laboratory centrifugal method.

fuges are operating propertly.

4. The amount of free water separable from oil before and after drying, which indicates whether wash water has been sufficiently removed before drying and whether drying is complete.

Efficiency of Plant Refining

The centrifugal method presented here is similar enough to centrifugal refining in the plant so that it is a good means of estimating the efficiency of the plant process. This can be expressed for intervals of hour, shift, day, or week as is appropriate. An essential requirement is an accurate accounting of wt of crude oil processed and refined oil produced so that the percent yield computed from wt can be compared with the percent yield as predicted by the centrifugal test method. The refining efficiency of a plant may be calculated as follows.

$$\text{Refining Efficiency} = \frac{\text{Actual Yield}}{\text{Predicted Yield}} \times 100$$

Figure 4 shows graphically the refining efficiency calculated on a weekly basis for a 5-week period. These data clearly indicate the close relationship that exists between the total refined oil obtained in the plant compared with that calculated from the laboratory centrifugal refining method data.

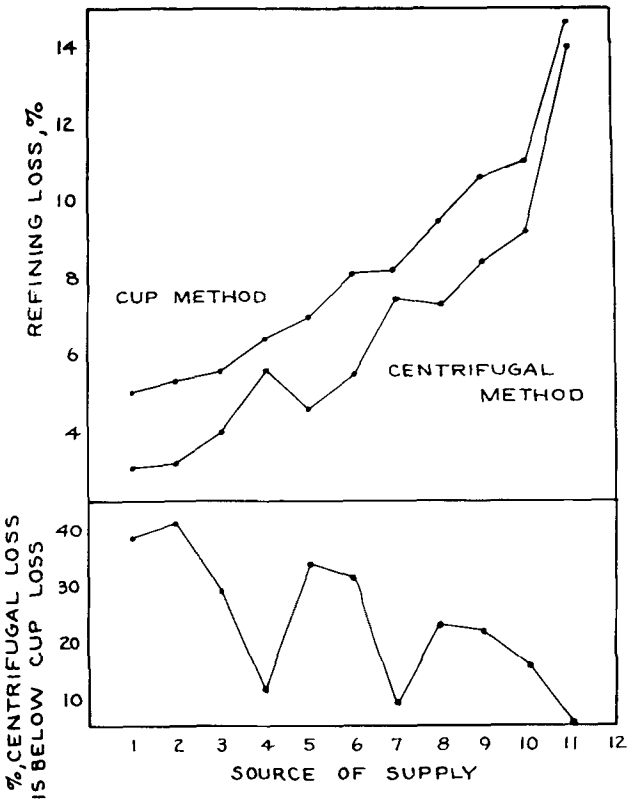

FIG. 5. Relationship between refining loss data by cup and laboratory centrifugal method.

It is known in the refining industry that the cup test is not an accurate index of the amount of refined oil that may be expected from the crude oil centrifugally refined. Crudes with similar cup loses may yield different amounts of refined oil. This clearly illustrated in Figure 5, which shows analyses made on crude oil from widely different sources and produced under different operating conditions. The data in Figure 5 are arranged in the order of increasing cup loss. The graph showing the percent the centrifugal loss is below the cup loss most clearly illustrates the difference in the characteristics of crude cottonseed oils from different sources. Similar differences, but

TABLE II

Example of Tests on Crude Cottonseed and Crude Soybean Oil

Sample	F.F.A. %	Cup Loss, %	% Loss and Color [1] by Centrifuge Test Using					
			15%			20%		
			2.5% Loss-Color	3.5% Loss-Color	5.0% Loss-Color	2.5% Loss-Color	3.5% Loss-Color	5.0% Loss-Color
Crude Cottonseed Oil								
1	1.4	7.0	3.9–.66	5.2–.59		4.9–.57	5.7–.56	
2	1.7	6.6	4.9–.60	4.2–.60		4.6–.56	4.5–.60	
3	2.0	7.0	5.9–.59	5.3–.55		6.1–.51	5.8–.51	
4	2.2	9.5		7.5–.75	8.2–.62		7.7–.62	8.1–.58
5	2.5	10.3		6.9–.78	7.5–.72		7.4–.70	7.4–.68
6	2.6	9.1		8.0–.64	7.2–.63		8.0–.58	7.6–.58
7	2.8	11.7		9.5–.57	11.4–.51		9.8–.55	13.7–.51
8	5.0	17.7		12.4–.73	12.8–.70		13.2–.70	13.1–.65
Crude Soybean Oil [2]			8%			10%		
			2% Loss	3% Loss		2% Loss	3% Loss	
9	0.5	3.3	2.4	3.2		2.8	3.2	
10	0.7	4.5	3.5	3.7		3.5	2.7	
11	0.7	4.9	2.9	3.1		3.2	2.9	
12	0.8	5.0	3.9	4.4		3.5	4.0	
13	0.8	4.9	3.3	3.4		3.1	3.3	

[1] Optical density at 500 mμ using a 25 mm round cuvette.
[2] Color was light enough in all cases so it did not have to be considered.

of a much smaller magnitude, have been observed in soybean oil.

Use in Conjunction with Trading

By proper utilization of the knowledge of actual refining characteristics of crude oils, as defined by the centrifugal method in contrast to the trading method (cup loss), the more valuable or profitable oils can be identified readily. Examination, by the centrifugal method of a cross section of crude cottonseed oils, revealed that in general the crude oils with lower refining losses are more profitable to refine in terms of yield per dollar invested than the high loss, discounted oils. Also, it becomes evident that crude oils from some mills yield a consistently better return than those from other mills. The same approach can be made when trading is on the basis of total neutral oil as determined by the chromatographic loss method (3). However, in the opinion of the authors, the advantage that might be gained under such conditions is lessened in that differences become less dramatic and the direction is reversed. This applies because chromatographic loss represents an estimate of the amount of oil available for recovery but without reference to the possibility of attaining such levels by specific processing techniques. Examples of the variation of the loss, characteristic of crude cottonseed oils, as determined by cup loss, centrifuge loss and chromatographic loss methods are given in Table III. These data indicate that while the chromatographic loss method gives the minimum loss that might be attained, the refinery loss will vary from this value depending on the characteristics of the crude.

TABLE III

Refining Loss by Different Methods for Crude Cottonseed Oils from Different Sources

Source	Refining Loss %, by Method		
	Cup	Centrifuge	Chromatographic
1	7.4	6.3	3.2
2	7.3	4.5	3.0
3	7.2	6.8	3.1
4	7.1	4.0	3.4
5	6.8	3.6	2.8
6	5.8	2.9	2.6

Analyses for each source are the average of analyses for 3 or more cars of crude oil.

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[Received May 9, 1963—Accepted September 10, 1963]

Quick and Simple Methods for Studying Crystallization Behavior of Fats

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Abstract

A simple method of obtaining reproducible cooling curves has been developed. A microscopical technique is described for determining melting point and transformation time of the unstable α-form, which has a marked influence on the consistency of commercial fats.

A correlation between the transformation time and the shape of the cooling curve has been found. Examples of the application of the cooling curve technique in factory control are given and discussed.

Introduction

THE CRYSTALLIZATION behavior of commercial fats used in margarine manufacture has been studied in order to investigate the causes of variations in the consistency of the margarine. For this purpose we have applied a special cooling curve method, and have also made microscopical examinations of the fats when crystallizing.

Cooling curve methods have long been employed to characterize fats of different kinds (1,2,3) and especially cocoa butter (4). A recent work describes the use of cooling curve analyses in conjunction with Differential Thermal Analyzing techniques (5).

Microscopical studies were made to investigate the behavior of fats when shock-crystallized, and to note the changes of the fat crystals occurring soon after chilling.

Experimental

Cooling Curves. As the cooling curve technique is empirical, the methods described in the literature give curves of different character, depending on the rate of cooling. In the following method the cooling rate is standardized by keeping the fat in a vacuum jacket flask in an ice-water bath. The fat is cooled evenly without stirring. In a horizontal center section of the flask crystallization occurs simultaneously all through the fat. The phase changes during crystallization accompanied by heat effects are detectable from changes in the slope of the curve. Most fats exhibit characteristic behavior, and minor changes in the composition of these fats are reflected by variations in the cooling curve.

Apparatus. The flask used is according to Shukoff (Fig. 1). It is essential to standardize vacuum in the jacket and the dimensions of the Shukoff flask so that the rate of cooling is the same for different flasks. Capacity of the inner tube of the flask is 30 ml and the jacket is evacuated to 10^{-2} mm Hg. Dimensions are given in Figure 1.

The flasks are most easily checked by making a cooling curve for a deodorized liquid oil, i.e., soybean oil. The temperature fall for a liquid oil in the Shukoff flask in an ice-water bath shall be from 40C to 18.5C ± 0.3 in 20 min.

The thermometer range is 0–50C with 0.1C subdivisions; Length is ca. 40 cm; Diameter of bulb 6 mm, length 12 mm. The thermometer is fitted to the flask with a ground joint, with the mercury bulb exactly in the center of the inner flask. The joint could be scratched, making the removal of the thermometer easier.

A Dewar bottle, ca. 1 liter is filled with ice-water at 0C. Times of cooling are measured with a stop watch.

Procedure. Heat the sample to 70C until all crystal