

In Graph No. 7 the titration curve for tannic acid, O amino benzoic acid and a mixture of equal parts of the two are shown. For the tannic acid curve and the O amino benzoic acid curve, 10 cc. of a solution of each were diluted separately to 110 cc. and titrated electrometrically with approximately  $N/10$  sodium hydroxide. The tannic and O amino benzoic acid curve was constructed by mixing 10 cc. of each acid solution diluting to 220 cc. and titrating 110 cc. of the resulting mixture. Here again the O amino benzoic acid shows a very decided effect on the titration curve of tannic acid which effect appears to be roughly additive. In the case of both tannic and pyrogallic acid difficulty was experienced in making readings for high  $p_H$  values. The highest  $p_H$  value obtained for each addition of sodium hydroxide was used rather than the lower ones obtained when equilibrium was established.

In Graph No. 8 we have shown the titration curves for 10 cc. of approximately  $N/10$  hydrochloric acid diluted to 110 cc. and for 10 cc. of hydrochloric acid plus 10 cc. of O amino benzoic acid diluted to 120 cc. Some effect of the amino benzoic acid on the titration curve of hydrochloric acid is here seen, but its influence is much less than in the case of the weaker acids. If the titration curve for the mixture is shoved to the left to the position occupied by the broken lines, the influence is more easily seen. The similarity between these two curves and those shown in Graph No. 1 is very evident. O amino benzoic acid apparently has very little effect on the titration curve of strong acids but a considerable effect on weakly acid substances. Gelatin, however, has no considerable effect on either.

The above curves are presented for the interest and value of them as such and due to the apparent lack of conformity to Loeb's theory as to the chemical amphoteric nature of gelatin, which of course now seems definitely established. It may be pointed out that the equivalent weight of gelatin is so high that the amounts used were not large enough to permit any appreciable effect on the titration curves of the acids worked with. Loeb, however, in constructing his titration curve for isoelectric gelatin worked with an 0.8% solution of gelatin. 0.8 of a Gm. of isoelectric gelatin was present in the 100 cc. of solution used for the titration.

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## A MODIFIED CALVERT TEST FOR DIETHYLPHTHALATE.

BY R. D. SCOTT AND E. G. WILL.\*

The writers have employed over a period of about two years a modified form of the Calvert test for diethylphthalate<sup>1</sup> in the examination of a large number of alcoholic beverages and medicinal preparations. The original Calvert test is briefly: To 3 or 5 cc. of the sample, in a test-tube, add 5 to 10 drops of phenol, 10 drops of concentrated sulphuric acid and heat slowly over a small Bunsen flame until most of the alcohol has been driven off and the sample assumes a red color. Cool, add 15-25 cc. of water, then add an excess of sodium or potassium hydroxide. A red color denotes the presence of diethylphthalate.

Numerous series of tests were carried out to study the effect of temperature

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<sup>1</sup> *American Journal of Pharmacy*, 94, 11, 702 (1922).

necessary for conversion and optimum concentration of phenol, sulphuric acid and alkali. As a result it was found that:

1. The temperature of a boiling water-bath is sufficient, if the reaction is allowed to proceed over night.

2. The amount of sulphuric acid may be materially reduced, thus reducing the volume of alkali added later, without affecting the conversion to diethylphthalate.

3. The sensitivity of the test is increased by the use of a larger proportion of phenol, possibly because evaporation of diethylphthalate may be thereby retarded, thus preventing its escape before reaction.

4. For convenience the phenol and sulphuric acid, diluted with alcohol, may be added together. Lessmann and Trumper<sup>1</sup> use phenol and sulphuric acid together in exact proportion to form phenol sulphonic acid. We have found, as noted above, that the sensitivity of the test is increased by using an excess of phenol. The proportions finally adopted were 250 Gm. of phenol and 15 cc. of concentrated sulphuric acid made up to one liter with 95 % alcohol; the mixture is designated as D. E. P. reagent. Exactly 10 cc. of this reagent is added to from 0.1 cc. to 5 cc. of solution to be tested, contained in a 50-cc. beaker.

5. The sensitivity of the test is much increased by carefully adjusting the amount of alkali finally added. On adding phenolphthalein to prepared buffer solutions it was observed that maximum intensity of red color developed at about  $p_H$  10.5. In more alkaline solutions no further increase in color strength was noted, but fading of color was observed to begin at about  $p_H$  12.7. At  $p_H$  13.1, or in a 0.1 *N* solution of sodium hydroxide, fading is more rapid, while in 10 cc. of *N* sodium hydroxide, the red color produced by 0.1 mg. of phenolphthalein faded in about four minutes. Accordingly, the addition of alkali should be so regulated that the final hydrogen-ion concentration ranges from  $p_H$  11 to  $p_H$  12.

This may be adjusted by running a control test taking 10 cc. of D. E. P. reagent, evaporating over night, adding 50 cc. of distilled water and one cc. of 0.1 per cent aqueous solution of Alizarine Yellow R. Titrate with *N* sodium hydroxide solution until the original light yellow color changes to a full orange shade; this color change takes place at about  $p_H$  11.5. Exactly this volume of *N* sodium hydroxide is then used in the test. If the indicator is not available, practically as satisfactory results may be secured by titrating with 0.2 cc. of 0.5 per cent alcoholic phenolphthalein solution to a faint pink color and then adding just 2 cc. more *N* sodium hydroxide than the volume required for this titration. Usually about 5.3 cc. of *N* sodium hydroxide solution is required.

A blank using the reagent alone and also a control consisting of the reagent plus 0.5 mg. of diethylphthalate are carried through with the sample to be examined. All are evaporated over night, 50 cc. of distilled water and the required volume of *N* sodium hydroxide are added to each.

Depending on the purity of the phenol used, the blank should be colorless to a light salmon or faint pink tint. Using definite amounts of diethylphthalate, 0.1 mg. should produce a light pink color, 0.5 mg. a light red and 1 mg. a red color. The colors persist indefinitely in the  $p_H$  range mentioned. To avoid the possi-

<sup>1</sup> *American Journal of Pharmacy*, 97, 8, 507 (1925).

bility of false tests, the presence of diethylphthalate in the sample examined should not be considered established unless the red color produced is at least equal in intensity to that produced by 0.5 mg. of diethylphthalate.

*Examination of Commercial Samples.*—Alcohol samples, rubbing alcohols and spirit of camphor may be run directly, using 0.1 to 1 cc. for the test. Beverage liquors, if colored, should be distilled. For example, 25 cc. of an approximately 50 per cent alcoholic preparation is distilled and the first 10 cc. of distillate used for the test. Aromatic spirit of ammonia should be distilled. Tincture of iodine should be reduced with zinc dust and distilled. Vanilla extract should be precipitated with basic lead acetate solution as recommended by Wales<sup>1</sup> and distilled before applying the test. In general, a control should be run on authentic preparations known to be free from diethylphthalate at the same time with the sample in question, to eliminate any possibility of a false test. However, it has been the writers' experience that samples which contained diethylphthalate gave full, clear, red colors, while samples which might be classed as giving false tests produced brown colors, or orange colors rapidly fading to brown.

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## A REVISION OF THE PENTANOLS.

BY S. M. GORDON.

(Continued from p. 322.)

### THE 3,5-DINITRO-BENZOATES.

3,5-Dinitrobenzoic acid was first prepared by Cahours in 1847 (*Jahresberichte*, 48, 533), its acid chloride by Behrend and Heymann in 1902 (*J. prakt. Chem.*, 65, 291). The first ester to be prepared was the ethyl ester obtained by Voit in 1856 (*Ann.*, 99, 105), by the action of ethyl alcohol on the acid, using sulphuric acid as the condensing agent. It was also obtained by Beilstein and Kurbatow in 1880 (*Ann.*, 202, 223), by acting on ethyl iodide with the silver salt of the acid. The ester in both cases melted at 91° C.

The methyl ester was prepared by Herre in 1895 (*Ber.*, 28, 596) by the action of the acid on methyl alcohol using gaseous hydrogen chloride as the condensing agent. This ester melted at 112° C.

Inasmuch as many of the esters of the alcohols of the methane series are liquid, the crystalline character and the definite melting points of these esters apparently suggested their use for the identification of the so-called fatty alcohols. Thus Mulliken in 1904 ("Identification of Organic Compounds," 1, p. 168), suggests that the alcohols be heated with 3,5-dinitro-benzoyl chloride for ten minutes, and that the reaction product be poured into water and the solid ester be recrystallized from a suitable solvent. He thus prepared the 3,5-dinitrobenzoates up to and including those of the two butyl alcohols.

In 1906 Cohen and Armes (*J. C. S.*, 89, 148), prepared the menthyl ester by heating molecular amounts of menthol with the acid chloride in a boiling water-bath for ten minutes.

In 1922 R. E. Kremers (*Jour. A. Ph. A.*, 12, 626) extended the use of this reagent to the identification of phenols, making use of a modified Schotten-Baumann

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<sup>1</sup> *J. Assocn. Official Agr. Chem.*, 9, 4, 477 (1926).