Quantitative Recovery of Volatiles from Fats and Oils by Combined High Vacuum Degassing and Thin Film Molecular Distillation

POUL ERIK BRANDT and **BIRTHE HORNDRUP JENSEN**, A/S GRINDSTEDVAERKET, Edwin Rahrs Vej 38, DK-8220 Brabrand, Denmark

ABSTRACT

An apparatus is described which in one unit combines conventional high vacuum degassing on cold finger with falling film molecular distillation. The upper part of the cold finger is for the collection of the most volatile substances, while the lower part is for the condensing of substances which are molecular distilled from a wiped falling film. All the connections in the glass apparatus are made from Teflon or Viton-O-rings, and the turning of the rotor in the molecular distillation part is carried out by means of a magnetic coupling. In this way, the risk for contamination is reduced greatly. As all volatile substances after the treatment of the oil are on the same cold finger, the collection can be made by a high vacuum distillation into a small glass chilled with liquid nitrogen. In the bp range of 40-450 C, the apparatus gives recoveries of volatiles in or below the ppm range between 71-114% with coefficients of variance between 5-23%. The recoveries are found with internal standards added before treatment of the oil. Below 70 C, the recoveries drop to some extent. The volatiles are substances with different kinds of functional groups, e.g. hydrocarbons, aldehydes, ketones, acids, esters, lactones, and sulfur containing substances.

INTRODUCTION

The volatile substances in fats and oils are subject to great interest because of their relation to many kinds of active substances.

Very different techniques have been used for the isolation of the volatile substances, but the best techniques generally involve, in one way or another, high vacuum degassing, molecular distillation, wiped falling film molecular distillation, and combinations of these.

De Bruyn and Schogt (1) developed a very useful high vacuum degassing technique which was suitable for quantitative removal of substances with bp up to 150 C. There are some problems with the recovery of the most volatile substances due to insufficient trapping, but the recovery of substances in the middle range is quantitative.

Lea and Swoboda (2) have used a similar technique. They have been able to extend the range of quantitative recovery of substances with bp up to at least 250 C, but they still had problems with the low boiling components.

Later, Angelini, et al., (3) introduced a modification to the degassing technique which consisted of the removal of the most volatile substances in a closed system, so that they could recover the most volatile substances quantitatively, but they could not reach as high in temperature as Lea and Swoboda.

Libbey, et al., (4) made a combination of high vacuum degassing and falling film molecular distillation.

In principle, this should cover a very broad range of bp, but, when tried on cheese oil, only relatively volatile substances are seen, probably because of a very complicated recovery procedure from the different liquid nitrogen traps.

In a comparison of high vacuum degassing, cold finger molecular distillation, and reduced pressure steam distillation, Forss, et al., (5) could show that the best method was combined high vacuum degassing and cold-finger molecular distillation. They tried this on 2-alkanones and n-alkanols from oils in a concentration range normal to fats and oils and showed good recoveries. Later, the same group (6) extended the useful bp range for their apparatus to substances with bp up to 300 C.

The last mentioned technique is a good one and probably sufficient for many purposes, but its upper limit for the recovery of stances is sometimes too low, e.g. when the quality of refined, deodorized oils are investigated. The deodorization normally removes substances with bp up to 300 C, but there are still many volatiles left. In this case, Libbey's, et al., method must be the most appropriate to start with, as it is continuous. However, it requires some improvements which will be described below.

DESCRIPTION OF APPARATUS

Some of the best features from the different kinds of apparatus mentioned in the introduction are used together with some new ones: it is made to a compact unit comprising only one cold-finger, which makes the recovery of volatile substances a simple matter; it contains no greased joints to give contamination; and the turning of the rotor in the molecular still is carried out by a magnetic coupling so that a greased stuffing box is avoided.

In Figure 1 the details of the apparatus are seen. They are as follows: (A) reservoir for the oil, (B) metering valve (Rotaflow TF 6/24), (C) drip catcher, (D) joint with Teflon and Viton-O-rings (Witeg 121, size 19), (E) tube to the high vacuum Hg-pump and pressure metering device (not shown), (F) cold-finger, (G) 50 mm O-rings connector (Kontes nr. K 671750-0050), (H) 2 in. pipeline precision glass tube from Quickfit (Trentham, Stoke-on-Trent, England), (I) 2 in. rotor with Teflon wipers and steel spirals (Carl Canzler type LG 50), (J) reservoir for purified oil, (K) stopcock to remove oil during a run (possibly no stopcock), (L) compressed air motor (infinitely variable), (M) magnetic coupling shown in detail in Figure 2. It is made from two concentric magnets (O) placed on both sides of the glass tube. The magnets are from a local made central heating circulation pump. In the middle of the inner magnet is placed a stainless steel T, (P) carrying the rotor (Q). All of this is held by a single steel ball (R) against the nylon plate (S). The friction is thus very low and so is the friction between the Teflon wipers and the glass wall. The low friction allows the small magnets to turn the rotor easily.

Figure 1B shows the apparatus in the recovery state. The molecular distillation unit is removed and replaced by a glass tube (T) to which a small conical glass tube (U) is connected by means of a joint (V), Kontes nr. K 671750-0009. The price for the apparatus as seen in Figure 1 is estimated to $700 when it is made in Denmark. The apparatus can be connected to any appropriate high vacuum line. If such a line is not available, another $2300 must be spent for a prepump, a mercury diffusion pump, pressure metering devices, and accessories.

EXPERIMENTAL PROCEDURES

The efficiency of the apparatus can be checked by

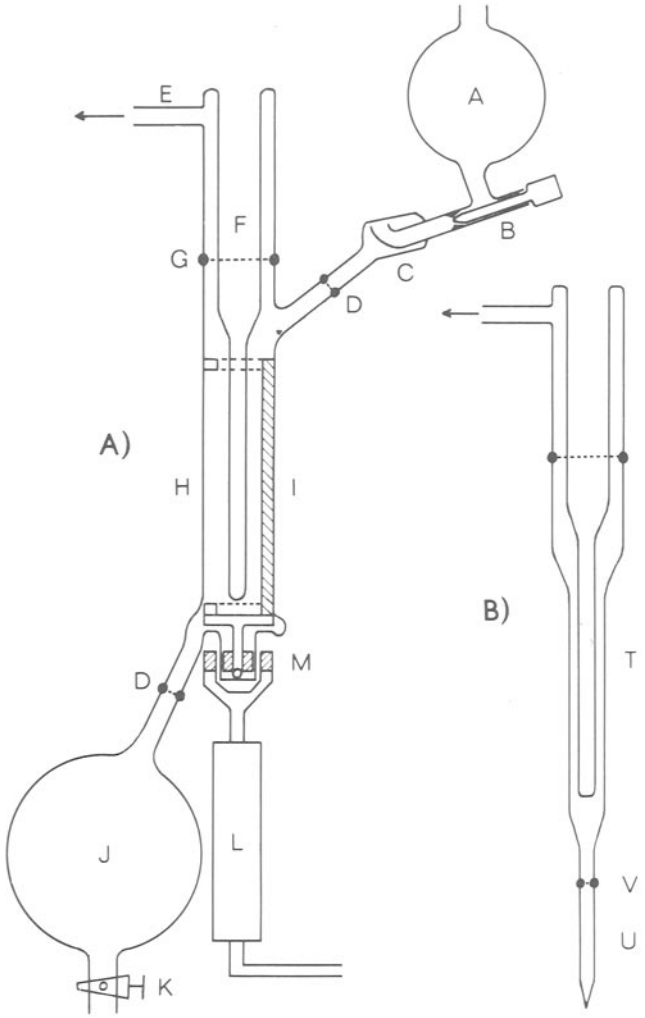

FIG. 1. Apparatus for combined high vacuum degassing and wiped falling film molecular distillation. A) Trapping of volatiles on the cold-finger. B) Recovery of volatiles from the cold-finger. *Labeled parts are:* A. Reservoir; B. Metering valve; C. Drip catcher; D. O-rings connector; E. Tube to vacuum pump; F. Cold Finger; G. O-rings connector; H. Precision glass tube; I. Teflon wipers; J. Reservoir; K. Stopcock; L. Motor; M. Magnetic coupling; T. Glass tube; U. Glass tube; V. O-rings connector.

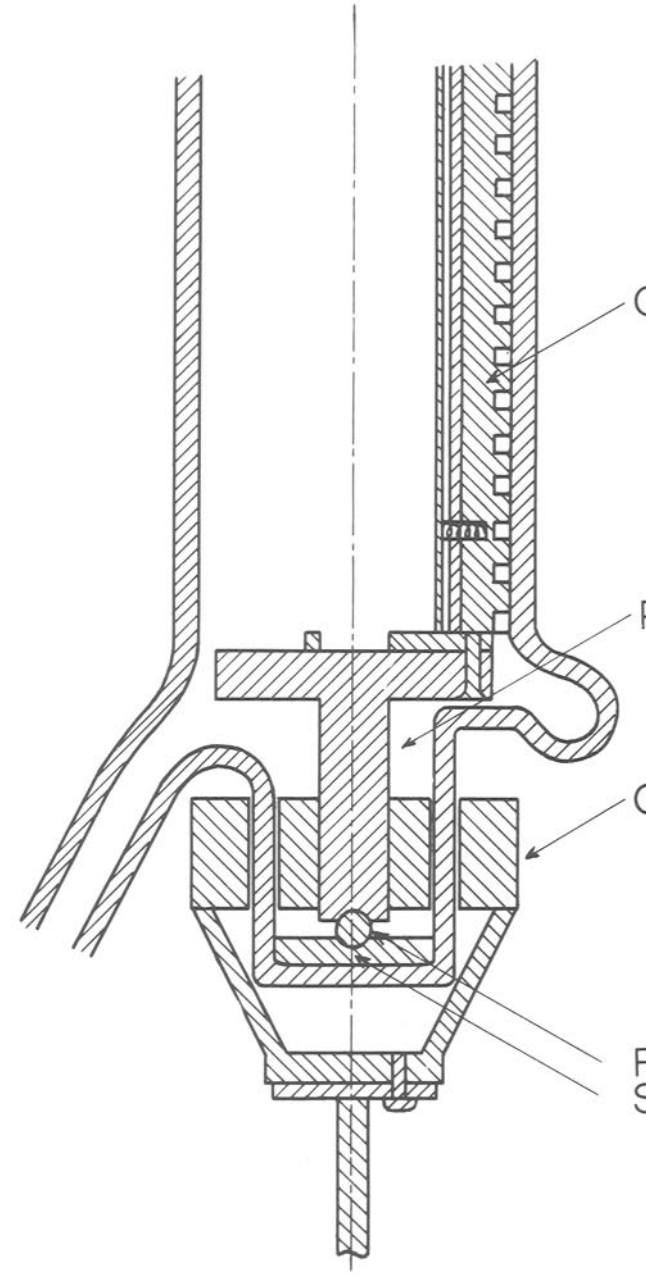

FIG. 2. Magnetic coupling in a molecular distillation apparatus. Labeled parts are: O. Magnets; P. Rotor carrier; Q. Rotor; R. Steel ball; S. Nylon plate.

measuring the recovery of known volatile substances from an oil and the coefficient of variance by this recovery.

A quantity of refined, deodorized soybean oil is purified further to remove residues of volatile substances. This is carried out in the apparatus described under testing conditions, except that a 25 C higher temperature is employed.

To the purified oil are added known amounts of different chemicals with different functional groups and bp. The chemicals are listed in Table I together with their bp and concentration.

Two other chemicals in known amounts are added as internal standards; they vary roughly 100 C in bp, and cover each end of the bp range. Besides being pure and stable, the substances chosen are volatile substances not normally found in fats and oils, and they should not interfere with other substances in the gas liquid chromatography (GLC) analysis later on.

The conditions of treatment of fats and oils in the apparatus may vary a lot according to the type of function and generally cannot be given as they interact. In the particular case we are dealing with, the conditions are: pressure, 10^{-3} mmHg; temperature, 50 C; residence time, ca. 15 sec, capacity, ca. 0.5 kg/h; and nitrogen consumption, ca. 1 liter/hr.

After the apparatus has been put together, the vacuum pumps are turned on. To avoid contamination a Hg-diffusion pump is used. The pressure is measured near the exit of the apparatus, and the temperature is measured close to the glass surface in the middle of the molecular still as is normal in falling film molecular distillation. After complete evacuation to roughly $5 \cdot 10^{-6}$ mm Hg, liquid nitrogen is poured into the cold-finger, and the addition of oil is started at an appropriate rate. The most volatile substances evaporate momentarily, and, in the high vacuum, a drip catcher is necessary to avoid triglycerides being blown onto the cold-finger. The vapors condense on the upper part of the cold-finger, while the oil smoothly runs to the molecular still where the higher boiling substances are removed and condensed on the narrower part of the cold-finger.

When the treatment of the oil has finished, nitrogen is introduced to break the vacuum, and the molecular distillation unit together with reservoirs is removed quickly. They are replaced by the glass tubes shown in Figure 1B. High vacuum is produced again, and the collection tube is chilled with liquid nitrogen. The cold-finger is heated slowly to room temperature, and, in the high vacuum, the volatiles

TABLE I

Recovery of Volatile Substances from Soybean Oil: Lower Boiling Fraction

Component	Boiling point C	Added ppm	Recovery %	Standard deviation[a]	Coefficient of variance %
Acetaldehyde	21	0.88	--[b]	--	--
Dimethylsulfide	37	0.50	71	0.059	12
Ethylacetate	77	0.38	88	0.082	22
2-Butanone	80	1.04	102	0.082	8
Diacetyl	89	1.22	95	0.12	10
Acetic acid	119	6.79	100	1.2	17
n-Hexanal	128	0.44	104	0.069	16
Acetoin	143	3.68	85	0.85	23
5-Methyl-2-hexanone[c]	145	1.63			
2-Heptanone	151	1.27	114	0.082	6
Butyric acid	164	4.44	99	0.60	13
2-Nonanone	194	1.09	98	0.12	11
2-Undecanone	229	1.25	104	0.11	9
Deltanonalactone	262	1.57	109	0.074	5
2-Tridecanone	263	2.30	112	0.18	8
Ethyl-5-oxo-nonanoate[c]	264	1.96			
Deltadecalactone	274	6.05	112	0.39	6
Deltadodecalactone	304	6.65	111	0.54	8

[a]The component of variance from the gas liquid chromatography procedure is subtracted.

[b]Recovery not measured because of steadily increasing values with time due to an autooxidation component.

[c]Internal standard.

TABLE II

Recovery of Volatile Substances from Soybean Oil in Low Concentrations and Internal Standards Added after Treatment

Component	Low concentration of volatiles		Internal standard added after treatment	
	Added to soybean oil, ppm	Recovery %	Added to soybean oil, ppm	Recovery %
Acetaldehyde	0.109	90	0.65	109
Dimethylsulphide	0.122	127	0.63	84
Ethylacetate	0.078	--	0.38	--
2-Butanone	0.076	--	0.45	52
Diacetyl	0.168	60	0.99	67
Acetic acid	1.05	7	5.84	76
n-Hexanal	0.094	86	0.56	83
Acetoin	0.619	52	3.01	79
5-Methyl-2-hexanone[a]	0.350	--	1.18	--
2-Heptanone	0.229	99	0.96	91
Butyric acid	0.709	22	3.54	74
2-Nonanone	0.212	113	0.94	87
2-Undecanone	0.230	105	0.85	77
Deltanonalactone	0.257	95	1.09	64
2-Tridecanone	0.282	103	1.49	68
Ethyl-5-oxo-nonanoate[a]	0.367	--	1.01	--
Deltadecalactone	1.13	94	6.39	61
Deltadodecalactone	1.16	96	6.16	65

[a]Internal standard.

will distill to the collection tube. When finished, the vacuum is broken again. If some high boiling substances are left on the cold-finger, they are washed down by a small amount of acetone, which also serves as an effective mixing agent for hydrophilic and lipophilic substances inclusive of water. Further amounts of acetone are added to give a homogeneous solution if necessary.

The volatiles are analyzed by GLC. The gas chromatograph used is a Perkin-Elmer 990 equipped with dual columns and flame ionization detector. The columns are 4 m x 1/8 in. stainless steel filled with 10% Free Fatty Acid Phase on Gas Chrom Q. The starting temperature is 50 C which is held for 5 min and then raised to 235 C with 5 C/min. Before analysis, the column is saturated once with the components of interest. The peaks in the chromatogram are integrated, and the amounts of the substances are calculated relative to the nearest internal standard (bp). Correction factors are applied.

RESULTS AND DISCUSSION

Table I shows the results of 11 equal experiments on 11 different days. Each concentrate from ca. 1 kg sample is run twice on the gas chromatograph so that the component of variance from the GLC procedure can be found and subtracted.

The recoveries from 40-300 C vary between 71-114%, and the coefficients of variance between 5-23%.

The recoveries in the low boiling end are, as expected, lower than 100% but still fairly good, at least, very reproducible, e.g. dimethylsulfide is recovered 71% with a coefficient of variance of 12%. The recovery might yet be a bit too high because of a background component not separated from dimethylsulphide (see Table II for inconsistency).

After all, one of the features of the method is that the volatiles are released successively and the last portion of them is only shortly exposed to the high vacuum.

In the other end of the bp range, the recoveries are a

TABLE III

Recovery of High Boiling Substances from Soybean Oil

Component	Boiling point, C	Added to oil, ppm	Recovery %
p-Tolylbenzoate[a]	316	6.20	--
Deltahexadecalactone	ca. 350	9.87	106
Deltaoctadecalactone	ca. 370	8.48	101
n-Triacontane	446	7.67	94

[a]Internal standard.

little higher than 100%. It might be due to the fact that small amounts of methyl, ethyl, and propyl fatty acid esters are left even in the purified oil. These esters are eluted with retention times equal to the lactones, and, therefore, they interfere.

Components like acetoin, acetic, and butyric acids have high standard deviations which can be attributed to their polarity. A fact is that they have a tendency to tail on the GLC column and, thus, to variate, because the absorption varies with the loading. Ethylacetate is eluted as a rider peak on acetone and, thus, also likely to fluctuate due to varying amounts of solvent.

Most of these problems can, therefore, be traced back to the GLC procedure and probably could be solved by means of an efficient capillary column. At least, it shows how careful one has to be in conducting recovery experiments of this type.

The concentrations of volatiles in Table I are more or less the concentrations found naturally in many products, and, for many purposes, the recoveries and standard deviations will suffice. Yet, it could be of interest to see the influence of concentration on recoveries, and some results are given in Table II. The concentrations are reduced 5-10 times compared to Table I. The results are the average of two experiments each run twice on the gas chromatograph. The standard deviations are, therefore, greater than in Table I.

The table clearly shows that there is a dependence, especially for the polar components like acetoin, acetic acid, and butyric acid, as previously mentioned. Also ethylacetate and 2-butanone gave problems as they could not be separated from the solvent. The reasons for the problems are two.

The gas chromatographic column will absorb the polar components in low concentration, and, because some higher boiling substances, like triglycerides, distill to the cold-finger and some water condenses on the cold-finger in the recovery state, a certain amount of acetone is necessary to make a homogeneous solution. This limits the amount of volatiles which can be injected into the gas chromatograph. In the higher temperature range, triglycerides evaporate very quickly. If the triglycerides are soft and low melting the capacity of the apparatus is reduced, because the distillate tends to drip from the cold-finger.

Another question of interest in the efficiency of the cold-finger. Table II gives the recoveries when the internal standards are added after degassing and molecular distillation. Again the results are based upon the average of two experiments each run twice on the gas chromatograph. The recoveries are less than in Table I, on an average, except for acetaldehyde and dimethylsulphide 73% compared to 102% in Table I. The efficiency of the cold-finger is, thus, in a range of 75%. The use of only one cold-finger is, therefore, justified, and it makes the recovery procedure much easier. It is, of course, understood that the loss of volatiles in the purified oil is of minor importance.

Still a further question is how high boiling substances can be recovered by the procedure. Table III gives a few figures in the high bp range. p-Tolylbenzoate is the internal standard. The results are the average of two experiments each run twice on the gas chromatograph. The temperature at the surface of the molecular still is 175 C. The bp of the deltalactones are only the best guesses from the bp of the lower homologues, but, in this case, the exact figures are not so important.

REFERENCES

1. De Bruyn, J., and J.C.M. Schogt, JAOCS 38:40 (1961).
2. Lea, C.H., and P.A.T. Swoboda, J. Sci. Food Agric. 13:148 (1962).
3. Angelini, P., D.A. Forss, M.L. Basinet, and C. Merritt, JAOCS 44:26 (1967).
4. Libbey, L.M., D.D. Bills, and E.A. Day, J. Food Sci. 28:329 (1963).
5. Forss, D.A., and G.L. Holloway, JAOCS 44:572 (1967).
6. Stark, W., G. Urbach, J.S. Hamilton, and D.A. Forss, J. Dairy Res. 40:39 (1973).

[Received December 5, 1974]