water, but insoluble in hot alcohol, while any gelatin is decomposed into bodies not precipitable by alcohol. The liquid is cooled and allowed to stand a few minutes to facilitate the separation of any insoluble caseinous matter; filtered, filtrate heated to boiling, one and one-half volumes of warm alcohol added and mixed. In the presence of 0.2 per cent. of gum tragacanth or agar-agar, a characteristic flocculent precipitate will *immediately* separate. Any turbidity, or slight precipitation on standing a few moments, should be ignored. The precipitated pectate may be dissolved in cold water and the solution saturated with ammonium sulphate for the purpose of demonstrating the absence of any appreciable quantity of proteids.

A second procedure, involving more or less complete preliminary removal of proteids and bases, with conversion of the gum into pectic acids, consists in boiling 10 cc. of the separated serum to 5 cc. after addition of one half cc. of concentrated hydrochloric acid. Two volumes of alcohol are then added to the hot liquid and the resulting precipitate washed two or three times with alcohol. The residue is boiled with 5 cc. of water and one drop of strong acetic acid and filtered hot. The resulting filtrate is rendered just neutral or very faintly alkaline, boiled and filtered. Finally 1 cc. of sodium hydroxide (1–10) is added to the filtrate, the latter boiled for a few seconds, followed by the addition of one and one-half volumes of alcohol, noting any precipitation of alkaline pectate.

NEW HAMPSHIRE LABORATORY OF HYGIENE.

THE DETECTION AND DETERMINATION OF BENZOIC ACID IN KETCHUPS, FRUITS AND CIDERS.

BY HARRY S. REED.

Received Sept. 6, 1907.

The following methods were worked out by the writer on occasion of being called upon to determine the presence of, and quantity of benzoic acid, in certain fruits, ketchups, ciders, etc. They are presented in the hope that some one may find them useful.

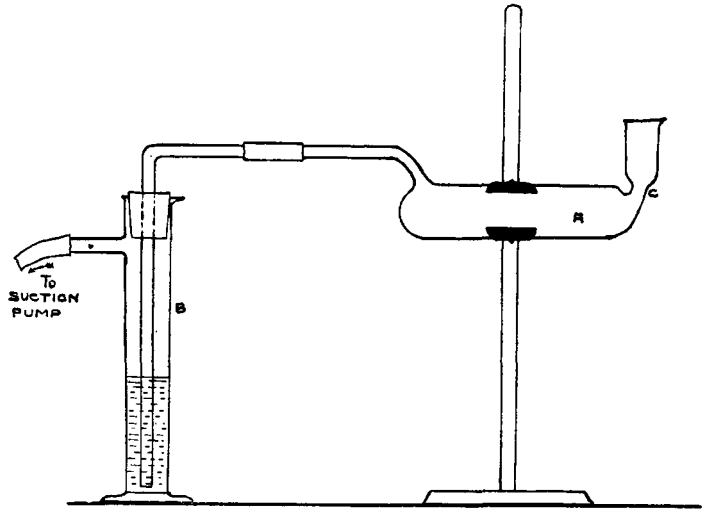
Detection of Benzoic Acid.—For this purpose a modification of Mohler's test is used. One hundred g. of the substance under examination is acidified with dilute sulphuric acid and thoroughly and repeatedly extracted with chloroform. The chloroform extract is separated from the water solution each time as far as possible by means of a separatory funnel. The last traces are then spun out with a centrifuge. The success of both qualitative and quantitative determinations depends largely on the care with which the extraction is made.

The chloroform extract is then placed in the reservoir (A) of the following apparatus:

(Capacity of A., 50 cc.)

(Capacity of B., half filled, 12 cc.)

(A) is detached, connected directly with a suction pump, and the chloroform allowed to evaporate spontaneously under a current of air. After the evaporation is completed, (A) is placed in a desiccator. When



perfectly dry it is again attached to (B) and completely submerged to the neck of the funnel (c) in a sand bath. The suction is now connected to (B), which contains approximately normal sodium hydroxide and the temperature of the sand raised slowly to 145°. It is kept at this temperature for a few minutes, and finally brought up to 260°. The benzoic acid is thus sublimed and then retained in (B) as sodium benzoate.

The water solution of sodium benzoate is next removed from (B), placed in a separatory funnel, acidified with dilute sulphuric acid, and extracted with chloroform. This chloroform solution of benzoic acid is now placed in a porcelain evaporating dish, and made alkaline with alcoholic potassium hydroxide. The residue obtained by evaporating the chloroform and alcohol from the above solution on a water bath is tested for benzoic acid by the same reactions utilized in Mohler's test, the procedure, however, is slightly different.

In the first place no water is added, as it was found that in case only a very small quantity of benzoic acid was present, it would be lost when the concentrated sulphuric was added to the water solution of benzoic acid. So the residue of potassium benzoate is decomposed directly by concentrated sulphuric acid and heated over an open flame until white fumes appear. The sulpho-benzoic acid now formed is oxidized to *m*-dinitrobenzoic acid and the organic matter oxidized by use of potassium nitrate. Very little will be necessary since if the extraction has been

carefully done, there will be very little organic matter to be disposed of. The acid solution of *m*-dinitrobenzoic acid is now cooled, diluted with water, cooled again, made alkaline with ammonium hydroxide and reduced with hydrogen sulphide. The reduction is accomplished by passing the gas through the solution in the same evaporating dish with which the test was started, necessitating no transference of the solution, and the least tint of cherry red color caused by the reduced product, the ammonium salt of *m*-diaminobenzoic acid, is readily discernible against the white background of the evaporating dish.

The Determination.—Quantitatively the method employed for the determination of benzoic acid is based on two conditions. The first, that chloroform very completely extracts benzoic from many other vegetable acids, as malic, tartaric, oxalic, etc., in water solution; and the second, that the calcium salt of benzoic acid is far more soluble in cold water than the calcium salts of the other acids mentioned.

The process consists in following the same method of extraction which is used in the qualitative test. Take the chloroform extract obtained from the water solution of sodium benzoate contained in (B) of the above apparatus, and allow this to evaporate spontaneously in a beaker. Add to this residue 25 cc. of milk of lime containing 0.0145 g. metallic calcium to each cubic centimeter. This milk of lime is prepared by acting on water with metallic calcium. Then 25 cc. of the milk of lime are poured into another beaker, and is to be subjected to the same treatment as the former. This serves as a blank. Returning to the beaker containing the extract, after the addition of the milk of lime its contents are evaporated to dryness on a water bath. The acids present in the extract are converted into calcium salts and the excess of calcium hydroxide largely into calcium carbonate. This residue is now taken up with 25 cc. of water, filtered and washed with 15 cc. of water. Care must be taken to use exactly the same quantities of water on the blank. The filtrate is allowed to run into a platinum evaporating dish, in which it is evaporated to dryness on a water bath. The residue should contain only calcium salts of benzoic and carbonic acids. These are now ignited over a blast lamp and burned to calcium oxide. The calcium oxide is dissolved with 2 cc. of twice normal hydrochloric acid and titrated back with normal tenth sodium hydroxide using phenolphthalein as an indicator. The amount of calcium present in the blank is subtracted from that found present in the test and the difference calculated to benzoic acid.

The chief objection to the above methods lies in the fact that it requires considerable time to carry them out successfully. I have no doubt, however, as to their exactness. The quantity of benzoic acid in cranberries gives excellent results. By drying the substance under exami-

nation very slowly at a low temperature, I have detected as little as forty-four hundred thousandths of one per cent. I give below the results of my last determination of benzoic acid in tomato ketchup.

Two samples were taken and to one, 0.12 g. of sodium benzoate (0.1 g. benzoic acid) was added. Original sample, sodium benzoate, found equals 0.0531 per cent. ; benzoic acid equals 0.045 per cent.

Original sample plus added sodium benzoate, sodium benzoate, found = 0.172 per cent. ; benzoic acid = 0.145 per cent.

Subtracting :—

0.172 — .12 (added) = 0.052 sodium benzoate.
0.145 — .1 " = 0.045 benzoic acid.

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SOLUBILITIES AND EXTRACTION VALUES OF FOOD COLORS.

BY EDWARD GUDEMAN.
Received June 28, 1907.

Few data are found in the literature on the solubilities and the extractive values of the vegetable and coal tar colors commonly used in foods. In collaborating with the Association of Official Agriculture Chemists, the following report was submitted to Prof. E. F. Ladd, Associate Referee on Colors. It was recommended by the Referee that special attention be given among other points, to investigations along the following lines :—

a—Solubility of coal tar and vegetable dyes, in various solvents, ether, acetic ether, petroleum ether, methyl and ethyl alcohols, acetones, etc., and mixtures thereof, arranging the compounds according to their solubility as—easily soluble, difficultly soluble and insoluble.

b—Extractive values of the various solvents for dyes in neutral, acid and alkaline solutions.

The terms "easily soluble", and "difficulty soluble" being very indefinite, the actual amounts of color dissolved and extracted were determined.

In determining the solubility of the colors, certain factors must be taken into consideration and considered as constants, *viz* : Amount of color to solvent ; time of bringing into solution, and temperatures.

In determining the extractive values, the constants must be : Amount of color in solution ; amount of solvent to solution extracted ; time of extraction and temperatures.

Working with colored food products, naturally colored or otherwise, the extraction values will be materially affected by the unknown factors, due to the composition of the food products, the presence of oils, fats, saccharine substances, nitrogenous matter, fiber, mineral substances (ash), etc., which may change the extractive properties of many solvents, and which in many cases act as mordants on the colors themselves, so that