roglucide of epihydrine aldehyde. It thus appears that the color obtained in the Kreis test on rancid fats is due to the formation of a phloroglucide of epihydrine aldehyde.

No direct evidence of the presence of acrolein or of free epihydrine aldehyde in rancid fats could be obtained, although some of the experiments would seem to indicate that the epihydrine aldehyde radical is present in the form of one of its simple compounds, possibly as an acetal, and that its formation is not dependent upon the action of the concentrated hydrochloric acid employed in the Kreis test.

However, that may be, it is certain that the Kreis test depends on the ultimate formation of the epihydrine aldehyde radical, and that the formation of oleic acid perioxide is the first of a series of reactions that may culminate in the production of this radical. The formation of C_9 aldehydes and acids in the development of rancidity is comprehensible enough, but the formation of C_7 (heptylic) and C_3 (epihydrine) aldehydes is somewhat puzzling. Only by the introduction of new double bonds into the oleic acid chain or into that of its C_9 cleavage products, does the further fragmentation of the molecule seem possible. Solway has suggested a plausible mechanism for the formation of heptylic aldehyde and acrolein in the oxidation of linolenic acid; and the accompanying adaptation of his scheme is suggested as a possible explanation of the processes at play in the development of rancidity.

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THE SULFURIC INDEX OF COTTONSEED OIL AND IN ADMIXTURES WITH OLIVE OIL

By James K. Morton and G. C. Spencer, Bureau of Chemistry, Washington, D. C.

Mazzaroni,[1] in determining the thermal index of oils by the Tortelli method, observed that the reaction of the oil and sulfuric acid was always accompanied by the formation of a gas, chiefly sulfurous anhydride, and that the quantity of gas given off varied with the nature of the oil under examination. This led to an attempt to measure the quantity of the gas liberated by passing it into an appropriate iodine solution and noting the quantity of iodine consumed. Mazzaroni termed this factor the "sulfuric index," a heretofore unrecorded constant of an oil.

The purpose of the work here reported was to utilize the principle advanced by Mazzaroni and to show to what extent the sulfuric index can be utilized as a means of identification of simple oils or of the constituent oils in mixtures.

It was necessary to devise an arbitrary procedure and apparatus in order to control every factor that enters into this determination.

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[1] *Staz. Sperim. Agrar. Ital.*, **48**, 583–594 (1915).

Oils of low index value, such as olive oil and tea seed oil, offer little difficulty in obtaining a fairly close agreement, even though the oils may differ widely in their source. Oils of high index value, of which cottonseed oil is an example, are sensitive and very wide differences may result with slight changes in apparatus or manipulation. The well-known variable constitution of oils obtained from different sources and the methods of extracting and refining also contribute to variable results.

In order that the sulfuric index of cottonseed oil should be representative of the different grades entering the trade, samples of oil were secured from many of the larger producers throughout the country. The low sulfuric index value of olive oil, which is subject to slight variations, has eliminated, for the purpose of this work, the necessity of extended research on this oil.

Apparatus

The apparatus (Fig. 1) consists of a Pyrex test-tube, 10 by $1^1/_2$ inches. The rounded bottom of this tube must be as nearly hemispherical as possible. A glass stirring paddle the blades of which are 3 cm. from tip to tip and 1 cm. deep, is provided. The blades conform in shape to the rounded bottom of the tube and are turned to give, as nearly as possible, an upward movement to the liquid. A three-hole rubber stopper closes the

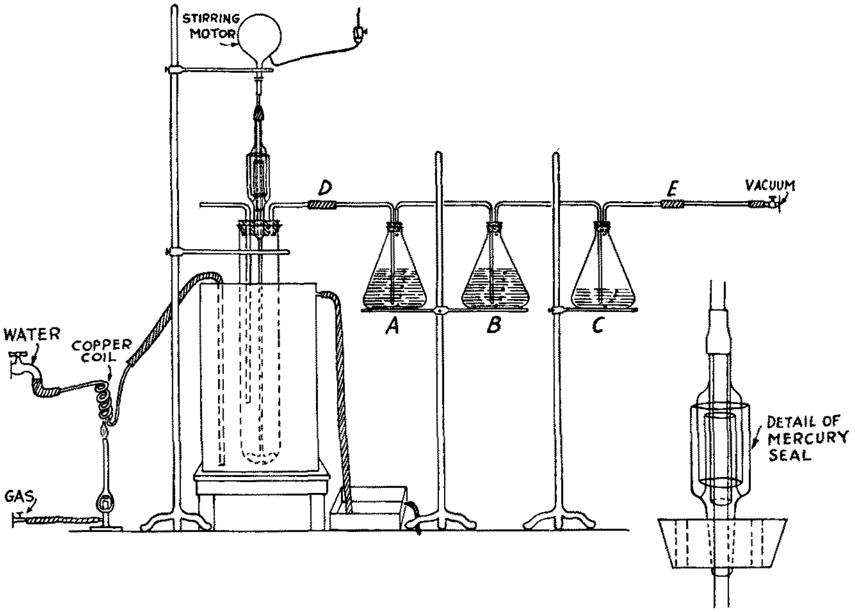

Fig. 1.—Apparatus set-up for the determination of the sulphuric index of oils.

tube, the center hole being large enough to admit a mercury seal, the other two holes carrying glass tubes of 4 mm. inside diameter. The shaft of the glass paddle passes through the mercury seal and is attached to the shaft of a stirring motor regulated to run at 300 r.p.m. The absorption end of the apparatus consists of three 200 cc. Erlenmeyer flasks each provided with a two-hole rubber stopper and glass connecting tubes. Glass tubing of 4 mm. inside diameter is used throughout.

The reaction is conducted in a constant temperature bath maintained at $25^1/_2$ to 26 °C. This bath can readily be constructed from an empty ether can. A $^3/_8$-inch overflow is provided about an inch from the rim.

Running tap water is passed into the can through a quarter-inch copper coil heated with a Bunsen flame, and the temperature of the bath is controlled by the rate of flow of the water and the heat applied. The authors have found this to be a very efficient and convenient means of bath control the variation not exceeding 0.5 °C. It has the advantage of being portable and easily manipulated. The test-tube can be so adjusted that tilting alone is sufficient to remove the bath without disturbing the apparatus above it. The overflow of the bath can serve as an additional bath in which the sulfuric acid and oil under examination may be brought to a uniform and constant temperature before making the determination.

The apparatus is assembled as shown in Figure 1. The intake tube in the digestion chamber extends to within $1^3/_4$ inches of the bottom of the digestion chamber. The intake tubes of the absorption flasks should extend to within a quarter of an inch of the bottom of the Erlenmeyer flasks, the outflow tubes in each case extending flush with the bottom of the rubber stopper. The apparatus should be adjusted so the the stirring paddle when in place will just clear the bottom of the tube and revolve freely

Reagents

(1) Sulfuric acid (98.5%) prepared by boiling the ordinary 95% acid in an open casserole to about two-thirds of its original volume. It is poured hot into a Pyrex Erlenmeyer flask and cooled under a calcium chloride tube. This acid must be carefully made to a uniform and definite strength and kept well protected.

(2) Iodine, tenth-normal solution.

(3) Sodium thiosulfate, tenth-normal solution.

(4) Starch, 0.5 per cent solution.

(5) Mercury.

Determination

Measure into the first 200cc. Erlenmeyer flask (A) enough tenth-normal iodine solution to assure an excess of about 15 cc.[2] and bring the volume to about 150 cc. with

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[2] The quantity of iodine required is indicated by the character of the oil and preliminary test.

water. To the second flask (B) add 5 cc. of the tenth-normal iodine solution and bring the volume to about 150 cc. To the third flask (C) add 1 gram of potassium iodide and 2 cc. of starch solution and dilute to about 100 cc. Connect the three flasks as indicated in Figure 1. Aspirate through the apparatus and regulate the rate to about 180 bubbles a minute.

Bring the sample of oil and the sulfuric acid to 25.5° to 26°C. in the constant temperature bath. Measure with a pipette 20 cc. of the oil and introduce it into the digestion chamber by placing the tip of the pipette near the bottom and touching the side of the tube. Be sure that no oil touches the side of the tube above the level that will be reached when the sulfuric acid is added. Allow the pipette to drain for 10 minutes. Carefully pipette 5 cc. of the sulfuric acid into the test-tube by placing the tip of the pipette just above the level of the oil, touching the side of the tube, and allow the acid to underlie the oil with as little disturbance as possible. All premature mixing must be avoided. Connect the test-tube with the stirring apparatus but do not let the paddle dip into the mixture.[3] Place the constant temperature bath directly under the test-tube. Raise the test-tube to its proper position and fasten in place. Make the connection to the absorption flasks at D. Elevate the constant temperature bath to submerge about 6 inches of the test-tube. Disconnect the aspirating tube at E.[4] Place a finger over the open end of the intake tube and start the stirrer. Steady the digestion tube with the hand to eliminate friction as much as possible. When the reaction subsides, as indicated by the backing up of the solution in the first flask release the finger from the intake tube, reattach the aspirating tube at E, and continue the aspiration at the predetermined rate. Stir for exactly 10 minutes. At the end of 30 minutes disconnect the absorption flasks at D and titrate the excess of iodine with tenth-normal thio-sulfate. The number of cubic centimeters of tenth-normal iodine consumed is the sulfuric index of the oil.

TABLE 1

SULFURIC INDEX OF COTTONSEED OIL

Source	Grade	Deter.	Max.	Min.	Ave.	Iodine number (Hanus)*
Miss.	Prime summer yellow	3	96.1	85.3	89.0	111.1
Ga.	Summer yellow	3	87.0	83.7	84.9	108.9
Tenn.	Prime summer yellow	3	96.2	91.0	92.7	111.6
Tenn.	Refined	2	85.0	74.5	79.7	111.0
Texas	Refined	4	56.37	51.50	53.8	104.0
Texas	Refined, winter pressed	3	69.0	66.7	68.1	102.0
Okla.	Refined	3	65.6	60.0	63.6	104.7
Okla.	Salad	2	79.67	76.9	78.3	106.5
N. Carol.	Refined	2	71.6	67.1	69.3	107.9
N. Carol.	Refined	4	88.0	70.7	81.4	112.2
	Cooking	2	56.2	56.0	56.1	104.0
	Salad	3	64.0	62.0	62.7	107.5
	Butter	5	68.1	56.0	62.6	106.1
	Winter oil	4	88.5	73.7	80.1	108.8

* Iodine numbers were determined by Walter F. Baughman, Oil, Fat, and Wax Laboratory, Bureau of Chemistry, Washington, D. C.

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[3] Care must be taken at this point to see that the paddle and test-tube are in correct alignment, permitting free movement of the paddle.

[4] Before starting the motor the aspirating tube should be disconnected from the end flask to permit the escape of air caused by the reaction in the digestion chamber.

TABLE II

SULFURIC INDEX OF MIXTURES OF COTTONSEED OIL AND OLIVE OIL

Sulfuric index of cottonseed oil	Per cent of olive oil added							
	10	20	30	40	50	60	75	100
86.6	60.7	42.0	26.0	17.2	11.5	6.7	3.2	2.54
	57.1	40.5					3.1	2.60
	59.1	39.0						
Iodine No.								
108.3	(105.5	102.8	100.0	98.2	96.5	93.7	89.6)	81.3

(Iodine value interpolated)

For comparison the iodine value is tabulated with the sulfuric index. The iodine value of cottonseed oil as recorded in chemical literature has a range of about 10 units. The sulfuric index range as found in this investigation is about 40 units (Table I). Hence the sulfuric index is more sensitive than the iodine number and close duplication of results will be more difficult.

In mixtures of olive oil and cottonseed oil the sulfuric index is not proportional to the quantity of either oil present. The addition of olive oil to cottonseed oil causes a marked reduction of the sulfuric index out of all proportion to the quantity added. Thus olive oil with additions of cottonseed up to 25 per cent shows but a slight increase in the sulfuric index, while cottonseed oil with 10 per cent of olive oil added shows a marked decrease in the sulfuric index.

It is believed that the addition of a low-index oil to a high-index oil not only reduces this index but also interferes with the heat of reaction of the high-index oil, resulting in a decreased proportional index of the higher oil.

TABLE III

SULFURIC INDEX OF VARIOUS OILS

Oil	Sulfuric index	Iodine value
Olive, California......	2.1	
	2.54	
	2.60	
	2.2	81.3
Italian...............	1.00	82.2
	1.21	80.0
Tea seed.............	1.62	83.0
Coconut.............	0.80	6.9
Sesame..............	52.67	
	51.97	109.1
Apricot.............	15.1	
	14.3	107.1
Peanut, cold pressed..	5.73	97.1
Sunflower seed	138.1	130.8

The sulfuric index value of a number of other oils was determined by this method and the results are tabulated in Table III.

The sulfuric index has a place in the record of analysis of cottonseed oil. The conditions entering into this determination can be controlled, but if the results are to have any value the method must be followed with care and expert manipulation. As a routine method it does not compare with that for the iodine number in the number of determinations that can be made in a given time, but as a means of identification of an unadulterated oil it compares favorably. The extent of adulteration of cottonseed oil with olive oil may be determined within a definite limit, but the reverse is not true. A large proportion of cottonseed oil can be added to olive oil, without increasing the index measurably.

Acknowledgment is made of the assistance given by Dr. G. S. Jamieson of the Oil, Fat and Wax Laboratory of the Bureau of Chemistry in securing for this investigation the oils under examination and for advice and comment.

BLEACHING STUDIES ON COTTONSEED OIL

BY FRANK C. VILBRANDT AND HERMAN J. BANKSTON, JR.

The production of a light, clear oil from dark-colored crude cottonseed oil is a difficult industrial undertaking and much time and money has been spent in this study. After the process of dragging down the fine meats and the proteins with soap formed in the oil, which in addition reduces the fatty acid content of the oil, many substances have been suggested for further bleaching the oil, but Fuller's Earth or certain clays are commonly used for this purpose.

There are many grades of this earth as well as many grades of oil to be bleached, some of the latter not responding to this treatment at all. Therefore many investigations have been made to determine whether the variability of the composition or of the procedure is responsible for the variations in results. Some emphasis has been laid upon the effects produced by these earths being dependent upon the quality of the earth, the quality of the oil and the skill of the workman in carrying on the bleaching operations. However, studies carried out by the Bleach Test and Fuller's Earth Committee, A. O. C. S., and embodied in their report[1] of August, 1921, indicated that the time and degree of agitation had no influence of the degree of bleach, that it was unnecessary to fix a standard procedure and the skill of the workman was not such an important matter in the bleaching of the oil.

Chemical analyses seem to throw no definite light on the mechanism of the bleach, for bleaches of the same formula often have different bleaching properties, while others with widely different composition have almost

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[1] *Cotton Oil Press*, V, 122 (1921).