done in a medium of phosphoric acid. In this solution the ferric ions are bound in a complex form, and do not react with iodide.

Therefore, if we wish to titrate iodide and ferrous iron together, the titration is done in the following way.

To 10 cc. of the liquid to be titrated is added a mixture of 80 cc. water, 10 cc. 25% phosphoric acid and 5 cc. 10% potassium cyanide.[1] Then 0.1 *N* potassium permanganate is added, until the liquid appears pink colored.

Then an excess of iodide is added, and the liberated iodine is titrated with thiosulphate, using starch as an indicator. If the permanganate number is A cc. 0.1 *N*, and the thiosulphate number B cc. 0.1 *N*, we have:

Iodide Content:	B × 12.69 Mg.
Ferrous Content:	(A − B) × 5.58 Mg.

Sucrose has but a very small disturbing effect in the titration with permanganate and therefore the method is recommended for a simple, rapid method for the titration of iodide and ferrous iron in syrup of ferrous iodide. Especially in scientific investigations, where the air and light decomposition is studied of a liquid containing ferrous iron and iodide, the method given above is of distinct advantage.

SUMMARY.

(1) The method of Lang is improved for the determination of traces of iodide with iodate as a reagent.

(2) The method of Lang is applied for the titration of iodide and ferrous iron in syrup of ferrous iodide.

PHARMACY LABORATORY OF THE UNIVERSITY,
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ISOPROPANOL AS A SUBSTITUTE FOR ETHANOL I. THE DETERMINATION OF SAPONIFICATION NUMBERS.*

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

Isopropanol is a member of the alcohol family whose appearance in the commercial field, either as a contribution from the petroleum-refining industry or as a foreign-made synthetic product,[1] has some interest to the pharmacist.

Fuller reported that not only is it superior to ethyl alcohol as a solvent but that it has greater antiseptic and disinfectant properties as well. He suggested[2] that the pharmaceutical profession has access to a solvent that might be capable

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[1] The potassium cyanide must not be added to the acidified mixture, which contains the ferrous iron, as there is formed a local excess of ferro-cyanide, and the liquid turns blue by air oxidation.

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[1] Anon, *Ind. Eng. Chem.*, 17, 822 (1925).

[2] JOUR. A. PH. A., pp. 1081-4, (December 1923).

of solving some of its most exasperating problems. This alcohol possesses also many possibilities from the analytical side, and it is the purpose of this paper to report on some experiments made with the view of demonstrating that it can be substituted without sacrifice of accuracy or convenience for other alcohols, particularly the ethyl form. When pure it is a colorless liquid possessing an odor decidedly more pleasant than its higher homologues and lacking their irritating qualities. It is not at all unpleasant to work with. Its boiling point does not lie much above that of ethanol and, like the latter, it is freely viscible with water in all proportions but it rectifies with greater ease. It will dissolve potassium hydroxide, but the carbonate is poorly soluble in it. It is also a good solvent for volatile oils, fatty oils, waxes, resins, etc.

Henriques[1] suggested some years ago that the saponification of a glyceryl ester by alcoholic potash proceeds in at least two steps, the first of which is the transposition of the glyceride into an ethyl ester, which is in turn saponified. Anderson and Pierce[2] elaborated on this idea and from their studies on the rates of saponification of an acetate in the presence of aliphatic alcohols it appears that with an increase in molecular weight among the monohydric alcohols that there is an increase in the velocity at which saponification takes place. On the basis of these facts Reid and his associates[3] demonstrated that normal butanol is an excellent medium in which to conduct the quantitative saponification of esters and found it to be superior to ethanol, for with its use they were able to very readily obtain satisfactory results and often without the use of any special precautions. Winkler[4] had previously called attention to the merits of propanol for the same purpose. In our case, *a priori* reasoning might have justified a statement of our conclusions without experimental evidence in at least one phase of this work, yet it seemed worth while to actually secure the necessary data in substantiation of any claims made. The investigation divided itself into two parts, the latter forming the subject of another paper.

1. Materials.—A commercial grade of isopropanol, "Petrohol," was treated with lime and distilled, that fraction boiling at 81.3° C. (unc.) being cut out for use. It was not water-free nor is it particularly desirable from theoretical grounds[5] that it be so for the purpose for which the alcoholic potash solution was subsequently to serve.

2.—Alcoholic potash solutions were prepared with the purified isopropanol and with ethanol purified with freshly precipitated silver hydroxide according to the procedure of Dunlap.[6] In each case forty grams of potassium hydroxide were dissolved in the alcohol and the volume made up to one liter. The precipitated potassium carbonate was removed by filtration. It is of interest to record here that whereas the ethanol solution turned a yellowish brown on standing, the isopropanol solution developed only a faint yellow color. From the analyst's view-

[1] *Z. angew. Chem.*, 338 (1898).
[2] *J. Phys. Chem.*, 22, 51 (1918).
[3] *Ind. Eng. Chem.*, 12, 129, 481 (1920).
[4] *Z. angew. Chem.*, 24, 638 (1911).
[5] Reid, *et al., loc cit.*
[6] *Jour. Am. Chem. Soc.*, 28, 395 (1906).

point, the ready preparation of so-called "water-white" solutions of this character is certainly a boon.

3.—As experimental material there were used four fatty oils, two waxes and two volatile oils. They were found to have the analytical constants as recorded in the following table. We believe them to be unadulterated.

TABLE I.—ANALYTICAL CONSTANTS OF EXPERIMENTAL MATERIAL.

	Index of refraction.			Iodine number (Hanus).			Acidity as
Substance.	Found.	Recorded.		Found.	Usual limits.		oleic.
Olive Oil	$1.4670^{25°}$	$1.4659–1.4685^{25°}$	(1)	79.4	77–95	(1)	..
Cottonseed Oil	$1.4701^{25°}$	$1.4698–1.4723^{25°}$	(1)	109.1	104–117	(1)	..
Cocoanut Oil	$1.4485^{40°}$	$1.4474–1.4495^{40°}$	(1)	8.9	8–9.5	(1)	..
Lard Oil	$1.4652^{25°}$	$1.4620–1.4660^{25°}$	(1)	66.0	67–88	(1)	16.9
White Wax	$1.4415°$	$1.4415°$	(2)	...	.....		..
Cetaceum	$1.4336°$	$1.4334°$	(2)	...	.....		..
Oil of Wintergreen (Synthetic)	$1.5360^{20°}$	$1.5379^{20°}$	(4)	...	.....		..
Oil of Peppermint	$1.4615^{20°}$	$1.4636–1.4643^{20°}$	(5)	...	.....		..

(1) Leach, "Food Inspection and Analysis," 4 ed., 528 (1920).
(2) Thurston, "Pharmaceutical and Food Analysis," 151 (1922).
(3) *Ibid.*, 156.
(4) *Ibid.*, 383.
(5) *Ibid.*, 352.

EXPERIMENTAL.

Saponification numbers of the fatty oils and waxes were determined according to the official method[1] of the Association of Official Agricultural Chemists. The volatile oils were assayed by the method of the U. S. P. IX. The reaction between the oils and the isopropanol-potash solution began almost immediately upon the addition of the saponifying agent and proceeded very smoothly. This suggests the thought that the usual thirty-minute saponification period, or "until completely saponified," may be materially shortened if isopropanol is to be used as the medium in which the reaction is to be conducted. The addition of the first few cubic centimeters of 0.5 normal hydrochloric acid solution to the resulting soap solution, in the titration of the excess of alkali, caused a slight cloudiness but this soon disappeared on the subsequent addition of more of the acid solution.

RESULTS.

In the following table we have recorded only averages, duplicate determinations in every case having fallen within the usual small range of experimental error. For purposes of comparison there have also been included the accepted values for authentic samples of the material in question. It is to be noted that all the values obtained are well within the limits for pure oils. For the fatty oils values were obtained by the isopropanol procedure which are between 0.2 and 0.3 per cent higher than those given with ethanol. The values for cetaceum were about 0.6 per cent higher for the isopropanol saponification and that for the white beeswax fell about 0.4 per cent short. The ester content of the ethereal oils both fell short of those obtained by the ethanol procedure.

It appears from these experiments that the values obtained when ethanol and propanol are used as saponifying mediums are substantially the same. The ad-

[1] "Methods of Analysis, A. O. A. C.," 2 ed., 288 (1925).

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.