oleic acid gave in concentration of 200 parts per million practically the same results, very little transpiration, green weight about half of that in the control solutions, and death of the plants in 12 or 15 days.

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THE COLORIMETRIC ESTIMATION OF BENZALDEHYDE IN ALMOND EXTRACTS.

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The recent successful application of the reaction with fuchsine-sulphurous acid to the colorimetric determination of acetaldehyde[1] and of citral[2] suggested its similar use for the estimation of small amounts of benzaldehyde. Such a method would find immediate use in the assay of commercial almond extracts, for which the methods at present given in text-books are entirely inadequate, yielding results often 40 to 50 per cent. too low. A procedure based on the colorimetric estimation has been worked out and is described in this paper.

Preparation of Reagents.

Fuchsine-Sulphurous Acid.—0.5 gram of pure fuchsine is dissolved in 100 cc. of water and a freshly prepared solution of sulphurous acid containing twenty grams of sulphur dioxide is added. When the solution is decolorized, sufficient water is added to make a liter. The amount of sulphur dioxide should be determined by titration with iodine, or, if freshly prepared, its strength can be determined with sufficient accuracy from its specific gravity as found with a Westphal balance. A convenient method of preparing the solution is to balance the fuchsine solution on a scale pan and then to pass in a current of sulphur dioxide until the weight has increased by twenty grams.

In order to get a colorless solution, pure fuchsine should be used, and the solution can be relied upon for about ten days, the sulphuric acid formed by the oxidation of the sulphur dioxide decreasing its sensitiveness so much in that time that it is better to use a fresh solution. This strength of sulphur dioxide was chosen after various experiments as giving less trouble in the use of alcohol containing traces of aldehyde, and being at the same time sufficiently sensitive. The difference in color produced by 0.05 milligram of benzaldehyde is readily detected.

It has been stated by Prud'homme[3] that benzaldehyde reacts but slightly with the ordinary fuchsine-aldehyde reagent and he has suggested

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[1] Tolman, THIS JOURNAL, 28, 1625.

[2] *Ibid.*, 1472.

[3] *Bull. soc. ind. Mülhouse*, 74, 169.

a more sensitive form of the reagent, in which sodium thiosulphate is used instead of sulphurous acid as the decolorizing agent. This statement does not agree with our experience, in which the fuchsine-sulphurous acid, prepared as described above, showed a distinct change in color with 0.05 mg. benzaldehyde in a volume of 50 cc. The modified reagent proposed by Prud'homme did not give satisfactory results in our hands. The reagent was inconvenient to prepare, owing to the separation of finely divided sulphur, which could not be removed by filtration. The reagent, furthermore, was too sensitive, giving a pink color when standing for a few moments in contact with the air, even in the absence of aldehyde.

Aldehyde-free Alcohol.—Considerable attention was devoted to the preparation of this reagent. We found it absolutely necessary to prepare it, although Vasey[1] says that he was able to secure a commercial cologne spirit sufficiently free from aldehyde to use.

Numerous experiments, the details of which need not be given here, were carried out to determine the most convenient method for preparing from commercial "cologne spirit" an alcohol which should be free from aldehyde as shown by the Schiff reagent, made up as described.

Methods involving oxidation of the aldehyde with silver oxide were given thorough trial. Winkler's method[2] as modified by Dunlap[3] gave an alcohol which showed considerable color with fuchsine-sulphurous acid, although the method was carried out exactly as prescribed.

Andrews[4] has recently described in connection with the determination of the refractive indices of alcohol-water mixtures a method for the preparation of pure alcohol, depending on treatment with quicklime and subsequent boiling with silver nitrate. The statement is made concerning the product that "no reaction for aldehydes could be obtained from it." In carrying out this method commercial "cologne spirit" was allowed to stand over quicklime, with frequent stirring, for four weeks. It was distilled twice from lime, collecting only the middle portion each time, boiled for ten hours with silver nitrate and then allowed to stand four days over the silver nitrate. The middle portion of the distillate from the silver salt gave a decided color with the Schiff reagent.

These oxidation methods with silver having failed in our hands to give satisfactory results, it was determined to resort to the methods involving the condensation of aldehyde with reagents to give non-volatile or difficultly soluble products. Of these the most promising appeared to be meta-phenylenediamine hydrochloride as used by Tolman and by Chace in the work already mentioned. After considerable work with this reagent

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[1] Analysis of Potable Spirits.

[2] *Ber.*, **38**, 3612.

[3] THIS JOURNAL, **28**, 395.

[4] *Ibid.*, **30**, 353.

we were enabled to prepare by means of it alcohol which was absolutely free from color when tested for aldehyde by our reagent. In order to secure a perfectly satisfactory alcohol, however, rather close adherence to certain details, which may be briefly mentioned here, is necessary.

The meta-phenylenediamine reagent seems to remove only comparatively slight amounts of aldehyde, so that it is essential that the alcohol be relatively pure before being treated with the reagent. Hence commercial alcohol should first be treated with some preliminary reagent which will remove the greater portion of the aldehyde. Tolman, Chace and others have employed the customary treatment with caustic potash for this purpose, but we have secured much better results and in a far less time by using the treatment with silver oxide, as suggested by Dunlap, as a preliminary step.

Although it is evident that the greater part of the meta-phenylenediamine takes no part in the reaction, we have been unable to secure good results by using a less proportion than 25 grams to the liter. Since this reagent is expensive, it would render the process a costly one were it not for the fact that the greater part of the excess, being only difficultly soluble in 95 per cent. alcohol, can be recovered unchanged at the end of the treatment. It is probable that if 3 to 5 grams of fresh reagent were added occasionally, 5 or 6 liters of purified alcohol might be obtained from 30 to 35 grams of reagent.

From the slight solubility of the meta-phenylenediamine in alcohol, together with the very large excess that it is necessary to use, it seemed probable that the reaction was very largely a question of the actual surface of reagent brought into contact with the alcohol. Such being the case, it seemed possible that the only purpose served by boiling for several hours, as recommended by those who have previously used this reagent, is to keep the mixture of alcohol and reagent constantly stirred. Experiment confirmed this view and it was found that the same results could be obtained by shaking the reagent and alcohol in a shaking machine at room temperature as by boiling for the same length of time. Allowing the meta-phenylenediamine hydrochloride and alcohol to stand for several weeks with frequent shaking proved sufficient to give a fairly good grade of alcohol. The best results, however, were obtained by keeping the mixture stirred up for several hours by simply drawing a rather vigorous current of air through it.

The method we have been using for some time may be summarized as follows, starting with commercial "cologne spirits:"

This is first treated with silver oxide exactly as described by Dunlap[1] and distilled. To the distillate is added 25 grams of meta-phenylenediamine hydrochloride per liter and a fairly rapid current of air drawn

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[1] *Loc. cit.*

through the solution for three hours. The alcohol is then distilled, the first 100 cc. being rejected.

The remainder of the distillate should give absolutely no color when tested for aldehyde in the manner described under the estimation of benzaldehyde. It will remain suitable for use for several weeks at least, if kept cold and in the dark, preferably in an ice-chest.

Determination of Benzaldehyde.—A standard solution of benzaldehyde containing for convenience one mg. of freshly distilled benzaldehyde in each cubic centimeter of aldehyde-free alcohol, should be made up. This dilute solution will keep well. For comparison, the ordinary Hehner's colorimeters are excellent, although for more accurate work we have used the Duboscq instrument with much satisfaction.

The most suitable range of color for matching is given by about 4 to 6 mg. of benzaldehyde in 25 cc. of alcohol. The color of the sample can be allowed to vary somewhat from that of the standard, since within reasonable limits the color is approximately proportional to the depth of the solution and the concentration of aldehyde. As a matter of convenience in reading, however, it is found best to have the concentrations approximate the limits given.

In general, in making the comparisons the precautions found necessary by Tolman[1] in his work on the aldehyde in whiskies should be observed. The method as used with commercial almond extract may be outlined as follows:

Since each cubic centimeter of standard almond extract contains approximately 8.9 mg. of benzaldehyde, an amount of extract containing enough benzaldehyde to give the color best suited for comparison would be too small for convenient measurement. Consequently 10 grams of extract are best diluted to 50 cc. with aldehyde-free alcohol. Two cc. of this dilute solution are placed in a Hehner colorimeter and made up to 20 cc. with aldehyde-free alcohol. Three standard solutions are made up containing 2, 4 and 6 mg. of benzaldehyde and placed in similar colorimeter tubes. The colorimeters are now transferred to a water bath at 15° and allowed to stand until the solutions reach the temperature of the bath. Then 20 cc. of Schiff's reagent, also at a temperature of 15°, are added, as rapidly as possible to all the tubes and after thorough mixing the tubes are allowed to stand ten minutes, after which time the unknown sample is matched with the nearest standard by drawing off the solution from one of the colorimeters until the depth of color is equalized. Within these limits the depth of color is proportional to the concentration of benzaldehyde.

A number of test analyses have demonstrated the accuracy of the

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[1] *Loc. cit.*

method and its convenience in the assay of commercial almond extracts. It is probable that it could be applied also to the valuation of almond oils.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE LEAD VALUE OF MAPLE PRODUCTS.

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The addition of lead subacetate or lead acetate to maple products in solution and a determination of the resulting precipitate constitutes one of the most important and most frequently used tests for purity of these products. Lead acetate when added to a pure maple product precipitates the malic and other organic acids, as well as chlorides, sulphates and carbonates, coloring and other organic matters. In cane sugar solutions this precipitation does not take place, and in maple products adulterated with cane sugar the precipitate decreases as the cane sugar increases.

The lead acetate precipitation methods may be divided into four classes: first, those in which the bulk or volume of precipitate is determined—Jones,[1] Hortvet,[2] Sy;[3] second, where the weight of the total precipitate is determined;[4] third, where the amount of acid radicals combined with the lead in the precipitate is determined, Hill and Mosher;[5] fourth, in which the amount of lead in the precipitate is determined, Winton,[6] and the method to be described in the following.

The Lead Value of Maple Products.—Since the preliminary note[7] on this method, sufficient data have accumulated and satisfactory results obtained on inspection samples of maple products, so that it is thought of interest to analysts to give the method in detail.

By "*lead value*" is meant the amount of lead precipitated by adding a solution of lead acetate to 100 grams of sugar or 100 cc. of sirup. The preliminary results with this method were obtained by the following procedure: to 50 grams of sugar or 50 cc. of sirup about 200 cc. of water were added, the solution heated to boiling, excess of a saturated solution of lead acetate added, allowed to settle and filtered. The lead was then determined in the precipitate by the usual method, as lead sulphate,

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[1] *17th Annual Rpt. Vermont Exp. Sta.*, p. 454.

[2] THIS JOURNAL, 26, 1532.

[3] *Ibid.*, Sept., 1908, p. 1429.

[4] Inland Revenue Dept., Ottawa, Can., Bull. 140.

[5] *Tech. Quarterly*, 1905, 146.

[6] THIS JOURNAL, 26, 1204.

[7] *J. Franklin Inst.*, 1906, 71.