Isolation of Volatile Constituents from Fats and Oils by Vacuum Degassing

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A description is given of an all-glass, high-vacuum (10^{-5} to 10^{-6} mm.) laboratory apparatus, to be used for the quantitative recovery of volatile constituents from oils and fats.

Up to 1 kg. of oil can be treated per day. To prevent decomposition of the oil, only moderately elevated temperatures are used. The distillate obtained can be transferred quantitatively to chromatographic columns.

Model experiments are described to show the efficiency of the degassing and the factors involved.

IN THE LAST DECADE considerable interest has been shown in the volatile substances in edible fats and oils in connection with stability problems. Certain disadvantages however attach to the methods of isolation.

Extraction procedures necessitate large volumes of solvent, which afterwards have to be removed by evaporation. Serious losses of the compounds sought can occur while traces of impurities in even highly-purified solvents thus become concentrated and contaminate the residue.

Steam distillation requires elevated temperatures, thereby promoting hydrolysis and decomposition reactions. In many experiments the distillate has to be extracted with the disadvantages just mentioned.

Alternatively, molecular distillation can be used. With the conventional apparatus high temperatures are required while the small amount of distillate, often containing substances of high molecular weight, has to be recovered from the relatively large condenser surface.

This paper describes a method embodying the following advantages. The use of solvent can be avoided. The volatile concentrate is obtained in a form suitable for subsequent analysis. Moderate temperatures can be used. The volatile matter is obtained in a straightforward way, which is less laborious and time-consuming than the conventional methods.

The technique described is a modification of molecular distillation (1) and has already been briefly mentioned in a preliminary publication (2). Because small amounts of material of a wide range of volatility are to be condensed in small cold traps, the apparatus differs from conventional molecular-distillation equipment.

In their publication on the volatile constituents of the onion Niegisch and Stahl (3) have described a high-vacuum degassing method, based on the same principle as ours. Their apparatus however differs in construction and use.

Apparatus and Operating Conditions

The degassing is carried out in batches in a flask of appropriate capacity; the upper limit of a batch is *ca.* 200 g. Using a suitable high-vacuum system, four to five batches can be treated simultaneously. Small amounts of 1 g. of oil or less can be treated without difficulty. During the course of the investigation it appeared that for our purpose three types of degassing units had to be developed.

a) Degassing Units

1. *The U-tube Unit (Figure 1).* In this unit, samples of from 1 to 40 g. are degassed in 80-ml. flasks, larger samples (to 200 g.) in 800-ml. flasks. To facilitate stirring and to enlarge the liquid surface, the bottom is flattened. The flask (A) is heated in an oil-bath placed on a hot plate with a magnetic stirrer. The unit is carefully evacuated. When strong foaming occurs, evacuation must be carried out very slowly, using a high stirring speed. After completion of the degassing the system is closed, the heating of the unit (A and B) is discontinued and dry nitrogen is carefully introduced through D. When atmospheric pressure has been reached, C is disconnected and quickly rinsed with a small volume of solvent. This unit is specially useful when the distillate obtained must be taken up in a small volume of solvent for further investigation (column chromatography; preparation of derivatives). The unit is fitted to the high-vacuum system at H (Figure 4).

2. *The Spiral-Capillary Unit (Figure 2).* With this apparatus quantitative transfer without use of a solvent is possible. Quantitative recovery however is limited to compounds with a boiling point below 150°C. at 769 mm. Degassing is carried out in the same way as described above. After completion of the degassing, S_1 and S_2 are closed and the contents of B are distilled into the capillary C. To this end B is turned upside down and is no longer cooled but gently heated (using e.g. hot air) while C is cooled, starting from the lower end and gradually raising the liquid nitrogen. C is subsequently sealed off and transferred to the gas-chromatography column,

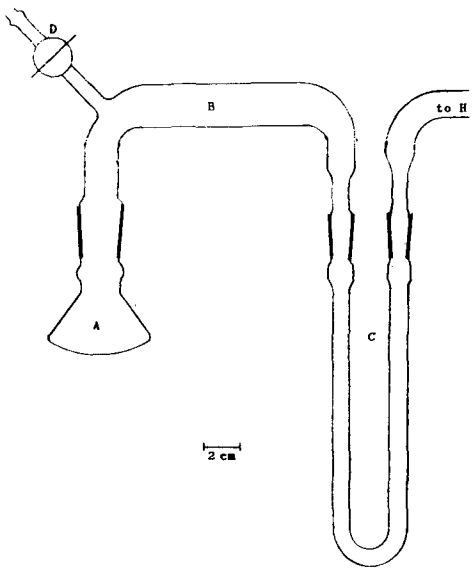

FIG. 1. U-tube apparatus. A. degassing flask with flattened bottom. B. connecting bridge wound with resistance wire. C. cold trap (internal diam. 8 or 14 mm.) placed in liquid nitrogen. D. dry nitrogen inlet.

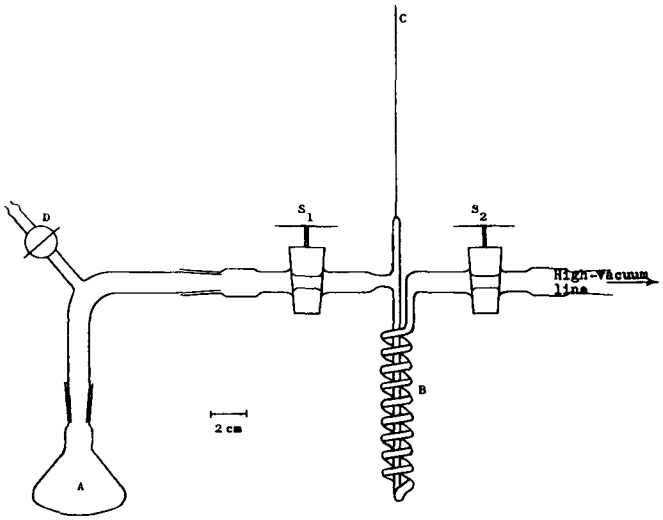

FIG. 2. Spiral-capillary apparatus. A. degassing flask. B. spiral collector placed in liquid nitrogen. C. capillary (2,5–3 mm.)

where it is crushed in a special device without disturbing the equilibrium in the column (Figure 2a).

The capillary is placed in space F; the crusher is then closed with the screw-cap A. The nitrogen supply is opened and flows through the crusher, at E, into the column. The capillary is also heated to the desired temperature in this way.

By turning handle B, the capillary is pressed by the pegs on spindle C against the wall of F, in which there are recesses, and crushed.

The degassing product is then brought onto the column by the carrier gas.

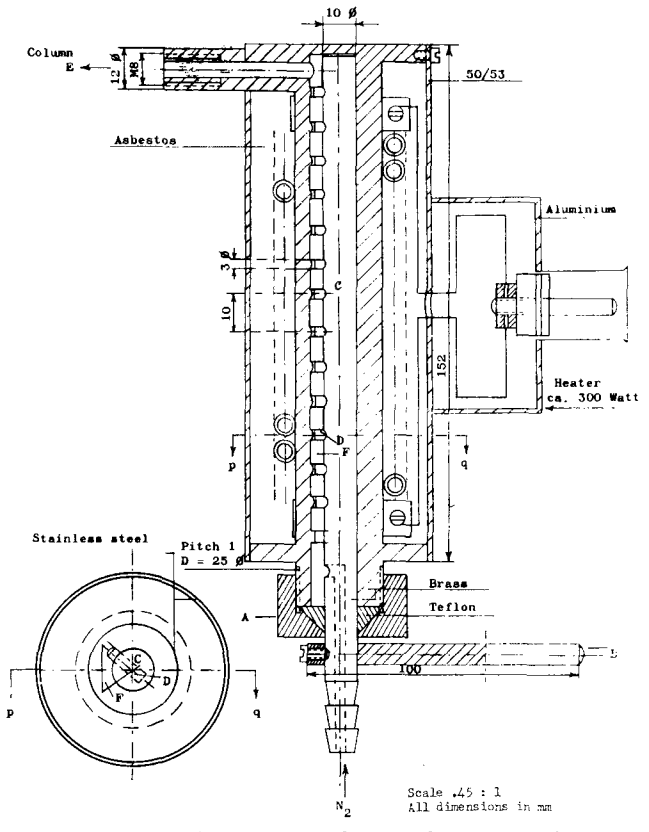

FIG. 2a. Capillary crusher for gas chromatography.

3. *The Cold-Finger Unit (Figure 3).* Because of its greater efficiency, small distance between evaporating and condensing surface, lower temperatures can be used in the cold finger unit than in the other degassing units. The increased efficiency can sometimes be a drawback, *e.g.*, where only the more volatile substances are of interest and the less volatile ones may interfere with the subsequent analysis.

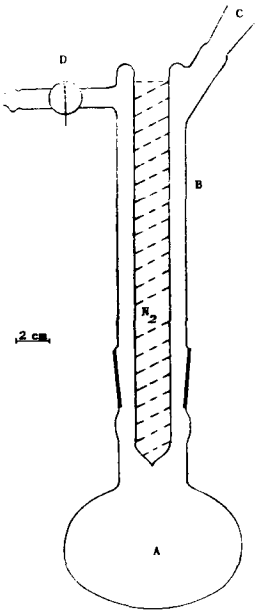

FIG. 3. Cold-finger apparatus. A. degassing flask. B. cold finger. C. side tube to high-vacuum line. D. dry nitrogen inlet.

After completion of the degassing and introduction of dry nitrogen a separating funnel is fitted into side-tube C. The tip of this funnel should touch the inner tube of the cold finger. With little solvent the condensed product can be washed down. This apparatus can be used for substances with relatively low volatility. When gas-chromatographic analysis of the distillate is desired, the side-tube has to be fitted with two taps B and C (Figure 3a). After degassing while A is kept filled with liquid nitrogen, dry nitrogen is admitted through C while B is closed. At atmospheric pressure flask A is quickly exchanged for capillary D or E, and the unit is evacuated. B is then closed, and the volatiles are distilled in D or E.

b) High-Vacuum System (Figure 4)

This system is based on the principles described by Riegel *et al.* (4). The pressure in the manifold A is maintained at 10^{-5} –10^{-6} mm. Hg. (The ultimate vacuum of pump C is better than 10^{-6} mm. Hg; displacement 12 l/sec.) The pressure in the exhaust line B is maintained at 10^{-3} mm. by pump E.

Traps F and F', cooled in liquid nitrogen, serve to prevent condensable gases from entering the pumps and mercury vapor from entering the manifold. A water-failure guard (5) protects the diffusion pump if water supply fails. The stopcock arrangement between A and B is sketched in Figure 4a. The exhaust line B serves to evacuate the degassing units to 10^{-3} mm. (in *ca.* 40 min.), which may then be connected to the manifold without causing an appreciable rise in pressure. Introduction of a new degassing unit does not impair the efficiency of a degassing already

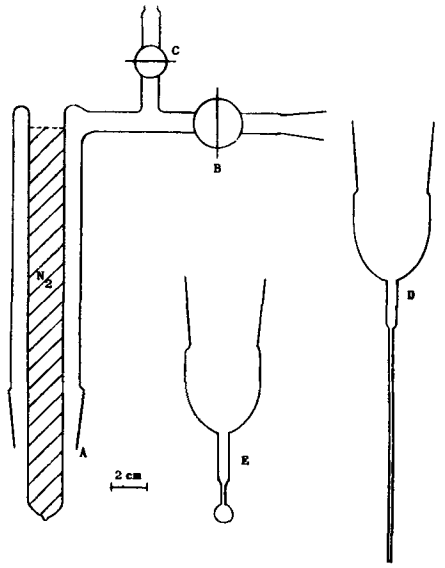

FIG. 3a. Variant of the cold-finger apparatus.

in progress. The pressure in the exhaust line is indicative of the rate of pumping. The initial pressure in the exhaust line should be 10^{-3} mm. Hg. Using a normal evacuation rate, a pressure increase of 1 mm. Hg per degassing unit on starting the evacuation is found. This increase is obviously dependent on the dimensions of the apparatus and the pump capacity. A better control on the evacuation rate is described below. When working with the spiral capillary unit, which is primarily designed for the isolation of highly volatile substances, evacuation needs special care and the simple use of L would not be satisfactory.

Precise control is achieved by the use of a precision vacuum valve (Figure 5), inserted between the degassing unit and the high-vacuum system. Evacuation takes place *via* D, B′, A, and C and is controlled by opening the valve slowly by means of the micrometer-screw. When a pressure of about 50 microns has been reached, E is opened to short-circuit valve A as the conductance of A is too low to give a good connection to the high-vacuum system.

In this way the evacuation rate is reproducible and can be satisfactorily controlled. The free air pressure in A is measured by gauge M. A Pirani gauge with four gauge heads and an ionization manometer were used for pressure measurements in the high-vacuum line and the degassing units. All the switches and pilot lights are mounted on a panel board.

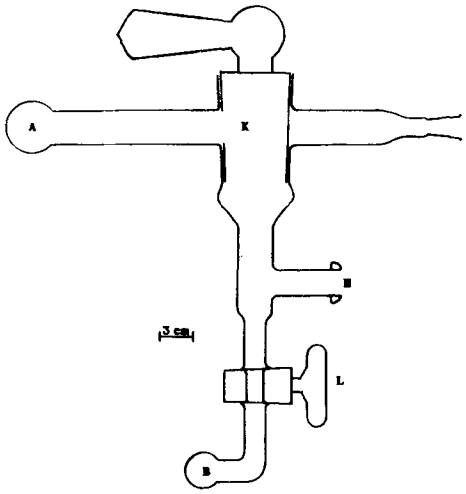

FIG. 4a. Stopcock-arrangement in high-vacuum system.

Evacuation of the apparatus can be carried out as follows. Close stopcocks K, L, O, and O′. Open P and P′. Cool the traps F and F′ with liquid nitrogen. Start the pumps E and D, close P and P′, and open O and O′. When the pressure in the manifold has dropped below 10 mm., start the diffusion pump

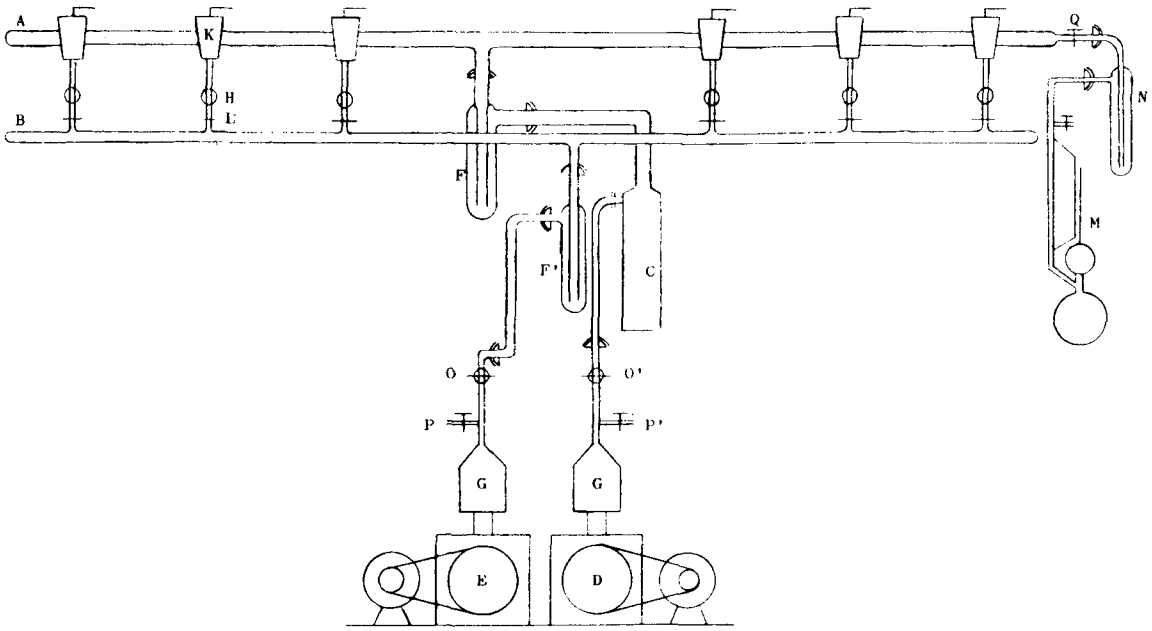

FIG. 4. High-vacuum system. A. manifold vacuum line. B. exhaust vacuum line. C. metal mercury diffusion pump (Leybold Hg 12). D,E. ordinary rotary pumps (Edwards' Speedivac 2 Sc 20). F,F′. Cold traps placed in liquid nitrogen. G. nonreturn valves. H. ground-glass ball-joint outlets. K. wide-bore stopcocks. M. McLeod pressure gauge. N. liquid nitrogen trap. L. narrow-bore stopcocks.

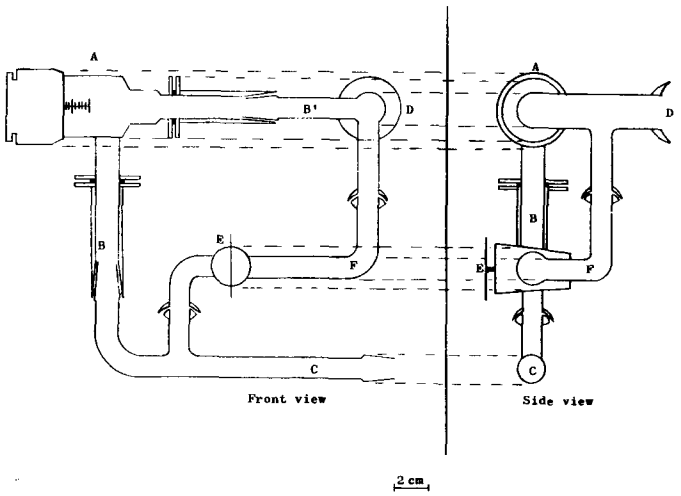

FIG. 5. Precision vacuum valve.

C. In a vacuum-tight system, high vacuum (10^{-5} to 10^{-6} mm.) should be reached in 15 min. After degassing, switch off pump C and allow to cool for about 20 min. Close stopcocks O and O', open P and P', and stop the pumps D and E. Connect the dry nitrogen gas supply to one of the joints H, and fill the system with gas through the stopcock K and L. Trap N, protecting the McLeod, must be cooled with liquid nitrogen. In the long run, dry ice-acetone cannot prevent mercury vapors from entering the system.

Ground-glass joints are lubricated with Apiezon L when used at room temperature, and with Apiezon T when used at elevated temperatures. For our purpose silicone high-vacuum grease was unsatisfactory as it contains volatile substances.

Model Experiments

To check the efficiency of the apparatus and the influence of temperature, time, pressure, concentration, etc., model experiments were carried out with various test solutions.

As volatile substances, aliphatic carbonyl compounds, cinnamaldehyde, cinnamic acid, phenanthrene, and pyrene, were chosen. The carbonyls can easily be determined as their 2,4-dinitrophenyl-hydrazones, the other compounds by ultraviolet absorption measurements. The concentrations of the volatile substances varied between 40 and 400 p.p.m.

As nonvolatile solvents, degassed peanut oil (PNO), di-n-octylphthalate (DOP), and di-(2-ethylhexyl- sebacate (DEHS) were used. It was found to be difficult to obtain a PNO of constant quality. Moreover development of flavors severely limited its storage properties. For the same reason DOP is not of general applicability. The distillate is sometimes contaminated by traces of this solvent. The best results were achieved with DEHS, which has a lower vapor pressure than DOP. After careful purification (molecular distillation and degassing), in DEHS, n_D^{25} 1.4488 (6) no decomposition takes place, and it can be used for about two months.

a) Comparison of the Three Degassing Units

For the recovery of a volatile compound from an oil or a nonvolatile solvent, the choice of the degassing unit is of great importance. Comparison of the three units gave the results shown in Table I.

TABLE I

Comparison of Degassing Units

Test solutions: phenanthrene (0.7 mg.) in 5 g. of DEHS; hexanone-2 and undecanone (0.8 mg.) in 15 g. DEHS
Pressure: $10^{-5} - 10^{-6}$ mm. Hg

Unit	Time (hrs.)	Temp. (°C.)	Yield (%)		
			Phenanthrene	Hexanone-2	Undecanone-2
U-tube	3	70	25[a]	.....	.....
Cold finger	1	70	90	.....	.....
Spiral capillary	3	50	....	100	18
Cold finger	2	50	....	100	100

[a] Poor reproducibility.

b) Influence of Stirring, Pressure, and Temperature

In molecular distillation (7) the diffusion of volatile compounds from the body of the liquid to the surface can become the rate-determining factor. To prevent this, stirring is essential. The following experiment is illustrative. Cinnamic acid (0.2 mg.) in DOP (5 g.) was degassed for 2 hrs. at 75°C. and 5.10^{-5} mm. The recovery was 45% without stirring and 74% with stirring. Variations in pressure from 5.10^{-5} to 10^{-6} mm. appeared scarcely to affect the yield.

The influence of the temperature is illustrated by some examples in Figure 6a. The yield increases strongly with the temperature, which is according to expectations. The choice of the type of unit is important (cf. the recoveries of cinnamic acid and phenanthrene having b.p. of 300 and 340°C. at 760 mm., respectively).

c) Time/Concentration Relation

Figure 6b shows the relation between recovery and time at three different temperatures, starting with the same initial concentration of phenanthrene (144 p.p.m.). Table II gives the results of a series of experiments, using various initial concentrations.

It can be assumed that the number of molecules leaving the surface of the liquid in unit time is, at any moment, proportional to the concentration in the liquid. Applying first-order reaction kinetics to this process, it follows that

$$-\frac{dc}{dt} = kc \text{ or } \ln\frac{c}{c_0} = -Kt.$$

Using the values in the last column of Table II, K was calculated and was indeed found to be constant: K = 0.25 hrs.$^{-1}$; standard deviation: 0.04.

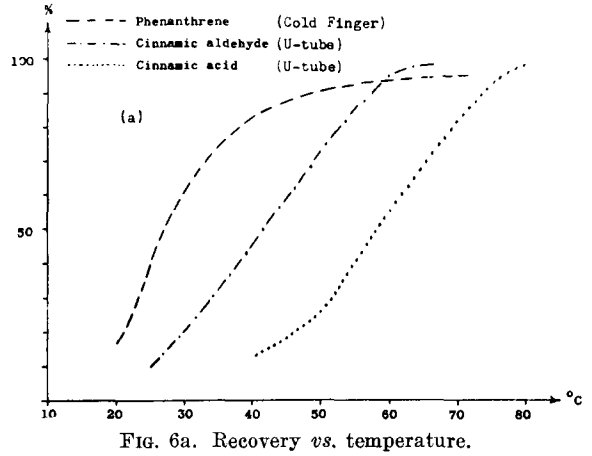

FIG. 6a. Recovery *vs.* temperature.

TABLE II

Degassing of Phenanthrene in DEHS (5 g.) at 25°C. and 10^{-5} to 10^{-6} mm. Hg in Cold Finger Unit

Expt.	Time (hrs.)	Initial concentration (p.p.m.)	Yield (%)	Residual concentration [a] (p.p.m.)
1	1	144	20	115
2	2	144	39	87
3	3	144	59	59
4	3	58	56	25
5	3	291	50	146
6	3	72	50	38

[a] Calculated by subtraction of the distillation yield from the initially dissolved phenanthrene.

Scope and Limitations of the Method

The aim of the degassing of fats and oils is twofold: isolation of volatile, odoriferous substances in a form which allows further investigation, and preparation of tasteless oil samples for stability studies.

Isolation of volatiles can be achieved with all three degassing units; each of them has its merits. Although the cold finger is evidently by far the most efficient, the spiral capillary is to be preferred when only the highly volatile substances are of interest. The U-tube is used for routine work, generally when larger amounts of distillate are expected and when higher temperatures are necessary. To overcome the relatively long distance between flask and condenser, the connecting bridge B (Figure 1) can be heated electrically to the same temperature as (or slightly higher than) the sample.

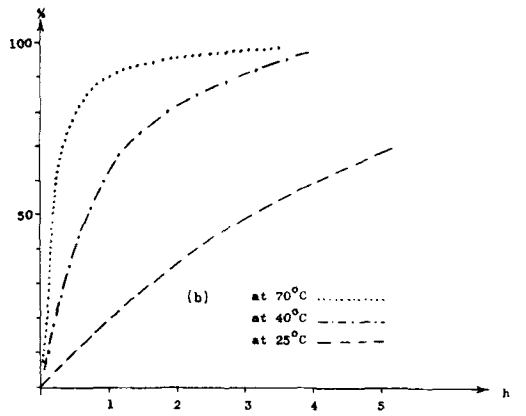

FIG. 6b. Recovery of phenanthrene *vs.* time (cold-finger).

When the total removal of volatile matter is required at the lowest possible temperature (*e.g.*, to prevent decomposition of the sample), the cold finger unit should be used. When, for example, PNO (peroxide content 4.4 mmole per kg.) with a definite "nutty' flavor was degassed for 3 hrs. at 60°C., the residual oil (peroxide content 4.3 mmole per kg.) was found to be completely tasteless. At the temperature used, no appreciable decomposition of peroxides had occurred, demonstrating that the peroxides of PNO are tasteless. This is in agreement with observations of Lea (8).

One of the drawbacks of the degassing method is that only small samples can be treated. By using the manifold a total of 1 kg. oil can be degassed per day. As flavor compounds often occur in extremely low concentrations, the distillate obtained may still be insufficient to permit unambiguous physical and chemical identification.

Water is always present in the samples to be degassed and forms another problem because it may interfere with subsequent analysis, *e.g.*, gas chromatography. Drying before degassing with conventional drying agents (*e.g.*, sodium sulfate) or with a molecular sieve of the Linde type does not always lead to satisfactory results.

The water may also be removed from the distillate by fractional distillation in accordance with the method of Niegisch and Stahl (3). Their degassing methods are similar to that described in this paper. In our method lower pressures are used, thereby reducing the degassing time. Moreover their trapping system is rather complicated and tends to spread the distillate over a much larger surface, which hampers the recovery.

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[Received May 18, 1960]

Filtration-Extraction of Safflower Seed on a Bench Scale

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Data are presented to show that filtration-extraction can be successfully applied on a bench-scale to extract whole or decorticated safflower seed to a residual lipids content in meal of about 1.0%.

Recommended procedure and operating conditions for processing this seed are given. These were found to be adequate within the limitations of the study and are not to be considered optimum. They are similar to those employed for filtration-extraction of most high-oil-content materials except that, for safflower, severe initial rolling is necessary and that efficient processing of decorticated seed requires an additional step of rerolling of the cooked materials prior to extraction.

Based on the close correlation obtained to date between bench- and industrial-scale filtration-extraction results for a wide variety of oil crops, there should be little difficulty encountered in the processing of safflower on a commercial scale.

SAFFLOWER, a relatively new cash oilseed crop in the United States, is now a well-established and profitable source of oil for the surface-coating industry and of protein for livestock feeds (1). Production of this seed has increased from about 34 million pounds in 1950 to about 228 million pounds in 1959 (2). Trade sources estimate the 1960 crop at 274 million pounds.

Safflower seed oil is a high-grade product for industrial and food uses. The meal is low in protein (18–

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