While these corrected values are independent of the aliquot size, it may be seen that the deviations from the theoretical values are considerably higher than those obtained by the modified Epton method. It should be pointed out however that in the methods of Barr, Oliver, and Stubbings the relationship between anionic and cationic agents is not claimed to be stoichiometric. The data generally are expressed in terms of known weights of a standard anionic compound.

In view of the difficulty of obtaining sodium alkyl sulphates in a state of absolute purity (1) it is considered that the mean error of 0.85% for the modified Epton method represents a comparatively high degree of accuracy. Furthermore the data obtained are based on a primary standard (potassium dichromate) which is completely independent of the material under test and which can be readily obtained in a highly purified condition.

Summary

In the determination of anionic surface active agents of the sodium alkyl sulphate type, the method of Epton (2) has been modified by the calculation of a blank to be added to the observed titration. Data obtained by this modified method indicate a mean error of 0.85%, based on the theoretical molecular weights of four purified sodium alkyl sulphates, as compared to mean errors of 3.8 and 4.3% for two other commonly used methods. Data obtained by the unmodified Epton method are shown to be dependent on the weight of sample taken for analysis whereas the modified method gave consistent results over a wide range of sample weights.

REFERENCES

1. Barr, T., Oliver, J., and Stubbings, W. V., J.S.C.I., *67*, 45-48 (1948).
2. Epton, S. R., Trans Faraday Soc., *44*, 226-230 (1948).
3. Lottermoser, A., and Stoll, F., Koll.-Z., *63*, 49-61 (1933).

[Received November 22, 1950]

A Modified Spinning Band Column for Low Pressure Fractionation

K. E. MURRAY, Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

THE examination of a number of fats and waxes in this laboratory has demonstrated the need for an efficient column to separate fatty acids and alcohols up to a chain length of 30 or more carbon atoms. With packed columns of high efficiency this has not been possible without some decomposition of the larger molecules, due to a considerable pressure drop between the kettle and still head. This large increase in pressure from still head to pot is not encountered in the spinning band type of column. Baker *et al.* (1) found a pressure drop of only 0.7 mm.[1] for a column 545 cm. in length and 6.7-mm. diameter when operated at 1-mm. pressure at the still head. A lower figure of 0.04 mm. is reported by Birch *et al.* for a column 85 cm. in length and 36-mm. diameter at a head pressure of 0.5 mm.

A spinning band column was therefore constructed with an internal diameter of 15 mm. and a working length of 145 cm. It had two new features which, it is believed, contribute to its high efficiency, particularly at operating pressures in the region of 1 mm. First, strips of stainless steel gauze, attached lengthwise to rotor, wiped the walls of the column and spread the descending reflux in an even film. Second, the rotor was accurately centered by means of bearings at intervals of 29 cm. to ensure even vapor and liquid conditions throughout the column.

Details of Column Assembly

The column and its accessories for operation under reduced pressure are shown diagrammatically in Figure 1 and details of the column head in Figure 2.

To reduce vibration the column and the rotor driving motor were mounted on a 2½-in. diameter steel pipe bolted to ceiling and floor. The glass tube of the column was held tightly in a 1-in. diameter aluminum tube (Figure 2-A) by a spiral of asbestos cord. This aluminum tube carried the weight of the lagging, gave an even distribution of heat, and protected the glass tube from fracture. Both the kettle (a 250-cc. flask) and the still head were sealed directly to the column. The kettle (Figure 1-A) was heated by a "Glas-Col" heater (B), separated from it by an air gap, and the temperature was controlled by a "Variac" transformer to give a constant pressure drop over the column measured by the butyl phthalate manometer (C). The need for mechanical stirring of the distilland below 2-mm. pressure has been stressed by Birch *et al.* (2), and this has been provided for by a small stainless steel impeller, 13-mm. diameter on a $\frac{1}{16}$-inch stainless steel rod attached to the bottom of the rotor and fitting loosely into a glass capillary sealed to the bottom of the kettle. The side arm of the kettle greatly facilitated charging and cleaning with solvents.

The column head is shown to scale in Figure 2. A water jacket (B) was provided to condense lower boiling materials, such as solvents. A part of the reflux was collected in a small weir at C which extended over approximately a quarter of the circumference of the tube. This weir, together with the volume of the capillary as far as the needle valve, had a capacity of 0.3 cc. The take-off was controlled by the intermittent operation of the d.c. solenoid needle valve (D) by means of a timing device (Figure 1-D), which consisted of a micro switch operated by a cam driven by a small synchronous motor (0.5 r.p.m.). The cam was made to give 10 seconds take-off in each 120 seconds. Fine control of the take-off rate could be made by adjustment of the vertical travel of the needle by means of the metal bellows attachment (F). Alternatively, changes in the take-off period could be made with different cams. This valve was well suited for

---

[1] Except where stated all pressures are given in millimeters of mercury.

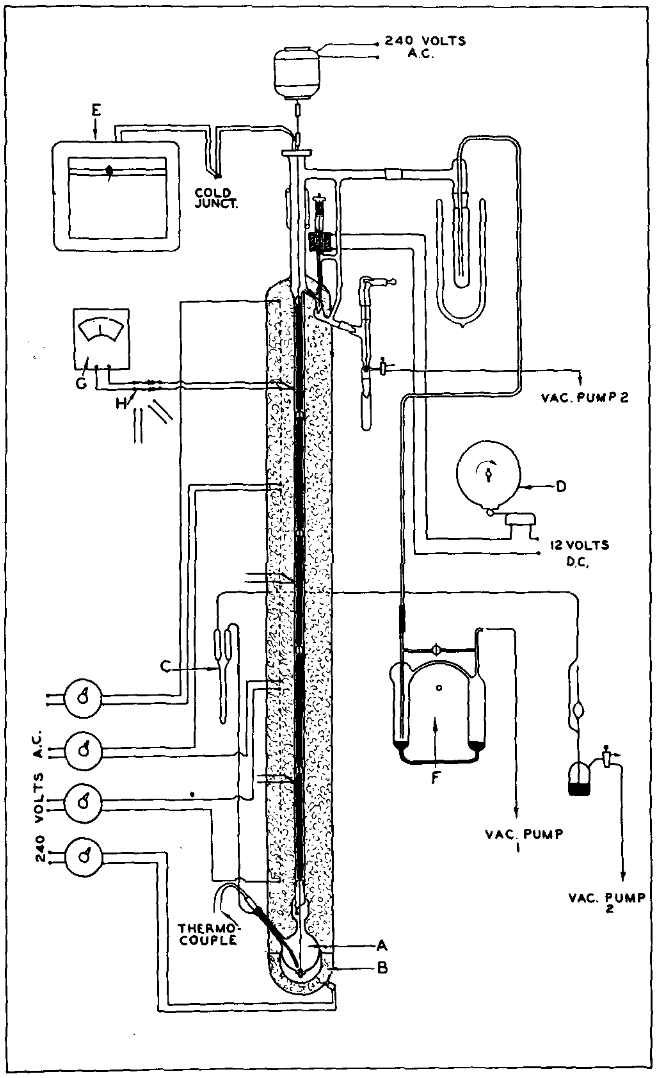

FIG. 1. Diagrammatic sketch of column and accessories.

the low take-off rates used with this column and has operated for long periods with little attention.

The thermocouple pocket and the gland for the rotor shaft were attached to the brass cover plate (G), which was clamped to the glass flange of the column head. The seal between the two is made by a $\frac{1}{16}$-in. thick neoprene washer lubricated with silicone vacuum grease. The rotor shaft of $\frac{3}{16}$-in. stainless steel passed through a close fitting bronze tube soldered to the cover plate, over which was fitted a 4-cm. length of pure rubber pressure tubing tightly fitting the shaft. The vacuum seal of this gland was made by a few drops of heavy silicone oil in a small reservoir (H) above the pressure tubing.

The head temperature was measured during distillations by a thermocouple (28 S.W.G. Iron-Constantan) at a point (J) and recorded on a Kent "Multilec" recorder (Figure 1-E) with a double range of 0-12 and 10-22 millivolts, using an ice cold-junction. The couple was calibrated to 0.2°C. The lower 5 cm. of the thermocouple pocket was wrapped in several layers of aluminum foil to shield the couple from radiant heating from the top winding.

The fraction cutter was similar in principle to that described by Birch *et al.* (2). It was heated to prevent solidification of the distillate by a removable copper sheet radiation shield mounted close to the back and sides of the cutter. Heat was applied by an electric winding on mica clamped to a fold in the copper sheet.

The manostat of Birch *et al.* was used, but with butyl phthalate as the sealing liquid. Its control of pressure to within ± 0.01 mm. in the range 0.50-2.00 mm. fulfilled the claims by these authors.

The column was lagged with two layers of magnesia-asbestos pipe lagging, each approximately 1 in. in thickness. Three windings of nichrome wire, each 150 ohms and covering 50 cm. of the column, were wound on the inner layer of lagging. At the midpoint of each winding a differential thermocouple (copper-constantan) was placed so that one junction was in contact with the glass wall of the column, and the other, silver soldered to a small copper plate, immediately under the winding, but insulated from it with mica sheet. Adiabatic conditions in the column were established by adjusting the voltage applied to each winding with a "Variac" transformer to give a zero reading on a center zero millivolt meter (G) connected through a selector switch (H) to the appropriate thermocouple.

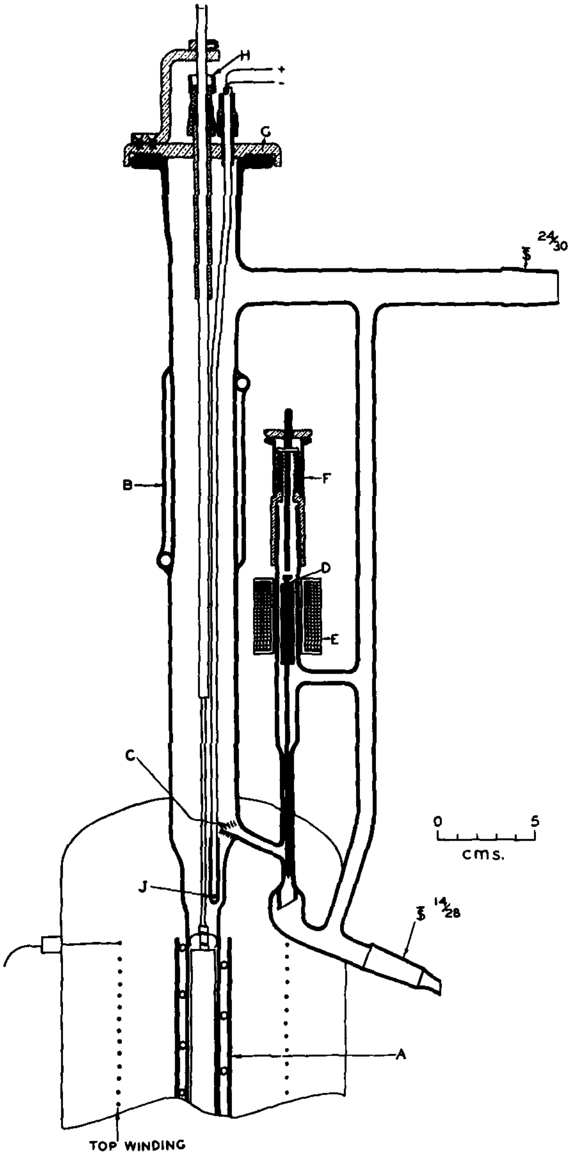

FIG. 2. Details of column head.

Description of Rotors Tested

The construction of the five types of rotors tested is shown to scale in Figure 3. All complete rotors were 145 cm. in length, excluding the two end bearings and had five blades each 28 cm. in length and 13 mm. in width. Details of these rotors are as follows:

Rotor A. The blades were flat and were made from 18 S.W.G. stainless steel. They were connected by short lengths of 1/16-in. stainless steel rod silver soldered into central slots. These rods also carried the star bearings which consisted of a nickel bushing and stainless steel arms (from 26 S.W.G. sheet), which were flexed to grip firmly the walls of the column and to center the rotor. Increased rigidity was given to the rotor by a 1/16-in. stainless steel rod silver soldered lengthwise by its ends to the center of each side of the blades.

Rotor B. The star bearings of Rotor A were replaced by a helix of 22 S.W.G. nichrome wire of 20 turns over each blade and attached to it by silver soldering to the top end of the blade and to a nickel sleeve over the 1/16-in. shaft at the lower end. This helix fitted the column tube closely and was intended to cause a downward wiping action on the column wall and so reduce the hold-up.

Rotor C. This differed from Rotor A by having its blades (22 S.W.G. stainless steel) shaped to the shallow S section shown in Figure 3. These blades, being more rigid than those of A, made the rotor run more smoothly.

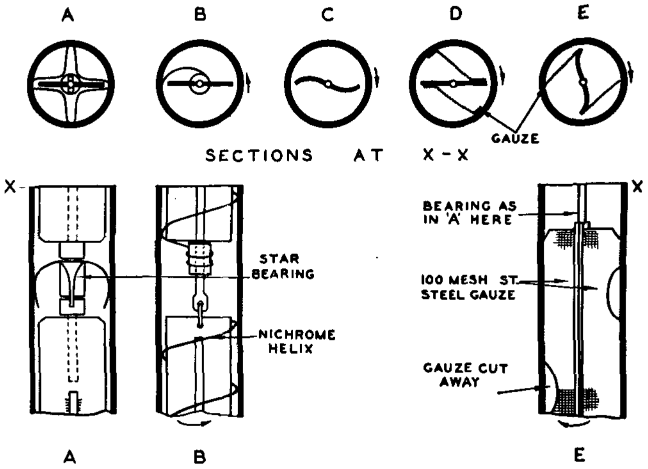

FIG. 3. Details of rotors.

Rotor D. Strips of 100-mesh stainless steel gauze were spot-welded along each side of the blades of Rotor A and bent as shown so that during rotation they wiped the column wall.

Rotor E. This design, developed from Rotors A, C, and D, was found to be efficient at reduced pressures. The bearings were the same as in A, the blades as in C rotating in the reverse direction, and the gauze wipers as in D. However, to reduce the rigidity of the gauze strips and so obtain a better and more gentle contact with the column wall, they were not bent over as in D, and semicircular sections 1.2-cm. diameter were cut from the strips at intervals of 3.8 cm., the cut-away sections in opposite strips being staggered.

Tests at Atmospheric Pressure

The column efficiency at atmospheric pressure was determined with the test mixture n-heptane—methylcyclohexane of approximately 80 mole % methylcyclohexane. The refractive indices of samples taken from the head and pot at equilibrium under total reflux (for 4-5 hours) were measured at 25°C., and the number of theoretical plates read from the nomograph of Brooks *et al.* (3) recalculated for 25°C. using the refractive index-mole fraction equation of Willingham and Rossini (4).

Comparison of Rotors. The efficiencies of the four rotors A-D were compared at a boil-up rate of 150 ml./hr. Rotor E is also included although it was constructed at a much later date. The results are set out in Table I.

TABLE I

Comparison of Rotor Efficiency

Rotor	Speed (R.P.M.)	Number Theoretical Plates
A	0	12.5
A	1420	70
B	0	7
B	1420	34
C	1420	58
C (in reverse)	1420	58
D	1420	42
E	1420	46

The effects of rotor speed, boil-up rate, and operation at reduced pressure were examined for the most efficient of these rotors (A).

Speed of Rotor. With the rotor speed made controllable by variable gearing, the column efficiency was measured at speeds in the range 0-1940 r.p.m. at a boil-up rate of 140-149 ml./hr. The results plotted in Figure 4 indicate that column efficiency increases with speed to 1400 r.p.m. and thereafter remains constant.

Boil-up Rate. Column efficiency was determined for boil-up rates over the range 77-465 ml./ hr. at a rotor speed of 1,420 r.p.m. The results plotted in Figure 5 show the decrease of column efficiency with an increase in the boil-up rate. It was observed that the pressure drop did not increase with boil-up rate, being almost constant at 0.25-0.30 mm.

Performance Under Vacuum

It remained to determine whether the high efficiency of Rotor A at atmospheric pressure was retained when operated at reduced pressure. As no test mixture has been described for testing column efficiency in the region of 70 theoretical plates at low pressure, an idea of the performance of Rotor A at low pressures was obtained by the fractionation of a mixture of n-hexadecanol and n-octadecanol as follows:

A mixture of 20 g. each of n-hexadecanol and n-octadecanol (Eastman) was fractionated at 0.50-mm. pressure with a take-off rate of 5 g./hr., a boil-up rate of approximately 100 ml./hr., and a rotor speed of 1,420 r.p.m. The poor separation of the two components shown (in Figure 6) by the curves of two such fractionations makes it clear that the efficiency of Rotor A is much lower than at atmospheric pressure. For reasons given in the discussion it was anticipated that a rotor would be more efficient under reduced pressure if provided with some means of gently wiping the column wall. Rotor E was therefore

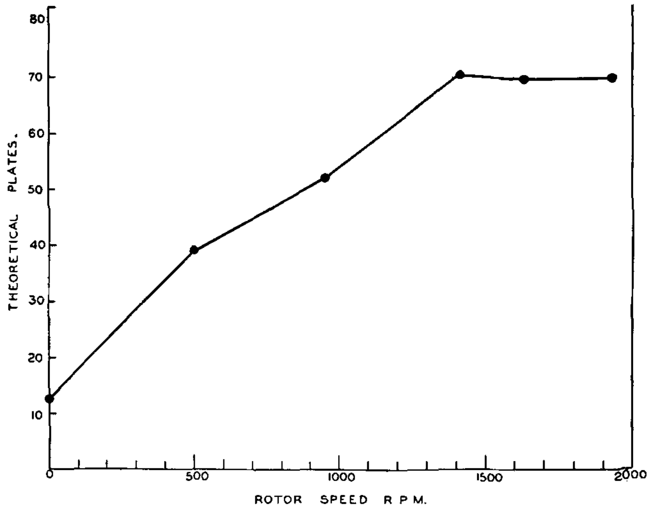

FIG. 4. Effect of rotor speed on efficiency at atmospheric pressure (Rotor A).

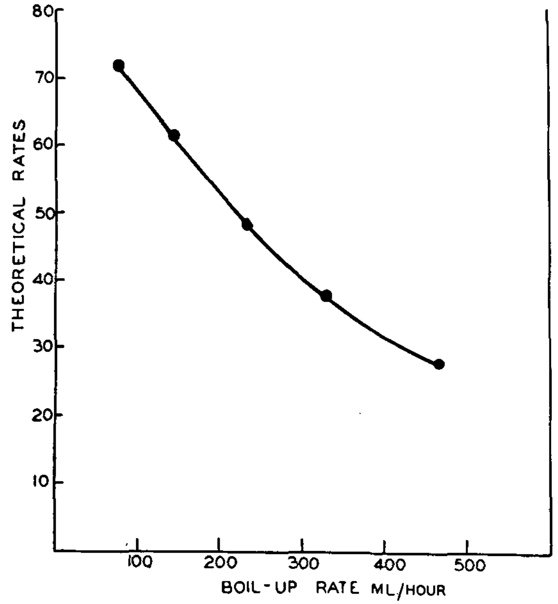

FIG. 5. Effect of boil-up rate on efficiency at atmospheric pressure (Rotor A).

constructed with gauze strip wipers and the outstanding improvement with it is seen in the result of a comparative fractionation of n-hexadecanol and n-octadecanol (Figure 6).

The following examples give some further idea of the performance and usefulness of Rotor E for vacuum fractionation, the rotor speed in all examples being 1,420 r.p.m.

a) Figure 7 shows the result of the fractionation of a mixture of n-tetradecanol, n-hexadecanol, and n-octadecanol at 1.00-mm. pressure. The charge was 54 g., the boil-up rate approximately 100 ml./hr., and the take-off 6 g./hr. Undistilled material was only 2.9 g. Sharp separations were obtained with almost flat plateaux and abrupt breaks.

b) The methyl esters of the acids from the seed oil of Terminalia Kaernbachiana have been fractionated at 1.00 mm. (5), and the distillation curves are shown in Figure 8. The recorded temperature during the first two distillations was high due to radiant heating from the top winding, and this was overcome in the third distillation in the manner already described. The sharp separations obtained even with the small charge of 33 g. (curve 2) demonstrates the usefulness of this column for this type of analysis. The fractions boiling on the plateaux can be combined, and the subsequent work in measuring their chemical constants is thereby much reduced.

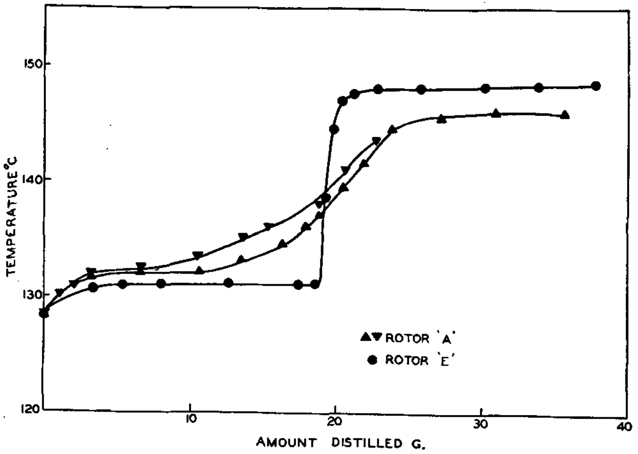

FIG. 6. Fractionation of n-hexadecanol and n-octadecanol at 0.50 mm. Comparison of Rotors A and E.

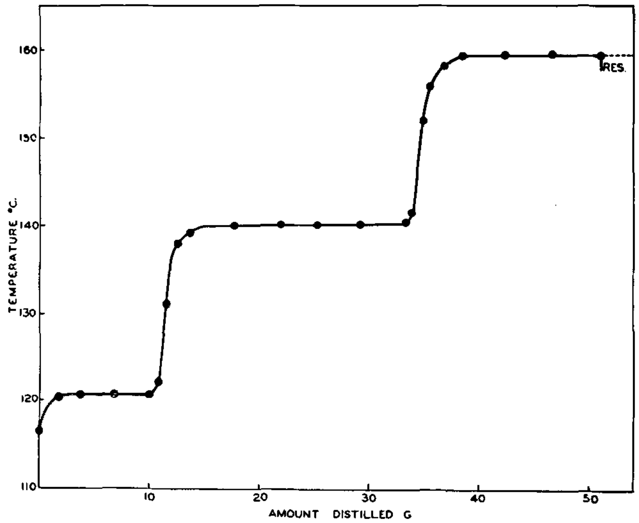

FIG. 7. Fractionation of n-tetradecanol, n-hexadecanol, and n-octadecanol at 1.00 mm. with Rotor E.

c) The low pressure drop of the column (0.4 mm. at 0.5 mm. head pressure) has made possible the fractionation of compounds of high molecular weight which in a packed column would suffer some decomposition. Thus it has been possible to make an analysis by distillation techniques of the alcohols of carnauba wax and to show they are chiefly the straight chain alcohols C_{30}, C_{32}, and C_{34}. A full account of this work will be published separately.

Discussion

The observed changes in performance of rotors with and without wipers calls for some consideration of the mechanism of fractionation in a spinning band column. The increase of column efficiency with rotor speed seems to indicate that several factors are of importance. Rotation mixes the faster moving central core of vapor with the slower moving layers near the column wall and forces all the vapor to take a long spiral path up the column. The resulting fast driven vapors near the column wall will cause a drag on the reflux which will spread in a uniform film moving in a spiral path downwards. Thus the relatively long countercurrent paths of vapor and reflux, the decrease of the gaseous diffusion barrier between the two, and the even distribution of reflux are all factors contributing to increased column efficiency. As a similar effect of rotation on efficiency has been observed in a column with a cylindrical rotor [Willingham *et al.* (6)], it is likely that the suggestion of Birch *et al.* that the efficiency of the spinning band column is explained by the pressure drop between front and rear faces of the rotor blade, creating conditions of evaporation and condensation at the reflux surface, concerns only a second order effect.

With a reduction of operating pressure the drag of vapor on the reflux will be diminished and with a rotor of type A will be so small in the region of 1 mm. that the reflux will run down undisturbed, thereby accounting for the poor fractionation with rotor A at 0.5 mm. With rotor E however the disappearance of vapor drag is less important because the wipers spread the reflux mechanically. It remains to explain why a rotor with wipers (D or E) is relatively less efficient than type A at normal pressure.

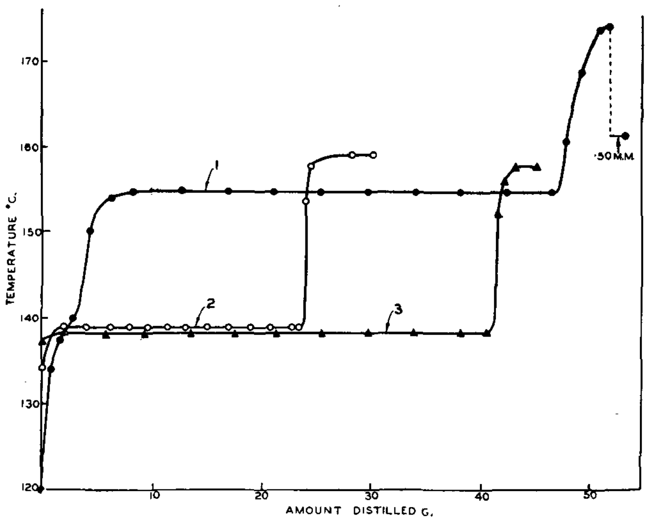

FIG. 8. Fractionation of the fatty acid methyl esters of Terminalia Kaernbachiana at 1.00 mm.

The vigorous action of the wipers on a reflux of low viscosity, formed by the test mixture, may generate a spray which is easily entrained by the fast moving vapors.

Comparison of this column with spinning band columns described in the literature is only possible at atmospheric pressure. Birch *et al.* reported an H.E.T.P. of 5.5 cm. for a column of 36-mm. internal diameter. For columns of 5 to 6 mm. internal diameter H.E.T.P. values of 7.8 and 7.1 (1), 3.12 (7), and 2.50 cm. (8) have been reported. The present column with rotor A had a plate equivalence of 70 under total reflux and therefore an H.E.T.P. of 2.07 cm. A semi-micro column 75 cm. in length and 6-mm. diameter with a type A rotor has recently been constructed in the Dairy Research Section of this organization, for which an H.E.T.P. of only 1.17 cm. was found (9). This improvement in efficiency of these two columns over earlier columns is attributed mainly to the centering of the rotors by bearings.

The spinning band column has several desirable features: a low hold-up, a low pressure drop, does not need preflooding, and is not subject, as are packed columns, to channelling. One disadvantage not eliminated in the present column is the low take-off rate (3-10 g./hr.), but with pressure control and automatic take-off this is compensated by the small attention needed, apart from changing receivers. The present work shows that for most efficient operation different types of rotors should be used at atmospheric and low pressures.

The column described has lately been reconstructed and the length of the rotor extended to 366 cm. Rotor E was remade, eliminating the use of silver solder. This is attacked by fatty acids and the copper salts formed would catalyze the polymerization of unsaturated fatty acids. No mechanical difficulty resulted from this extension, but it was found that the rotor speed could be reduced to 700 r.p.m. without decrease of efficiency.

Acknowledgments

This work formed part of the research program of the Organic Section of the Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia. The writer gratefully acknowledges the practical assistance and suggestions contributed at times by members of this Division, in particular W. G. Jones, S. E. Powell, J. Mills, R. B. Morrow, and R. Schoenfeld.

Summary

A spinning band fractionating column is described for operation at pressures down to 0.5 mm. of mercury. A study has been made of various designs of rotor. One type consisting of flat blades of stainless steel interspaced with bearings at regular intervals, which centered it in the column, gave an H.E.T.P. of 2.07 cm. at atmospheric pressure. At low pressures (0.5 mm.) its efficiency was found to be small, and a more suitable rotor has been developed in which strips of stainless steel gauze are attached to the blades. These wipe the walls of the column and provide an even film of reflux. Sharp separations of fatty acid methyl esters, fatty alcohols, and acetates have been made, using this rotor at pressures of 0.5-2.0 mm. On account of the low pressure drop (0.4 mm. mercury) it is possible to fractionate compounds with 30 or 32 carbon atoms without decomposition.

REFERENCES

1. Baker, R. H., Barkenbus, C., and Roswell, C. A., Ind. Eng. Chem., Anal. Ed., *12*, 468-70 (1940).
2. Birch, S. F., Gripp, V., and Nathan, W. S., J. Soc. Chem. Ind., *66*, 33-40 (1947).
3. Brooks, F. R., Nelsen, F. M., and Zahn, V., Petroleum Refiner, *27*, 620-21 (1948).
4. Willingham, C. B., and Rossini, F. D., J. Res. Nat. Bur. Stand., *37*, 21 (1946).
5. Clark, E. J., Hatt, H. H., and Troyahn, W. J. To be published.
6. Willingham, C. B., Sedlak, V. A., and Rossini, F. D., Ind. Eng. Chem., *39*, 706-12 (1947).
7. Björkman, A., and Olavi, S., Svensk, Kem. Tids., *58*, 145-50 (1946).
8. Koch, H., Hilberath, F., and Weinrotter, F., Chem. Fabrik, *14*, 387-90 (1941).
9. Bennett, G. R., and Forss, D. Unpublished work.

Tables for the Conversion of Spectrophotometer Readings to A.O.C.S. Photometric Color Values

EGBERT FREYER and V. B. SHELBURNE, Spencer Kellogg and Sons Inc., Buffalo, New York

ALTHOUGH the spectrophotometric method for determining oil colors possesses obvious advantages over the old method employing Lovibond color glasses used in the Wesson oil colorimeter, one disadvantage which is being felt by some laboratories results from the added work and time required to obtain color readings, compared to the older method. While the manufacturer of the spectrophotometer currently being most widely used in determining oil colors is supplying scales in terms of the A.O.C.S. color components corresponding to the readings at the four wavelengths, it is understood that only two components will be covered on one scale strip, thus requiring changing the scale on the instrument during the course of determining the color of an oil. When a large number of oils are being read however, this becomes less objectionable because it is no doubt customary to make all readings on a group of oils at