	Olive Oil.	Rapeseed Oil.	Mixed Oils (75 Olive + 25 Rape).
Iodine value	83.5	99.9	87.9
Saponification number	....	....	190.3
Refractive index at 25°	1.4678	1.4720	1.4687
Critical temperature of dissolution or Valenta number	69.2°	83.4°	72.0°

The above results show how closely this mixture of olive and rapeseed oils approaches the constants of a pure olive oil. It will also be noted that figures are stated for the critical temperature of dissolution or Valenta number. In the experience of this laboratory, the Valenta number is the most satisfactory means of detecting this particular adulterant. The details of this test are herewith abstracted from "The Technical Handbook of Oils, Fats and Waxes," Percival J. Freyer and Frank E. Weston, Volume II, 1920, Cambridge University Press.

> Prepare a standardized solvent by taking equal volumes 92% ethyl alcohol and pure amyl alcohol and add water until pure almond oil gives a corrected turbidity at 70° C. when tested in the following manner. To 5 cc. of the standardized solvent add an equal volume of the dry oil to be tested; warm until clear; allow to cool and note temperature at which the first sign of turbidity appears during stirring. A correction for acidity is added to the recorded temperature and the result is termed the True Valenta Number.

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A NOTE ON THE TITRATION OF BORIC ACID.*

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INTRODUCTION.

The titration of boric acid has warranted the attention of the analytical and physical chemist. The acid in aqueous solution behaves like a weak monobasic acid having a dissociation constant of 6.6×10^{-10} at 25° C. The end-point in titration with alkali occurs at about p_H 11 (1). The change in the hydrogen-ion concentration upon the addition of various types of polyhydric alcohols has been observed for years. Mannitol and glycerin augment the dissociation constant of the acid roughly ten-thousand-fold. This change has been studied by Hildebrand. The properties of the mannitol-boric acid complex were studied by Maugauini (2) in 1890. This investigator emphasized the importance of having the solution of the polyhydric alcohol concentrated and furthermore showed that upon dilution the complex was completely hydrolyzed. Very recently Dodd (3) studied the accuracy of the titration with various indicators and found phenolphthalein the most satisfactory.

Based upon theoretical considerations Prideaux (4) titrated boric acid in aqueous solution using tropeolin O as an indicator. The p_H range of this indicator is approximately 11.1 to 12.7. This investigator determined the p_H of a solution containing equal molar quantities of boric acid and sodium hydroxide and found it to be approximately 11. He titrated boric acid in 0.2 to 0.3 molar solution, using about 0.2 cc. of 0.04 per cent solution tropeolin O as an indicator. His results were

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concordant. Likewise upon theoretical considerations nitramine (picrylmethylnitramine) should also serve as an indicator for the titration of boric acid in aqueous solution.

These methods were studied to determine their applicability as a Pharmacopœial method.

EXPERIMENTAL.

A solution of boric acid of U. S. P. purity was prepared 1.250 Gm. in 25 cc. Twenty-five cubic centimeter portions of this solution were titrated with carbon dioxide free sodium hydroxide solution in normal concentration. Glycerin neutral to phenolphthalein was employed throughout. One series was run by the present U. S. P. method, another by the method of Prideaux using tropeolin O as an indicator and a third by adding glycerin to discharge the pink color produced by phenolphthalein at the end-point and further titrating until it re-appears. This modification (5) was suggested to the Pharmacopœia Revision Committee by the Pacific Coast Borax Company.

TABLE I.

	I. U. S. P. Method Gm. Found.	II. Modified U. S. P. Method, Gm. Found.	III. Aqueous Solution Using Tropeolin O Method, Gm. Found.	
1.	1.220	1.234	1.261	1.242
2.	1.220	1.240	1.259	1.270
3.	1.232	1.248	1.252	1.262
4.	1.252	1.240	1.252	1.255
5.	1.228	1.240	1.259	1.258
6.	1.222	1.243	1.278	1.271
7.	1.220	1.240	1.259	1.271
8.	1.230	1.243	1.252	1.271
9.	1.228	1.243	1.270	....
10.	1.228	1.240	1.271	....
Gm. mean	1.225	1.241	1.262	
Mean per cent of H_3BO_3	98.0	99.5	100.9	

The probable error of a single determination was calculated by the formula $r = \pm 0.6745 \sqrt{\frac{\Sigma (v^2)}{n-1}}$. The probable error of the mean of the determinations was calculated by the formula $R = \pm 0.6745 \sqrt{\frac{\Sigma (v^2)}{n(n-1)}}$. v is the deviation from the mean and n the number of observations.

I U. S. P.

$r = \pm$ 5.4 mgm. or $\pm$0.43 per cent
$R = \pm$ 1.7 mgm. or $\pm$0.14 per cent

II Mod. U. S. P.

$r = \pm$2.4 mgm. or $\pm$ 0.19 per cent
$R = \pm$0.77 mgm. or $\pm$ 0.06 per cent

II Trop. O

$r = \pm$7.7 mgm. or $\pm$0.6 per cent
$R = \pm$1.6 mgm. or $\pm$0.13 per cent

When nitramine was used as an indicator concordant results were obtained only with great difficulty. When the solution of boric acid was saturated with sodium chloride to depress the hydroxyl-ion concentration caused by the hydrolysis of mono-sodium borate, neither with tropeolin O nor with nitramine was the end-point sufficiently sharp for an official method.

DISCUSSION.

The statistical analysis of the raw data shows the modification of the U. S. P. method most satisfactory from the standpoint of accuracy in procedure. Furthermore, this method gives results which are closest to the theoretical. The probable error of a series of determinations is practically negligible.

The values obtained with tropeolin O are somewhat higher than the theoretical. This is what one would expect from theoretical considerations of boric acid and the transition range of the indicator. The indicator begins to change at about the theoretical end-point of the titration. However, the transition range is not sharp and generally an excess of alkali must be added to obtain the reddish brown tint. The transition range of the indicator is between approximately p_H 11 and 13, the reddish brown color appears definitely at about p_H 12. The hydrogen-ion concentration at the true end-point of the titration may be calculated from the following equation:

$$[H^+] = \sqrt{\frac{Kw \times Ka}{c}}$$

in which Kw = 10^{-14} and Ka the dissociation constant of boric acid = 6.6×10^{-10}, and c, the concentration, which is about 0.1 molar:

$$[H^+] = 8.1 \times 10^{-12} \text{ and } p_H = 11.2.$$

Thus it becomes necessary to add sufficient normal alkali solution in excess of the true end-point to change the p_H from approximately 11.2 to 12 in order to reach the midway transition range of the indicator. Supposing the final titration volume to be 50 cc. our problem becomes quite simple. One cc. *N* sodium hydroxide diluted to 100 cc. is equivalent to 0.01 *N* solution or 10^{-2} or in terms of $[H^+]$ as the negative exponent of 10, we have 10^{-12} or p_H 12. For 50 cc. approximately 0.5 cc. is required. The theoretical amount of 1 *N* alkali for 1.25 Gm. of boric acid is 20.2 cc., hence, 0.5/20.2 = 0.0248 or 2.48 per cent excess. By knowing the theoretical quantity of alkali required and matching the color of the indicator at this hydrogen-ion concentration, results in accordance with theory can be obtained. This procedure, in the authors' opinion, is not suitable for an official assay.

In the modification of the U. S. P. assay 1.25 Gm. of boric is employed, dissolved in 25 cc. of distilled water and 25 cc. glycerin. The boric acid is approximately 0.2 molar and the glycerin about 3.5 molar at the end of the titration. After the appearance of the pink color this is discharged by the addition of 25 cc. additional glycerin, increasing the molar concentration of glycerin to approximately 7.

Mellon and Morris (6) studied the potentiometric titration of boric acid in the presence of various polyhydric alcohols. These workers used boric acid in approximately 0.11 molar solution and four moles of glycerin to one mole of acid. The hydrogen-ion concentration of the glycerin-boric acid complex with this proportion of glycerin taken from the curve of these investigators is approximately p_H 4.6. The present authors determined the hydrogen-ion concentration electrometrically of 1.25 Gm. of boric acid dissolved in 25 cc. of distilled water and 25 cc. of glycerin and found it to be 8×10^{-4} or p_H 3.1. When 25 cc. of additional glycerin was added the hydrogen-ion concentration was increased to 1×10^{-3}, p_H 3.0 indicating that the additional glycerin slightly augmented the hydrogen-ion concentration of the complex. After the discharge of the pink color with the additional amount of glycerin the p_H of the solution was 7.5 indicating that the mixture was well on the acid side of the incipient color change with phenolphthalein. To restore the pink color (p_H 8.3) it requires about 0.25 cc. 1 N sodium hydroxide solution, which gives results in accordance with theory. The dissociation constant of the glycerin-boric acid complex calculated from the [H$^+$] in 0.2 molar solution is $Ka = \frac{(10^{-3})^2}{0.2} = 5 \times 10^{-6}$, which indicates clearly that the complex is a relatively strong acid.

SUMMARY.

1. The titration of boric acid has been studied.
2. The modified Pharmacopœia method herein described is satisfactory for an official method of assay.
3. The P.E. of an individual determination by this method is 0.19 per cent, *i. e.*, the chances are even that one in two determinations will be either mean ± P.E. or that it will differ from the mean by more than one P.E.

BIBLIOGRAPHY.

(1) H. T. S., Britton, "Hydrogen Ions," D. Van Nostrand, New York (1929), p. 143.
(2) *Z. physik. Chem.*, 6 (1890), 58.
(3) *Analyst*, 50 (1930), 23.
(4) *Z. anorg. Chem.*, 83 (1913), 362.
(5) *General Circulars of the Revision Committee of the U. S. P. X.*
(6) *Ind. Eng. Chem.*, 16 (1924), 123.

ASSAY FOR ALKALI SALTS OF ORGANIC ACIDS.*

BY JOSEPH L. MAYER.

The United States Pharmacopœia on page 431 directs that alkali salts of organic acids be assayed by the following method:

> "Heat about 2 Gm. of the salt, accurately weighed, in a platinum or porcelain crucible, heating at first very gently, then gradually raising the temperature until the salt is thoroughly carbonized. (Caution.—Do not use platinum crucibles for lithium salts.) The final temperature must not exceed a dull red heat and the flame of the burner must not come in contact with the carbonized mass. After allowing the carbonized mass to cool, moisten with distilled water, ignite again and repeat the moistening and igniting until a white residue is obtained. Then disintegrate the ignited mass with the aid of a stout glass rod and transfer the mass and crucible to a beaker. Add 50 cc. of distilled water and titrate with half-normal sulphuric acid, using methyl orange T.S. as indicator. The number of cc. of half-normal sulphuric acid used, multiplied by the proper equivalent of the salt, represents the amount of salt present in the quantity taken."

This procedure has several defects; for example:

If a sufficiently large dish be substituted for the crucible, not only is it easier to obtain a white residue but there is no need to "transfer the mass and crucible to a beaker," the result being that the titration can be done without danger of loss.

Believing that residual titration would give better results than the direct method recommended by the U. S. P., the following experiments were made:

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