



Fig. 2.

a 100-ml. volumetric flask with ether, and made to volume with this solvent.

The optical density of this solution was determined directly in the Beckman Spectrophotometer at wavelengths of 652.5 and 660.0 millimicrons.

### Results

Chlorophylls A and B were isolated from the Fuerte and the Nabal varieties of the California avocado. Figures 1 and 2 show the spectral absorption curves of ether solutions of the chlorophylls isolated from the Nabal variety.\* The absorption maxima of

both the chlorophylls isolated from both varieties are in fair agreement with those obtained by Zscheile and Comar (2). The difficulty of preparing highly purified chlorophyll solutions from the avocado is indicated by the presence of several small peaks in the wavelength range of 4500 to 5500 Å in the curve for chlorophyll A, Figures 1 and 2. These are probably due to the presence of decomposition products such as Pheophytin A. The results obtained indicate that chlorophylls A and B are the principal green pigments of the edible portion of the Fuerte and Nabal varieties of the California avocado.

The quantitative determination of the chlorophylls by calculation from the optical densities at wavelengths of 652.5 and 660.0 millimicrons was conducted on both the Fuerte and the Nabal varieties according to the method of Comar and Zscheile (7) and Comar (8). By this method the Fuerte avocado was found to contain 21.57 micrograms of chlorophyll A and 15.57 micrograms of chlorophyll B per gram of edible portion. The Nabal avocado contained 19.93 micrograms of chlorophyll A and 11.90 micrograms of chlorophyll B per gram of edible portion. No attempt was made in this work to relate chlorophyll content to degree of maturity, degree of ripeness, or to season of the year. Further investigations along this line are contemplated.

### Summary

It has been shown that chlorophylls A and B are the principal green pigments of two varieties of the California avocado. Chlorophylls A and B have been determined quantitatively in those two varieties.

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\* Figure 1 covering the range of 3800 Å to 5000 Å, inclusive. Figure 2 covering the range of 5000 Å to 7000 Å, inclusive.

## A Rapid Method for Estimating Glycerol in Kettle Soap

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Soapboiling has not yet completely emerged from the state of art to one of science. This is probably because the initial processing of kettle soap during the saponifying and salt washing procedures is easily controlled by eye and taste. It is not necessary to control them chemically at these stages of manufacture in order to make a suitable soap. The "fitting" stage, which is the final adjustment of caustic soda and salt content must be done with more care if a good product is desired. At this stage, the "art" of the soapboiler calls into play his sense of taste and

his sense of feel as well as his eyesight. By touching the soap to his tongue he determines whether or not the proper adjustment of caustic has been made and by sight he judges whether the kettle soap is "boiling properly." He may even use a trowel to see how the soap slides off the flat blade. Then using his "art" he adjusts the kettle with salt, caustic soda, or water until a proper "fit" is obtained.

After the fitted soap has stood for a few days and the kettle has settled out its excess salt and caustic, the soap is ready for further processing. If the "fit-

ting" is done by "art" there is no assurance that the kettle soap will settle properly and failures to obtain quality soap means the loss of time on a kettle while it is being "refitted" and resettled.

Science has generally penetrated into the "art" of soapboiling at least to the extent of a controlled "fit" and it is now possible to make certain that there will be no losses of time due to improper settling by a control of the caustic soda and salt balance on the fitting operation.

Tests have also been devised for the control of the amount of glycerine left in a kettle soap. The dichromate method is in popular use. It is an old method but by application of new features it has been speeded up considerably (1, 2). For testing in the laboratory it is an excellent method but for use by the soapmaker in determining whether he has extracted the glycerine to a low enough figure, it is still rather slow, taking about three hours. The soap maker would like to have a test that will give him results while the kettle is being fitted. In case the test shows too much retained glycerine he can then easily convert his "fitting" operations to washing operations with no lost time. If the test is satisfactory he can proceed with the fit by adjusting his caustic and salt.

Publications exist on the extraction of glycerine from kettle soap (3, 4, 5) but the usual method adopted is a routine processing formula. This calls for a set procedure in boiling the soap and a set number of glycerine extracting "salt water washes." The number of washes is set by sampling succeeding washes and testing them at leisure in the laboratory. The number of washes required to bring the glycerine down to a set figure is thus found and it is assumed that if the same procedure is followed again the same results will be obtained. This would undoubtedly be true if the same procedure could be repeated exactly, but variables such as the amount of water used in a wash, the time of settling each wash, and the varying amounts of glycerol present in reclaimed salt from the glycerine plant usually connected with a soap plant make the "set" procedure not so set and introduces errors.

However, by the use of a quick glycerol test which can be used after the "set procedure" method has been followed, the soapboiler can tell whether he has already accomplished his glycerine extraction or whether an extra wash or two must be used.

Since the amount of glycerine contained in kettle soap does not affect its usability for quality soap to any great extent, except in special cases, a glycerine retention test is of value only from an economic point of view or when conditions make it necessary to extract all the glycerine practical from the soap. Good practice usually calls for a retention of not over 0.8% of glycerol on the basis of the anhydrous soap.

In order to reach the above figure it is first expedient to experiment to find a good "set procedure" for processing. In actual manufacturing operation, the set processing procedure is followed and a sample is taken from the kettle when the soap has settled on the final wash and is ready to be boiled up on the "fitting" operation. At this stage the anhydrous soap content of the kettle soap will be about 65% and if the figure of 0.8% glycerine basis of the anhydrous soap content is wanted it would mean that the test on the whole kettle soap (including water in the

soap) should not be over 0.52%. During the settling operation after a "fit" a bit more of the glycerine settles out so the test is on the safe side. If the kettle tests as desired, the soapmaker proceeds with his "fitting" but should the test be too high, he converts the "fit" to a wash with no lost time and tests again until the glycerine content is correct.

Accuracy of about 0.1% of glycerine in kettle soap can be obtained by the following tests depending on the operator's sense of interpolation of color standards. No greater accuracy is needed for this practical manufacturing control test. The test can be made within one-half an hour.

The authors do not claim this test to be new, but merely a novel adaptation of the old dichromate method to speed it and adapt it to practical control work.

### Method

#### 1. Scope:

This method covers a procedure for the evaluation of glycerine retained in kettle soap. It is sufficiently quick and accurate enough so that it can be used as an operating control test.

#### 2. Apparatus:

- 1—Rough balance accurate to about 0.1 gram
- 2—250-ml. beakers
- 1—400-ml. beaker
- 1—500-ml. volumetric flask
- 1—1000-ml. volumetric flask
- 1—25-ml. automatic pipette
- 1—10-ml. pipette
- 1—50-ml. graduate
- 8—Rubber stoppered pint bottles
- 9—Comparator tubes (rubber stoppered, 5/4", calibrated mark).

#### 3. Reagents:

*Potassium Dichromate Solution.* Dissolve 74.564 grams of C. P. Potassium Dichromate in distilled water and make to 1 liter with more distilled water.

*Sulfuric Acid.* Pour a volume of C. P. Sulfuric Acid into an equal volume of distilled water and allow to cool.

*Lead Sub Acetate (Powdered).* Basic Dry Powder, for sugar analysis by the Horne Method.

*C. P. Glycerine.* 95% Glycerol content, U. S. P. grade of Glycerine.

#### 4. Preparation of Standard Color Solutions:

Dilute 100 grams of 100% glycerine (105.3 grams of 95% glycerine) to 1000 ml. Take 10 ml. of this solution A and dilute to 1000 ml. Put 10 cc. of this solution B into a 250-c.c. beaker and add enough water so that the total volume will be at least 100 ml. Add 25 ml. of glycerine analysis dichromate solution and 50 ml. of 1:1 H<sub>2</sub>SO<sub>4</sub>. Boil vigorously for two minutes. Cool and dilute to 500 ml. This makes a standard colorimetric solution for 0.1% glycerine value when a 10-gram sample of Kettle Soap is used on the test. Fill a comparator tube to the mark with the oxidized standard solution.

The table below shows the number of ml's of solution B (0.001 gm. Glycerine per 1 ml.) required to be oxidized to give standard color solutions for comparing the percentage of glycerol when 10-gram samples of material are being tested. Preserve the standard oxidized glycerol color samples in pint bottles with rubber stoppers. Temperature does not change the color of the standards.

Percent Glycerol the Standard Color Represents							
0.1	0.3	0.5	0.7	0.9	1:1	1:3	1:5
Ml's of Solution B to be Oxidized							
10	30	50	70	90	110	130	150

Make up a complete set of solutions for the comparator tubes by oxidizing the required ml's of solution B. Fill the tubes to the mark with the respective color standard and store in a test tube rack. Plug the ends with rubber stoppers while not being used for comparisons. When excessive evaporation is observed, discard the old sample and refill the comparator

tube with fresh solution from the appropriate pint reserve bottle.

#### 5. Procedure:

Weigh out into a 250-ml. beaker 10 grams of the soap to be tested, using a rough balance ( $\pm 0.1$  gram). Add about 100 ml. of distilled water and boil to dissolve. When thoroughly dissolved add successive portions of powdered lead subacetate and boil until the soap and salt are completely precipitated. A little experience will enable one to tell when the soap and salt are completely precipitated. Usually about 5 grams of dry powder will be sufficient. Boil until the precipitated soap is coagulated and the solution is clear. Decant into a 250-ml. beaker and wash out the original beaker once with about 10 ml. of hot water. Add 1 to 1 C. P. sulfuric acid until the excess lead is precipitated. This point has been reached when no further precipitate is formed on the addition of more  $H_2SO_4$ . Filter into a 400-ml. beaker, add 25 ml. of dichromate solution, 50 ml. of 1:1 sulfuric acid, and boil vigorously for at least two minutes.

Pour into a 500-ml. volumetric flask, cool under running tap water, and make up to the mark with distilled water. Mix

well, and pour into a  $5\frac{1}{4}$ " comparator tube, to the mark. Match against standard samples by looking through the length of the solutions at a frosted 75-watt light bulb fastened to a table. Estimate any glycerol colors falling between two standard sample colors.

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# Progress Report of the Committee on Analysis of Commercial Fats and Oils

## October, 1943

### Thiocyanogen Numbers

A year ago this Committee recommended the adoption of revised constants for the calculations involved in the determination of thiocyanogen values. We now submit the formulae for these calculations based on the proposed constants.

The suggested constants were:

Acid	Pct.	Iodine Value	Thiocyanogen Value
Linolenic.....	X	273.7	167.1
Linoleic.....	Y	181.1	96.7
Oleic.....	Z	89.9	89.3
Saturated.....	S	0	0

When the iodine and the thiocyanogen values are determined on the fatty acids the calculations are as follows:

When no Linolenic acid is present:

$$181.1 Y + 89.9 Z = 100 \text{ I.V.}$$

$$96.7 Y + 89.3 Z = 100 \text{ T.V.}$$

$$S = 100 - (Y + Z)$$

$$Y = 1.194 \text{ I.V.} - 1.202 \text{ T.V.}$$

$$Z = 2.421 \text{ T.V.} - 1.293 \text{ I.V.}$$

$$S = 100 - (Y + Z)$$

When Linolenic acid is present:

$$273.7 X + 181.1 Y + 89.9 Z = 100 \text{ I.V.}$$

$$167.1 X + 96.7 Y + 89.3 Z = 100 \text{ T.V.}$$

$$X + Y + Z = 100 - S$$

$$X = 1.5902 \text{ T.V.} - 0.1290 \text{ I.V.} + 1.3040 S - 130.40$$

$$Y = 1.3565 \text{ I.V.} - 3.2048 \text{ T.V.} - 1.6423 S + 164.23$$

$$Z = 1.6146 \text{ T.V.} - 1.2275 \text{ I.V.} - 0.6617 S + 66.17$$

When the iodine and thiocyanogen values are determined on the mixed triglycerides the calculations for the hypothetically pure triglycerides are as follows:

Glyceride	Pct.	Calculated from Fatty Acids	
		Iodine Value	Thiocyanogen Value
Linolenin.....	X	261.8	159.8
Linolein.....	Y	173.3	92.5
Olein.....	Z	86.0	85.5
Saturated and Unsaponifiable.....	S	0	0

When no Linolenin is present:

$$Y = 1.246 \text{ I.V.} - 1.253 \text{ T.V.}$$

$$Z = 2.525 \text{ T.V.} - 1.348 \text{ I.V.}$$

$$S = 100 - (Y + Z)$$

When Linolenin is present:

$$261.8 X + 173.3 Y + 86.0 Z = 100 \text{ I.V.}$$

$$159.8 X + 92.5 Y + 85.5 Z = 100 \text{ T.V.}$$

$$X + Y + Z = 100 - S$$

$$X = 1.6610 \text{ T.V.} - 0.1332 \text{ I.V.} + 1.3056 S - 130.56$$

$$Y = 1.4137 \text{ I.V.} - 3.3449 \text{ T.V.} - 1.6441 S + 164.41$$

$$Z = 1.6839 \text{ T.V.} - 1.2805 \text{ I.V.} - 0.6615 S + 66.15$$

These constants are based on the assumptions that the addition of thiocyanogen to the fatty acids and the triglycerides is on a strictly stoichiometrical basis. This relationship has not been definitely proved. Several samples were analyzed during the past year in an attempt to show whether or not this relationship would hold true. The results are shown in the following tabulation:

	IODINE NO.—FATTY ACIDS						
	1	2	3	4	5	6	Average
Cottonseed—A.....	112.4	112.8	112.7	114.3	112.3	112.5	112.8
Cottonseed—B.....	112.3	112.8	113.1	113.5	112.0	112.1	112.8
Soybean.....	134.2	133.5	134.0	134.2	133.0	135.2	134.0
Peanut.....	99.4	98.7	99.5	99.5	99.7	100.1	99.6
Corn.....	125.6	132.1	132.2	131.9	133.0	131.7	131.1

	IODINE NO.—GLYCERIDES						
	1	2	3	4	5	6	Average
Cottonseed—A.....	107.0	106.9	108.5	108.5	108.0	108.0	107.8
Cottonseed—B.....	108.8	107.9	109.8	109.0	109.5	109.3	108.9
Soybean.....	129.2	129.7	129.7	129.7	130.0	129.8	129.6
Peanut.....	95.7	94.8	98.0	95.5	97.7	96.3	96.4
Corn.....	126.9	127.1	127.9	127.5	128.5	127.2	127.0