

Steam Distillation-Solvent Extraction Recovery of Volatiles from Fats and Oils

Roy Teranishi,* Edwin L. Murphy, and Thomas R. Mon

This system combines steam distillation and liquid-liquid extraction to recover volatiles from fats and oils. Oil is pumped in at the top of a spinning-band distillation column, in which the oil is heated to 100 °C and spread to a thin film. As the oil film drops down to the pot, steam, which is introduced at the bottom, travels upward to strip the volatiles from the oil. The steam distillate is extracted in a liquid-liquid extractor incorporated in the system, and the extracted water is recycled as steam. Stripped oil in the pot serves as a liquid seal to force steam up the column. The level of the oil in the pot is maintained automatically by an overflow system. Many liters of oil can be pumped through this system to be stripped of volatiles by steam. The volatiles can be isolated easily from the small amount of solvent recycled in the liquid-liquid extractor.

Steam distillation, sweeping with an inert gas, and high vacuum distillation are some methods used to remove volatiles from lipids (Teranishi et al., 1971; Chang, 1976). Buttery and co-workers (1973) have shown that the air/solution partition coefficient of the C₈ aldehyde is 500 times less in a vegetable oil system than in a water system. If we extrapolate to C₁₀, we note that the difference is over 10 000. These data explain why it is so difficult to obtain volatiles from lipid systems by sweeping with an inert gas or by high vacuum distillation. If an inert gas is used to sweep volatiles from a lipid, volatiles are diluted in the gas, and the dew point becomes so low that it becomes very difficult to condense the desired material quantitatively. A similar situation exists with high vacuum distillation with difficulties in getting the volatiles away from the lipid phase and also in condensing the desired material.

Offending odors can be blown out of oils with steam, a well-known commercial practice. In order to study the odor qualities of odoriferous materials blown out of oils, such materials must be collected and isolated. The principal advantage in using steam is that the volatiles are easily condensed with water. The disadvantage of having the volatiles in a dilute solution in water is overcome by the simultaneous liquid-liquid extraction. This combination of a liquid-liquid extractor with a continuous steam distillation system permits the isolation of odoriferous materials from large amounts of oil in one step. Recycling of both water-steam and solvent affords minimal introduction of artifacts.

EXPERIMENTAL SECTION

Materials. Oleic acid, commercial grade, Neo Fat 94-04, 400 lbs. in a 55-gal drum, was purchased from Armac Chemical Division, La Mirada, Calif. Distilled water was used in the steam generator. Ethyl ether, reagent grade, was purchased from J. T. Baker Chemical Company, Phillipsburg, N.J.

Distillation Equipment. The semi-works spinning-band distillation column, stainless steel mesh band, 23 mm × 91 cm, with automatic takeoff, was purchased from Nester/Faust, now part of Perkin-Elmer Corporation, Norwalk, Conn.

Extractor. The liquid-liquid extractor was made from glass ball and socket and standard taper joints and Pyrex tubing by one of the authors (R.T.).

Pump. The Zenith metering pump, size 1/2, was purchased from the Zenith Product Company, West

Newton, Mass. The pump was driven by an electric motor equipped with a variable-speed transmission, Graham Transmissions, Inc., Model No. 29MW45, output 0-24 rpm, purchased from Graham Transmissions, Inc., Menomonee Falls, Wis.

Procedure. Figure 1 shows a flow diagram of the entire system. Oil, or heated fat, is pumped to the top of a spinning-band column, which is heated to 100-105 °C. The oil is wiped to a thin film by the rapidly spinning band. As the film falls to the pot, it is in contact with steam, which is introduced at the pot. The steam and volatiles from the oil are condensed and extracted with a liquid-liquid extractor. The extracted water flows into a steam generator, and the water is continuously recycled as steam. The volatiles are extracted into a small volume of ethyl ether, which is also being continuously recycled. The ether can be stripped with a small distillation system to isolate the volatiles.

Figure 2 shows the head of the spinning-band column. The oil is added where the reflux is normally returned to the column. All the steam and volatiles, as well as any condensate, are taken off to the condenser of the liquid-liquid extractor. The spinning-band column is heated to 100-105 °C. The oil is quickly heated so that only the top few centimeters of the column show an emulsion of water and oil. The oil is swept downward as a thin film by the spinning band as the steam rises upward to strip off the volatiles.

Figure 3 shows the liquid-liquid extractor and steam generator. Condensate from the spinning-band column is extracted by the solvent being recycled continuously. The second, lower condenser is to maintain the temperature of the condensate low enough to make certain that only the ether in the solvent pot boils. The heights of the solvent overflow and water overflow systems must be adjusted to keep ether from overflowing into the steam generator and water from overflowing into the solvent pot. Also, the water overflow must go into a chamber large enough that the walls are not wet. If the walls do wet, water and then ether are siphoned into the steam generator, where the ether vaporizes almost explosively, a dangerous and undesirable situation, to say the least. If the proper levels are maintained, the overflow water smoothly flows into the steam generator pot, where the rate of steam throughput is controlled by the current passed through the heating mantle under the steam generator pot. Similarly, the rate of solvent recycled to extract the volatiles is controlled by the current passed through the heating mantle under the solvent pot.

Figure 4 shows the spinning-band distillation column pot. Volatiles in the oil are carried out with the steam,

Western Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Berkeley, California 94710.

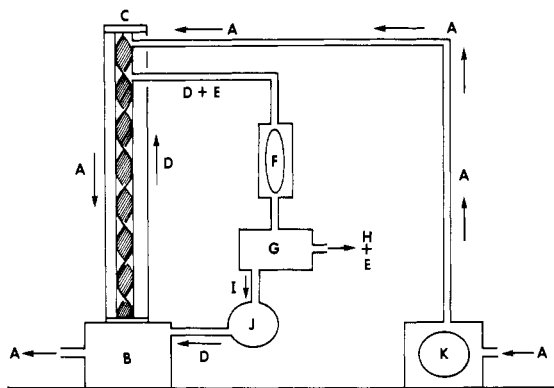


Figure 1. Flow diagram of entire system: (A) oil to be extracted, (B) spinning-band distillation pot, (C) spinning band column, (D) steam, (E) volatiles, (F) condenser, (G) liquid-liquid extractor, (H) solvent, (I) water, (J) steam generator, (K) pump.

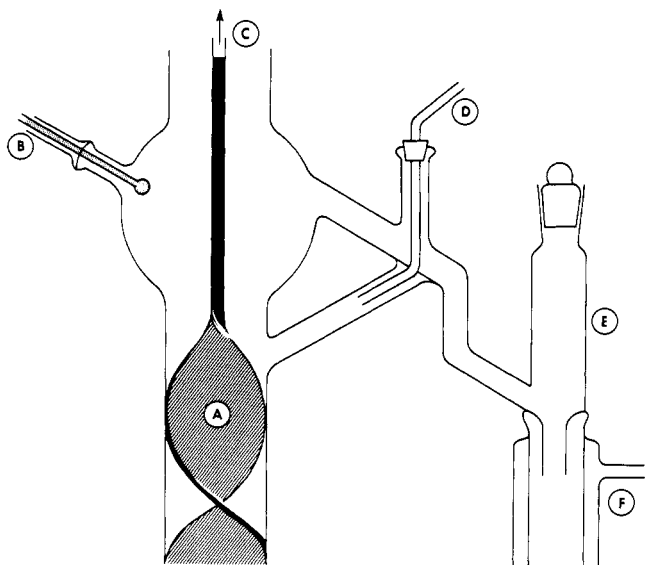


Figure 2. Spinning-band still head: (A) spinning-band column, (B) thermometer, (C) to motor, (D) oil input, (E) takeoff, (F) condenser.

which is introduced into the pot where the thermocouple is normally situated to indicate the pot temperature. The spent oil in the pot forms a liquid seal so that the steam is forced up the column. The level of the pot oil is maintained by adjusting the tilt of the stainless steel tubing connected to the bottom of the pot. The pot is covered with a heating mantle and is maintained at about 150 °C to make certain that the steam does not condense in the pot and that only oil flows out the bottom of the pot.

RESULTS AND DISCUSSION

As any researcher in flavor has found, if the desired sensory properties are destroyed or if off-flavors are developed (so that the good characteristic odors are masked beyond recognition), the isolation process being used must be discarded for one that will succeed, no matter how tedious and time consuming the successful one is. Many flavor studies cannot reach the point of correlations between chemical structures and sensory properties because not enough material can be isolated for definitive work. This system described here is applicable only in situations in which volatiles will survive steam distillation conditions, but where applicable, this system will permit processing large amounts of starting material to yield sufficient isolated material for detailed studies.

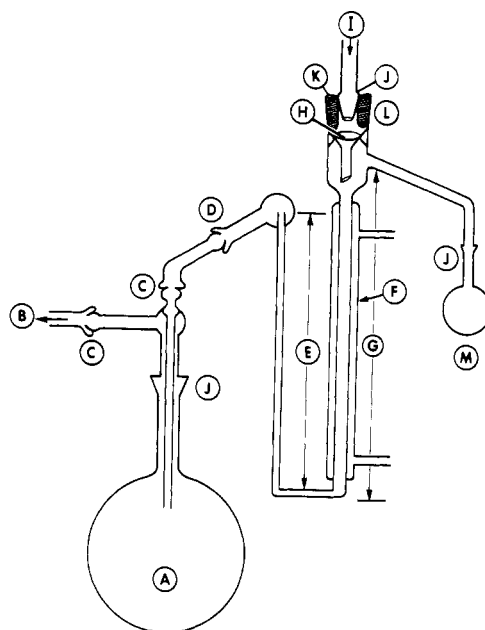


Figure 3. Liquid-liquid extractor and steam generator: (A) steam generator pot, 1000-mL round-bottom flask heated with glass-col mantle, (B) steam to spinning-band column, (C) 18/9 ball-socket joint, (D) 28/15 ball-socket joint, (E) 22 cm height, (F) condenser, (G) 30 cm height, (H) funnel, (I) condensate from spinning-band column, (J) 24/40 standard taper joint, (K) bushing, (L) 34/45 standard taper joint, (M) solvent pot.

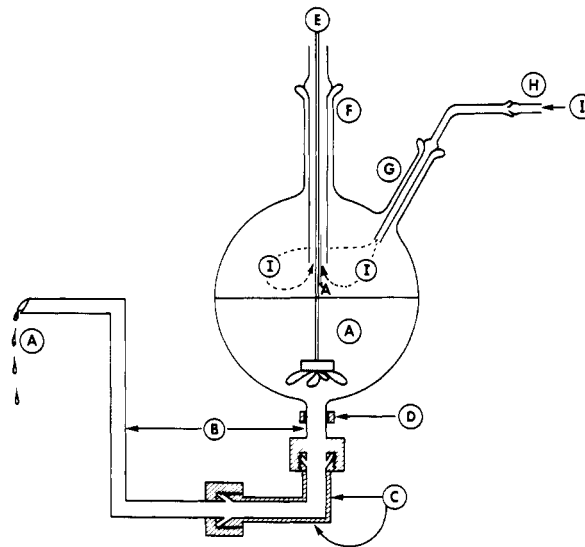


Figure 4. Spinning-band distillation pot: (A) spent oil, (B) $\frac{1}{4}$ in. o.d. s.s. tubing, (C) s.s. "L" joint, (D) glass to metal seal, (E) spinning-band column, (F) 29/26 standard taper joint, (G) thermocouple well used as steam inlet, (H) 18/9 ball-socket joint, (I) steam.

The air/solution partition coefficients mentioned earlier (Buttery et al., 1973) are for equilibrium conditions at 25 °C. The conditions in the spinning-band column are far from equilibrium, but there are two advantages: the oil and steam flow countercurrent and the temperature is elevated to 100 °C so that the organic material vapor pressures are considerable higher than at 25 °C. However, at this time, the effectiveness of stripping can only be evaluated qualitatively by sniffing the oil going in and the oil coming out and noting whether the oil coming out has considerably less odor. The quantitative effectiveness can be assessed only by a detailed study similar to that by Schultz et al. (1976). This type of study is also needed to

establish optimum conditions.

The spinning-band column is especially well suited for this system because there is very little pressure drop across this type of column. For this reason only a very small amount of liquid is needed to form a liquid seal to force the steam up the column. Also, because of the rapidly spinning band and stirrer in the pot, there is little bumping and surging, and thus, the simple overflow system works very smoothly.

Artifacts from large amounts of steam are greatly reduced since only a very small amount of water is used. Artifacts from the solvent are also kept at a minimum since only a small amount of solvent is used and high-purity material can be afforded. Mechanical losses are kept down because few manual transfers are necessary. Entrainment losses are kept to a minimum because so little solvent need be removed, especially compared with amounts necessary in conventional steam distillation and separatory funnel extraction methods.

Oleic acid, commercial grade, Neo Fat 94-04, 400 lbs (182 kg), was pumped through at a rate of 500 mL per hour. The entire amount of 182 kg was processed in 16 days of continuous operation. Initially, about 600 mL of distilled water was placed in the steam generator pot and was recycled as steam at a rate of 200 mL of water condensate per hour. About 100 mL of water was lost in the 16-day operation. The ether solution containing volatiles extracted from the steam distillate was removed every day or so from the liquid-liquid extractor system. A flask containing fresh ether can be exchanged without shutting

down the steam distillation because the exchange of ether flasks takes such little time. The rate of ether being recycled was 100 mL per hour. From the 182 kg of commercial oleic acid processed, 200 g (0.11% w/w yield) of steam volatile material was isolated. This isolate has the same qualitative attractancy to coyotes as did the starting material. The more difficult quantitative tests have not yet been carried out. Fractionation and identification of components are in progress.

LITERATURE CITED

- Buttery, R. G., Guadagni, D. G., Ling, L. C., *J. Agric. Food Chem.* 21, 198 (1973).
 Chang, S. S., Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, AGFD-132.
 Schultz, T. H., Flath, R. A., Mon, T. R., Teranishi, R., Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, AGFD-131.
 Teranishi, R., Hornstein, I., Issenberg, P., Wick, E. L., "Flavor Research: Principles and Techniques", Marcel Dekker, New York, N.Y., 1971, pp 47-50.

Received for review December 13, 1976. Accepted February 28, 1977. This paper was presented by Roy Teranishi in the Symposium on Methods for Isolation of Trace Volatile Constituents, Agricultural and Food Chemistry Division, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, AGFD Abstract No. 155. Reference to a company and/or product named by the Department is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

A New Strategy for the Analysis of Complex Flavors

C. L. Teitelbaum

The problem of isolating the components of very complex flavors can be approached by the sequential use of separation techniques in which each step uses a different set of physical properties to effect separation. Thus, one can successively use adsorption (silica gel chromatography), partition between two phases (normal or reversed phase partition chromatography), and vapor pressure (gas chromatography). An isolation scheme based on this concept is presented and its application to the analysis of cocoa butter demonstrated.

The isolation of the trace components of flavors has been pursued with increasing sophistication over a period of many years. The development of gas chromatography gave promise of a route that would lead to the identification of the important constituents of even the complex flavors found by fermentation and/or heating. Yet, as the techniques became increasingly powerful, the problems correspondingly appeared to become more complex with the desired constituents found to be buried in the chromatograms under far larger quantities of compounds of little interest.

After the early stages of development, two ways of using gas chromatography were pursued. In the first, highly

efficient capillary columns were used as in the work of Vitzthum et al. (1975) on the volatile components of roasted cocoa. However excellent their chromatographic results, there is still considerable doubt that the characteristic flavor components have been isolated, at least in quantities sufficient for identification. In addition, it is very desirable to be able to pinpoint the areas of a chromatogram where the components with the characteristic aromas or flavors occur so as to avoid spending inordinate amounts of time isolating and identifying compounds of little importance to the flavor. This is extremely difficult to do with capillary columns. The quantities are commonly too small for collection for evaluation and the gas flow rate is so low that effluent splitting is a problem. Even without an effluent split, sniffing the outlet port is a very tedious and unproductive effort.

General Foods Corporation, Technical Center, Tarrytown, New York 10591.