vantages gained by using the latter are (1) rapid saponification, (2) a reagent apparently less subject to the disturbing effect of aldehyde resinification, and finally, (3) a chemical is available around which no legal restrictions as to sale or use have been thrown.

TABLE II.—SAPONIFICATION NUMBERS OF FATTY OILS AND WAXES AND ESTER CONTENT OF VOLATILE OILS.

Substance.	Saponification number. Ethanol KOH.	Isopropanol KOH.	Recorded values.	Ester content. Ethanol KOH.	Isopropanol KOH.	U. S. P. IX.
Olive Oil	191.9	192.3	185–196 (1)	..	..	....
Cottonseed Oil	190.5	191.2	193–195 (2)	..	..	....
Cocoanut Oil	254.7	255.5	246–260 (3)	..	..	....
Lard Oil	193.1	193.7	190–198 (4)	..	..	....
White Wax	93.6	93.2	90– 98 (5)	..	..	....
Cetaceum	127.0	127.8	123–135 (5)	..	..	....
Oil of Wintergreen (Synthetic)	...	...	....	98.4	98.1	Not less than 98
Oil of Peppermint	...	...	....	13.0	12.4	Not less than 5

(1) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6 ed. Vol. I, 397 (1921).

(2) *Ibid.*, 396.

(3) *Ibid.*, 399.

(4) Leach, *loc. cit.*, 528.

(5) Lewkowitsch, *loc cit.*, 400.

SUMMARY.

Isopropanol may be substituted without sacrifice of accuracy or convenience for ethanol as a medium in which to conduct the quantitative saponification of fats, oils and waxes.

ISOPROPANOL AS A SUBSTITUTE FOR ETHANOL. II. THE TITER TEST.*

BY H. A. SCHUETTE AND LOYD E. HARRIS.

The present recognized methods[1] of the Association of Official Agricultural Chemists for determining the so-called titer test or solidifying point of the mixed insoluble fatty acids of fats and oils are two, namely the modified Dalican procedure in which either an alcoholic or an aqueous solution of sodium hydroxide is used as the saponifying agent and the more recent glycerol-potash procedure. There is not much to choose from between the titers obtained by either method, for they are substantially the same. Choice of saponifying medium at the present day, no doubt, favors glycerol, although it is not improbable that a denatured ethyl alcohol containing some methanol, for example formula number 30, offers possibilities as a substitute for 95 per cent ethanol in this case. For reasons[2] which we have already pointed out, higher homologues of ethanol are to be preferred for conducting saponifications. They are good solvents for fats, oils, and waxes, which property admits

---

* Read before the Scientific Section, A. PH. A., Des Moines meeting, 1925. A contribution from the Laboratory of Foods and Sanitation, Department of Chemistry, University of Wisconsin.

[1] "Methods of Analysis," A. O. A. C. 2 ed., 285 (1925).

[2] See this issue of the JOUR. A. PH. A.

of lower saponifying temperatures. Overheating, with a resulting scorching of the soap, thereby becomes a negative consideration.

Experiments made in this laboratory[1] showed that no consequential difference in the titer test of fats and oils results when the latter are saponified with sodium butoxide in butanol. Objections to the practical use of this observation can only be based on the irritating fumes of the butanol and probably to the cost of the solvent in quantity routine work. Such objections do not apply to isopropanol which is not at all unpleasant to work with. Its odor is described as being rather mild.

For the purpose of conducting the investigation herein recorded, comparative titer tests were made on the fatty acids prepared by the glycerol potash method with those in which isopropanol was substituted for ethanol. Saponifications were conducted on a steam-bath, which at once eliminated a precaution necessary in the glycerol potash procedure where it is required to keep the temperature at a point very near 150° C., when the isopropanol solution was used.

EXPERIMENTAL.

1. Materials.—Nine fats and oils were selected for this study. They were olive, menhaden, cottonseed, soya bean, cocoanut, and lard oils, and oleo stearin, oleo oil, and a tallow. With the exception of the last three, which is rather to be expected since they are manufactured products whose composition can be varied almost at will, all possessed analytical constants lying within the range of samples of known history. Their analysis is recorded in Table I.

2. Glycerol-potash Solution.—The solution recommended by the Association of Official Agricultural Chemists[2] was prepared. It consists of 25 grams of potassium hydroxide in 100 cc. of U. S. P. glycerol.

3.—A practically saturated solution of potassium hydroxide in isopropanol was prepared. The alcohol had been dehydrated over lime and had a boiling point of 81.3° C. (unc.). Titration against a standard acid solution showed the saponifying agent to contain 7 grams of potassium hydroxide per 100 cc. of solution. A normal solution of potassium hydroxide was found to readily saponify all the oils except cocoanut oil. Attempts to prepare a sodium hydroxide solution lead only to one whose strength was 0.7 normal which was found to be inefficient for saponification within the limits of time, size of sample and quantity of saponifying agent set for our experimentation.

Note.—A number of possibilities were tried in order to ascertain the best saponifying solution using isopropanol as solvent. A molar solution of sodium in this alcohol was prepared with the aid of heat but when the isopropoxide was cooled to room temperature it congealed. Saponification was attempted with it, however, using 150 cc. of the warmed and liquified solution to 50 cc. of olive oil. After heating on the steam-bath for three hours it was found that the reaction was not complete. Half-molar sodium isopropoxide which remains a liquid at ordinary temperatures was also tried, using the same proportions, but without satisfactory results.

1. Apparatus.—Standard thermometer.—The prescribed official titer thermometer[3] was used. It was calibrated against one of known accuracy.

---

[1] Unpublished thesis of J. H. Draize, University of Wisconsin, 1922.

[2] *Loc. cit.*

[3] *Loc. cit.*

2. *Titer Tube.*—An unsilvered Dewar flask of 50-cc. capacity was used in place of the calorimeter which usually serves in this test. The latter is made by placing a tube, 25 by 100 mm. into a 16 oz. wide-mouth bottle. The dimensions of the inner tube of the Dewar flask were substantially those as given above.

Preparation of Insoluble Fatty Acids.—The fats and oils were saponified in duplicate. In one case soaps were made by the official glycerol-potash procedure and in the other by the following which was developed as a result of numerous trials made to determine the optimum conditions for readily and completely saponifying all the fats and oils used in this study. We believe that it is applicable to all classes of fatty oils inasmuch as a representative group had been selected for study.

Fifty cc. of oil or melted fat and 175 cc. of the isopropanol-potash solution (7 grams in 100 cc. of the alcohol) were heated for 30 minutes on a steam-bath in a 500-cc. round-bottom flask which had been provided with a reflux condenser. After saponification about two-thirds of the alcohol was recovered by distillation, water added to the residue and the solution poured into a large metal crucible. The mixture was heated on the steam-bath, with occasional stirring, until the odor of isopropanol had disappeared. Finally this soap was transferred to an 800-cc. beaker containing 500-cc. of boiling water and the solution boiled to remove whatever alcohol might not have escaped before.

The fatty acids were liberated in each case by the careful addition of 50 cc. of dilute sulphuric acid (1 + 3). They were then washed repeatedly with boiling water to remove the mineral acid. The fatty acids so purified were dried for 20 minutes in an oven at 100° C., transferred to the titer tube, and the titer taken as directed by the official method. The only new feature which was introduced was the use of a more efficient titer tube.

The proximate composition of the mixtures of insoluble fatty acids, which were obtained by following the glycerol-potash method of saponification on the one hand and the isopropanol-potash method on the other, was then compared by making a determination of the iodine number, the melting point, and the index of refraction. Iodine numbers were determined by the method of Hanus and the melting points by the capillary tube method.[1]

RESULTS.

That the composition of the resulting mixed insoluble fatty acids is substantially no different from that obtained by the glycerol or by the isopropanol methods of saponification is apparent from the practical concordance of the melting point, titer test, index of refraction, and iodine absorption values which follow. Except for the titer test, averages only are recorded, for which see Table II. There have also been incorporated into a third table such titer tests and melting points, pertinent to this investigation, which we have been able to find in the literature. With the exception of oleo stearine and tallow, whose histories are obscure, the values found by us fall within the published limits.

The above results show, we believe, that no consequential difference in the titer test occurs with a change of method of saponification of the fat or oil in question. The use of an isopropanol-potash solution eliminates the careful observation

---

[1] "Methods of Analysis," A. O. A. C., 2 ed., 284 (1925).

and constant stirring of the other saponifying procedures. The danger of scorching the soap is also removed and with it the possibility of a low titer test.[1] Saponification is more rapid, a consideration to be taken into account in routine quantity work.

SUMMARY.

Isopropanol-potash has been shown to possess possibilities as a substitute for glycerol-potash, or for alcoholic potash (ethanol), in the saponifications preliminary to the determination of the solidifying point of the insoluble fatty acids of fats or oils. It is a safe and rapid reagent to work with.

TABLE I.—ANALYTICAL CONSTANTS OF FATTY OILS.

Fatty oil.	Index of refraction. Found.	Index of refraction. Usual limits.	Iodine number (Hanus). Found.	Iodine number (Hanus). Usual limits.	Acidity as oleic.
Olive	1.4670^{25°	1.4659-1.4685^{25°	79.4	77– 95	..
Menhaden	1.4770^{25°	....	135.9	145–170[1]	..
Cottonseed	1.4701^{25°	1.4698–1.4723^{25°	109.1	104–117	..
Soya Bean	1.4732^{25°	1.4729–1.4742^{25°	128.8	121–143	..
Cocoanut	1.4485^{40°	1.4474–1.4495^{40°	8.9	8– 9.5	..
Lard Oil	1.4652^{40°	1.4620–1.4660^{25°	66.0	67– 88	16.9
Oleo Stearin	1.4600^{40°	1.4524–1.4580^{40°	42.95	8 –27	..
Oleo Oil	1.4525^{60°	1.4573–1.4593^{40°	12.4	40– 50	12.7
Tallow	1.4480^{60°	....	15.8	.....	..

All references are to Leach, "Food Inspection and Analysis," 4 ed., 528 (1920) unless otherwise stated.

[1] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6 ed., Vol. II, 426 (1921).

TABLE II.—COMPARISON OF TITER TESTS, INDICES OF REFRACTION, MELTING POINTS, AND IODINE NUMBERS OF INSOLUBLE FATTY ACIDS.

Saponifying medium. Fatty acids from.	Glycerol potash. Index of refraction.	Glycerol potash. Iodine number (Hanus).	Glycerol potash. Melting point, ° C.	Titer tests, ° C.	Isopropanol potash. Index of refraction.	Isopropanol potash. Iodine number (Hanus).	Isopropanol potash. Melting point, ° C.	Titer tests, ° C.
Olive Oil	1.4530[2]	85.5	29.8	26.8	1.4523[2]	85.8	29.8	26.65
				26.7				26.6
Menhaden Oil	1.4650[2]	137.5	33.1	29.7	1.4642[2]	137.3	33.0	29.3
				29.6				29.4
Cottonseed Oil	1.4550[2]	110.2	38.4	33.2	1.4542[2]	110.2	38.2	33.15
				33.6				33.05
Soya Bean Oil	1.4650[1]	130.6	22.8	21.6	1.4645[1]	130.9	22.8	21.4
				21.6				21.3
Cocoanut Oil	1.4351[2]	9.0	25.2	23.5	1.4350[2]	9.1	25.1	23.45
				23.55				23.5
Lard Oil	1.4525[2]	66.5	37.3	34.3	1.4495[2]	67.2	37.4	34.6
				34.3				34.45
Oleo Stearin	1.4435[3]	48.0	43.7	41.0	1.4450[3]	47.8	43.8	41.15
				40.8				41.2
Oleo Oil	1.4430[3]	16.3	42.6	40.2	1.4425[3]	16.2	42.5	39.55
				40.2				39.6
Tallow	1.3950[4]	16.2	53.0	51.4	1.4400[4]	16.3	53.1	51.7
				51.55				51.75

[1] At 25° C. [2] At 40° C. [3] At 50° C. [4] At 60° C.

---

[1] *U. S. Bur. Chem. Circ.*, 22 (1904).

TABLE III.—MINIMUM AND MAXIMUM RECORDED TITER TESTS, MELTING POINTS, IODINE NUMBERS, AND REFRACTIVE INDICES OF INSOLUBLE FATTY ACIDS.

	Titer test.		Melting point.		Iodine number.		Refractive index at 60° C.	
Fatty acids.	Min., ° C.	Max., ° C.	Min., ° C.	Max., ° C.	Min.	Max.		
Olive Oil	17.2[1]	27.0[2] 26.4[1]	19.2[5]	31.0[5]	86.1	90.2[5]	1.4528[5] 1.4410[4]	..
Cottonseed Oil	28.5[2]	38.5[2]	34.0[7]	40.0[7]	105	115[7]	1.4460[7]	..
Soya Bean Oil	22.5[2]	25.0[2]	26.0[3]	29.0[3]	122[6]		1.465	27.5°[6]
Cocoanut Oil	21.5[2]	26.0[2]	24.0[3]	27.0[3]	8.3	9.3[8]	1.4295[8]	..
Lard Oil	34.5[2]	39.5[2]	..	..	..	...	....	..
Oleo Stearin	48.0[3]	51.0[3]	..	..	..	...	....	..
Tallow (Beef)	43.0[9]	45.0[9]	43.0[9]	47.0[9]	25.9	41.3[9]	1.4375[9]	..

[1] Lewkowitsch, *loc. cit.*, Vol. I, 517.

[2] Fryer and Weston, "Oils, Fats and Waxes," Vol. I, 70 (1918).

[3] Leach, *loc. cit.*, 528.

[4] Lewkowitsch, *loc. cit.*, 519.

[5] *Ibid.*, Vol. II, 351.

[6] *Ibid.*, 119. [7] *Ibid.*, 197. [8] *Ibid.*, 659. [9] *Ibid.*, 779.

THE PREPARATION OF TRIBROMHYDRIN AND PROPADIENE.*

BY M. W. TAPLEY AND P. M. GIESY.

In the course of the research on anesthetics being carried out by our laboratories it was desired to make sufficient propadiene for physiological investigation. Upon looking up the literature, the most feasible method for our purposes was found to be that of Gustavson and Demjanoff.[1] This method requires 1,2-dibrompropylene which, in turn, is prepared from tribromhydrin (1,2,3-tribromopropane).

Most methods of preparing tribromhydrin require heating at an elevated temperature in a sealed tube, the best method being that of Kronstein.[2] In this method a mixture of propylene dibromide with bromine in the presence of iron wire is heated in a closed tube in a water-bath for two hours. The resulting reaction gives an almost quantitative yield of tribromhydrin. The method has, however, the drawback of requiring the reaction to be carried out in a bomb tube, which was highly undesirable from a laboratory point of view. To avoid this the following modified method was evolved:

A mixture of 200 Gm. of propylene dibromide and 300 Gm. of bromine was placed in a 500-cc. round-bottom reaction flask and a small bundle of iron wire (20 Gm. of card teeth) added. The flask was then gently heated under a reflux condenser with the free flame, the heating being gradually increased until hydrobromic acid was no longer evolved. This required from one to two hours. The resulting mixture was distilled under vacuum and then redistilled at atmospheric pressure. The fraction boiling from 219° to 221° C. was collected. Yield, 78% of the theoretical, based on tribromhydrin.

The conversion of tribromhydrin into 1,2-dibrompropylene was accomplished by the method of Gustavson and Demjanoff,[1] which consists in dropping small

---

* Read before Scientific Section, A. PH. A., Des Moines meeting, 1925.

[1] *J. Prakt. Chem.*, [2] 38, 202 (1888).

[2] *Ber.*, 24, 4246 (1891).