TABLE II

Refinery	Oil	No. of tank cars	% FFA	Cup loss (%)	Plant loss (%)		Caustic
					Mod. soda ash	Full soda ash	
A	Corn	1	2.0	7.2	4.28	....	5.90
A	Corn	1	1.2	5.0	2.85	....	3.23
B	Soybean	150	....	....	3.18	3.72	....
C	Linseed	15	1.2	....	2.46	....	....
D	Soybean	2	0.4	3.4	2.13	....	....
D	Deg. soybean	10	0.7	1.9	0.72	....	....
D	Mixed soybean	13	....	2.2	1.30	....	....
D	Deg. soybean	13	....	3.6	2.63	....	....

Refinery	Oil	No. of tank cars	% FFA	Cup refining		Modified soda ash refining	
				% Loss	Bleach	% Loss	Bleach
E	Cotton	17	1.4	8.0	2.5	4.68	2.4
E	Cotton	8	....	6.7	3.4	4.69	2.7
E	Cotton	2	....	7.5	3.2	4.50	2.8

oil, using the assumption that all the sodium of the soda ash is available for neutralization. On oils of low FFA we, at present, use a minimum treat of 1% of 22° soda ash.

After mixing in a mixing zone, the oil is heated to at least 180°F., and here again proper control of the temperature is important. A reasonable temperature range would be between 180 and 200°. The heated oil is then degassed in the gas vent tank and centrifuged.

The cooler should cool the primary refined oil to about 100°F. and is followed with a decolorizing caustic treat, which will depend to a large extent on the crude oil. Soya oils can be lightly washed with 8 to 12° Bé. caustic, prime cotton oils can be rerefined with low treats of 20° Bé. caustic, and dark cotton oils may require up to 3% of 26° or 32° Bé. caustic adequately to reduce color. It is important to note that, in the absence of soap from primary neutralization, excellent colors may be obtained from dark oils without seriously affecting the overall loss results. Generally the rerefining centrifuges will require between 20 and 30% water flush to assist in the discharge of the traces of soap removed.

By means of the low primary treat, the refining soapstock will be above 35% TFA, usually falling between 37 and 40%. This materially reduces the problems of acidulation and even produces a salable material as is. The most important trend of recent times in this regard is the work being done through the efforts of Refining Unincorporated and B. H. Thurman to prove beyond question that this particular type of soda ash soapstock, having a low excess of free carbonate or bicarbonate, is both palatable and nutritional as an additive to cattle feed. Preliminary reports from the Chicago stockyards and several state universities are very encouraging, based on tests made from materials supplied in quantity from the Sharples Refinery.

Data

It is readily recognized that data based on laboratory analysis or on an arbitrary selection of cup loss values could lead to doubt. For this reason we have chosen to relate each run to the Wesson loss or the chromatographic loss of each crude and to associate most modified soda ash runs with a run of equal length, using the same crude supply but operating as a caustic refinery. In each case we have taken pains to carry out the caustic run according to the best known techniques available to our experienced refiners, and in some cases this attention to detail has led to a better caustic refining than might be expected from day to day plant operation.

Table I shows the results of these comparisons.

On a basis involving much less control, this process has been operated successfully by a number of commercial refiners. Table II shows the data available to us for general publication from these installations.

Both of these tables show a superiority of ½ to 1% in refining loss for the soda ash process over the caustic process. Refinery E reported in Table II shows a reduction in bleach color of cotton oil below the bleach color established in the settlement cup refining, and this advantage has been maintained over a period of at least one year. During this period savings over cup refining losses have averaged about 30%.

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Surface-Tension Determinations with a Precision Micro Capillary Rise Apparatus[1]

C. S. NEVIN,[2] Department of Chemistry, North Carolina Agricultural Experiment Station,
Raleigh, North Carolina

THE MORE COMMONLY used procedures for measuring surface tension, such as the ring detachment method (13, 9), the drop weight method (14, 15), the bubble pressure method (24), the hanging drop method (10), and the classical capillary rise method (15, 21, 22), are either very time-consuming, employ a complicated apparatus, require a large sample, do not give absolute values, and thus require correction factors or are extremely tedious techniques. Since the author desired a quick, micro method for determining surface tensions, he tried Ferguson's method (5) with a series of methyl esters of normal saturated fat acids. Although the results (20) were encouraging, they showed that Ferguson's method needed refine-

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[2] Present address: Stamford Research Laboratories, American Cyanamid Company, Stamford, Conn.

TABLE I

Surface Tensions at Various Temperatures

Compound	Surface Tension in Dynes/cm.										
	20°C.	25°C.	30°C.	40°C.	50°C.	60°C.	70°	75°C.	80°C.	90°C.	$-\frac{\Delta\gamma}{\Delta t}$
Benzene—Experimental values	28.83[b]	28.19	27.56	26.28	25.01	23.73	22.46	......	21.18[b]	......	0.1275
Benzene—I.C.T.[a] values	28.86	28.20	27.56	26.26	24.99	23.72	22.49	......	21.26	......	......
n-Pentadecane	......	......	26.05	25.24	24.44	......	22.83	......	......	21.22	0.0804
Methyl laurate	......	......	......	27.09	......	25.43	......	24.18	23.76	......	0.0834

[a] International critical table values (16).
[b] Extrapolated values.

ment in order to obtain precise and accurate measurements of surface tension. This paper reports a micro apparatus which has improved ease of operation, precision, and accuracy.

Experimental

Apparatus. An open end U-tube manometer is joined by means of a "T" seal to 7-mm. glass tubing. Extending to the left, this tubing terminates in a female, standard taper, ground glass joint, where specially prepared capillaries are attached. Extending to the right, the glass tubing connects with a large air reservoir (enclosed in a Dewar flask) which in turn connects with rubber tubing, forming a part of the pressure assembly. The rubber tubing passes first through a Hoffman tubing compressor and then feeds between two close-set metal rollers which form a seal by compressing the tubing. Behind the manometer is a white cardboard straight-edge, which is vertically adjustable for sharpening and enlarging the manometer fluid meniscus. Strapped to the side of the manometer is a thermometer for measuring the manometer fluid temperature.

The apparatus is enclosed within an asbestos board box with only the female standard taper joint emerging from the left-front. Two windows of plate glass are mounted on the asbestos box: one on the right-front for viewing the manometer, the other on the right-top for illumination from the fluorescent lamp hung above the apparatus.

In operation the specially prepared capillary is enclosed in a constant temperature air bath similar to earlier descriptions (20, 5). The capillary is illuminated by a substage microscope lamp fitted with a 6-volt bulb. The glass face of the lamp has been replaced by a nontransparent plate with a 0.5-cm. diameter tube, which guides a small beam of light up to the glass face of the air bath and directs the light upon the end of the capillary. A 20-diopter, double-convex lens is mounted adjacent to the lamp to facilitate viewing the end of the capillary.

The capillaries were prepared from thick-walled, precision-bore, borosilicate glass tubing. The working end was ground to a plane perpendicular surface in a manner similar to that described by Ferguson and Hakes (6), and the opposite end was sealed to a male, standard taper, ground glass joint. For surface tension determinations the previously described procedure for cleansing a capillary (20) is followed.

Measurement of Associated Physical Constants. The diameter of the capillary was measured at the plane perpendicularly ground end by means of a microscope equipped with a calibrated scale micrometer eyepiece. All measurements agreed within ± 0.025 revolutions of the micrometer eyepiece drum, which was equivalent to slightly less than ± 0.00005 cm. Each capillary was measured at 16 different diameters evenly spaced around the circumference, and the mean radius was taken as being one-half of the mean diameter. The maximum out-of-round varied from 0.00020 to 0.00030 centimeters.

Densities of the manometer fluid, n-dodecane, were determined, using a calibrated, modified Sprengel-type pycnometer. Values of $D_4^{25} = 0.7453$, $D_4^{30} = 0.7417$, and $D_4^{35} = 0.7380$ with a limit of error of less than ± 0.0001 g./ml. were obtained. In calculating surface tension, the manometer fluid density used in the formula was read from a precise graph of density *versus* temperature.

Manometer readings were made with an accuracy of ± 0.001 cm. by a Gaertner micrometer slide cathetometer, which was calibrated against an Invar steel standard meter bar certified by the International Bureau of Weights and Measures at Sevres, France, and by the U. S. National Bureau of Standards. The thermometers used in this work were checked over the range of usage against a thermometer graduated in 0.1°C. which had been recently calibrated by the U. S. National Bureau of Standards.

The acceleration of gravity has been accurately determined at North Carolina State College in Raleigh, N. C., and is reported as 979.777 dynes (19).

Procedure. The previously described procedure (20) is followed except for the method of pressure application. This is accomplished by feeding rubber tubing through the metal rollers for rough pressure adjustment, and by tightening the Hoffman tubing compressor for fine adjustment.

Results

Surface Tension of Benzene. Benzene was chosen as a "standard" because its surface tension has been exhaustively studied and has a value in the range of most surface-active agents. The benzene used was Standard Sample No. 210a-8S provided by the U. S. National Bureau of Standards. Data covering various physical properties of this or similarly purified benzene can be found in the literature (7, 8). The refractive index of the benzene was determined in this laboratory with a Bausch and Lomb, precision, Abbé-type refractometer which had been thoroughly calibrated with National Bureau of Standards samples. The value obtained, $n_D^{40} = 1.48827$, compares very closely to the result reported in above cited literature.

Surface Tension of n-Pentadecane. Benzene is not an ideal material to use as a "standard" because it is very volatile above 40°C., is limited as a liquid to the narrow temperature range of 5.5°–80.1°C., and is readily contaminated by acquiring moisture from the atmosphere. In order to extend the temperature range of surface-tension measurements and to utilize a more stable compound, n-pentadecane was chosen for study. A highly purified and reproducible sample was obtained from the U. S. National Bureau of Standards

(Sample No. 581–58). Recent data covering the physical properties of purified n-pentadecane are reported by Schiessler *et al.* (23) and by Vogel (25). A refractive index value, $n_D^{40}=1.42416$, obtained in this laboratory with the n-pentadecane sample compares favorably with the cited literature.

Surface Tension of Methyl Laurate. Since the prime purpose of developing this apparatus was for the determination of surface tensions in the field of fats and fatty acid derivatives, a sample of methyl laurate was studied in order to show the utility of the method. The methyl laurate was prepared by direct esterification of commercial lauric acid and methanol, using dl-camphorsulfonic acid as a catalyst. The unsaturated esters were removed by sulfonation, followed by hydrolysis and aqueous washings. The crude methyl laurate was then purified by distillation through a low pressure fractionation column packed with multiple turn glass helices.

The refractive index and the density of the purified methyl laurate were determined as follows: $n_D^{40}=1.4238$, $D_4^{40}=0.8538$. These values compare favorably with those found in the literature (18, 1, 2).

Table I presents the experimentally obtained surface tensions at various temperatures. The values for benzene and n-pentadecane were obtained by regression calculations of more than 60 measurements made at six different temperature levels. For comparison, corresponding values for benzene are presented from the International Critical Tables (16). These latter values were compiled from capillary height determinations made by Richards and Coombs (21), Richards and Carver (22), and Harkins and Brown (15).

Discussion

Surface Tension Values. Calculations were made, using the differences in dynes/cm. between the experimentally obtained values and the International Critical Table values for the surface tension of benzene. From 16 measurements, using six different capillaries, at two temperature levels, the average difference at 95% confidence limits was 0.026 ± 0.0073, the average difference at 99% confidence limits was 0.026 ± 0.0101, and the standard deviation was 0.013 dynes/cm.

The surface tension values obtained for n-pentadecane are as precise as the benzene values and were much easier to obtain because of the lower volatility of n-pentadecane. Comparison of the experimental results with values reported by Vogel (25) and by Jasper *et al.* (17) shows fair agreement.

To emphasize the simplicity, speed, and accuracy of this modified micro capillary rise method only six surface tension determinations (two each at 40°, 60°, and 80°C.) were made in acquiring the experimental values for methyl laurate. The actual measurements require but a few minutes; however 5–20 min. are necessary for aerating the capillary and for permitting the test liquid to assume the temperature of the air bath. The surface tension values obtained by regression calculations with these six measurements compare very closely to previous values reported in the literature (12, 20, 26).

Parachors. Table II presents parachors calculated according to Gibling's (11) system. The experimental parachors were determined, using liquid densities obtained from the literature (2, 7, 8, 23), and the $\Delta D/\Delta t$ values were indicated. Vapor densities were calculated from molecular weight-boiling point correlations, as reported by Boyd and Copeland (3). The saturated vapor densities of benzene are great enough to be appreciable while those of n-pentadecane and methyl laurate are negligible. Correlations between the calculated and the experimental parachors is excellent for benzene and good for n-pentadecane and methyl laurate.

TABLE II
Parachors at Various Temperatures

	Benzene	n-Pentadecane	Methyl laurate
Calculated parachor[a]	206.2	631.7	573.5
D_4^{20} (g./ml.)	0.8790	0.7685	0.8695
$\Delta D/\Delta t$	−0.00106	−0.00067	−0.00078
Experimental parachors			
40°C	206.3	630.4	572.5
50°C	206.4	630.9	......
60°C	......	......	574.2
70°C	206.3	631.7	......
80°C	206.2	......	575.1
90°C	......	631.7	......

[a] Gibling's system.

Apparatus Refinements. By replacing the previously employed liquid-leveling bottle pressure system with rubber tubing passing between metal rollers, a steady method of applying an unvarying pressure is obtained. The inclusion of the Hoffman tubing compressor provides a delicate means of final pressure adjustment. By replacing ordinary capillary tubing with precision-bore capillary tubing, diameter measurements made at the plane perpendicularly ground end of the capillary can be assumed to remain constant for the short distance of 0.5 to 1.0 cm. along the length of the capillary. The experimental results of surface-tension measurement prove this assumption to be valid.

The use of n-dodecane provides a stable manometer fluid whose absolute density does not vary. Earlier workers used the density values for the manometer fluid at 20°C. in their calculations of surface tension. In this study variations in the density of the manometer liquid with changes in room temperature have been taken into account.

Previous instruments were operated by observing the reflection from the surface of the test liquid of the filament of an open incandescent lamp. By channeling a small beam of light up to the glass face of the constant temperature air bath, it is possible to observe the light beam's reflection from the surface of the test liquid within the capillary without having interference from light glare reflected from the glass face of the constant temperature bath.

The incorporation of the Dewar flask, the asbestos box, and fluorescent lighting is necessary for precision measurements since the apparatus is highly sensitive to environmental variations in temperature.

The method is based upon the premise that with a horizontal capillary there exists no hydrostatic pressure due to the weight of the test liquid. Therefore the female standard taper joint at the left of the apparatus must be leveled, and care must be taken to see that the capillaries are attached properly to the male standard taper joints so that they are held level.

Although extensive studies have not been made, the surface tensions of a variety of liquids have been measured with this apparatus, and it has been found applicable to organic, aqueous, clear, colored, and opaque liquids or solutions. Furthermore the method can be adapted for interfacial tension determinations although, as yet, only crude results have been obtained.

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Summary

Details of apparatus construction and refinements are presented for a micro capillary rise method of determining absolute values of surface tension. Experimental values of surface tension for benzene, n-pentadecane, and methyl laurate are recorded and compared with previous literature values. Parachors are determined. The method requires a minute amount of sample and is simple, quick, precise, and accurate.

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The Trans Fatty Acids of Margarines and Shortenings[1, 2]

AHMED FAHMY MABROUK[3] and J. B. BROWN, Departments of Agricultural Biochemistry and Physiological Chemistry and The Institute of Nutrition and Food Technology,
The Ohio State University, Columbus, Ohio

A PRESENT TREND in the American diet is the rapid increase in use of shortenings and margarines. For example, in 1953 the consumption of margarine in the United States exceeded that of butter for the first time; lard consumption has declined along with the increase in use of shortenings.

Margarines and shortenings can be, and sometimes are, formulated by blending natural fats, but currently it is almost the universal practice to use hydrogenated fats for this purpose. This use of what one might properly call a "synthetic fat" as a major item in our diet makes the problem of the composition of hydrogenated fats important, and more particularly that of the nature of the unsaturated acids in these fats. The unsaturated acids in natural fats are almost always of the so-called *cis* configuration, the principal exception being vaccenic acid, *trans*-11-octadecenoic acid, which has been found in small amounts in several animal fats (4). Recent work in this laboratory (5) has shown that summer butterfat contains up to 9.5% *trans* acids. In contrast to the natural fats, hydrogenated fats are known to contain large quantities of *trans* acids, not presently known to occur naturally. Another important difference in composition between the hydrogenated fats and the oils from which they have been made is their content of essential fatty acids. Hydrogenation destroys a major part of these acids, thus impairing their nutritive value in this respect.

The almost hopelessly complex nature of the mixed fatty acids in hydrogenated fats can best be pointed out by citing a few of the numerous investigations of the chemistry of hydrogenation of fatty acids and their esters and glycerides, which involves more than simple addition of hydrogen to double bonds. Various types of isomerization take place in this process so that in partially hydrogenated products there is always an increase in the number and types of fatty acids present in the product. Thus Moore (16) showed that, in the course of hydrogenating ethyl oleate, the resulting iso-oleic acids consisted of a mixture of 8-, 9-, and 10-octadecenoic acids. Likewise Hilditch and Vidyarthi (8), Benedict and Daubert (3), and others (15, 17) found that partial hydrogenation of oleic acid and its esters resulted in formation of numerous positional and geometric isomers of oleic acid. The trans 6-, 7-, 8-, 9-, 10-, and 11-octadecenoic acids, described by Huber (9) melt much higher than the corresponding *cis* isomers, and at least several of them are responsible for a considerable part of the desired high melting point of commercial hydrogenated fats.

The partial hydrogenation of a dienoic acid, such as linoleic acid, or of its esters, results in a still more complicated mixture of products including numerous octadecenoic acids, (16, 8, 20) both *cis* and *trans*, as well as various isomers, both positional and geometric, of linoleic acid itself. Most of these isolinoleic acids have not been identified reliably. Hydrogenation of the 12,13-double bond to give oleic acid is always accompanied by less reaction of the 9,10-double bond to give 12-octadecenoic acid (24). (Cf. also 1, 6, 14, 20, 22.)

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[2] Presented at the June, 1955, meeting of the Institute of Food Technologists, Columbus, Ohio.

[3] Supported by a study leave, Cairo University, Giza, Egypt. Present address: Faculty of Agriculture, Cairo University.