It is sometimes observed that the reaction time for dehydrated material is less than that for the freshly blanched material. This may be due to loss of ascorbic acid or to regeneration of the enzyme. Table I gives evidence of such regeneration in cabbage extract.

This test is not supposed to fix the proper amount of blanching, but only to show when that amount has been obtained. The proper amount of heating naturally varies with each kind of vegetable, but when it has once been determined there should be no difficulty in specifying this amount in terms of the peroxidase value, and in using the peroxidase value as a means of factory control thereafter.

Summary

The method described appears to meet the requirements for a simple, swift test for the blanching of vegetables, even if extracts of them are highly colored. It is particularly applicable to control of the blanching time of cabbage, which has been a problem in the dehydration field. No doubt the test may be used in other fields, such as blanching before quick-freezing. As a result of this work a new method for the determination of ascorbic acid is suggested, the details of which will be presented in another paper.

Acknowledgment

The aid of A. K. Balls, of the Enzyme Research Laboratory of this bureau, is gratefully acknowledged.

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Agricultural Chemical Research Division Contribution No. 87.

Preparation of Diphenylthiocarbazide and Diphenylthiocarbazone (Dithizone)

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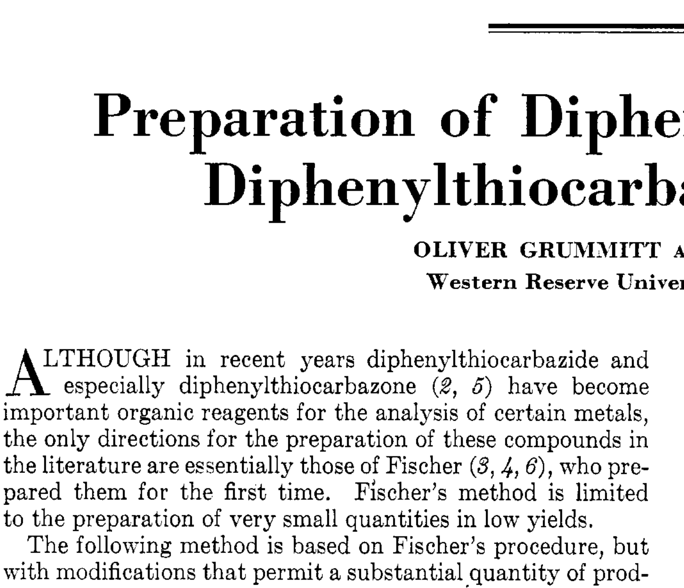
ALTHOUGH in recent years diphenylthiocarbazide and especially diphenylthiocarbazone (*2*, *5*) have become important organic reagents for the analysis of certain metals, the only directions for the preparation of these compounds in the literature are essentially those of Fischer (*3*, *4*, *6*), who prepared them for the first time. Fischer's method is limited to the preparation of very small quantities in low yields.

The following method is based on Fischer's procedure, but with modifications that permit a substantial quantity of product to be made at one time. The reactions involved are:



$$2\,C_6H_5NHNH_2 + CS_2 \longrightarrow C_6H_5NHNH\underset{\|}{\overset{}{C}}SNH_3NHC_6H_5 \quad \text{I} \quad (C_6H_5NHNH\text{–}C(=S)\text{–}SNH_3NHC_6H_5)$$

$$\longrightarrow (C_6H_5NHNH)_2C{=}S + H_2S \quad \text{II}$$

$$2\,(C_6H_5NHNH)_2CS \xrightarrow{NaOH} C_6H_5N{=}NC({=}S)NHNHC_6H_5 \;(\text{III}) + C_6H_5NHNHC({=}S)NH_2 + C_6H_5NH_2$$

The condensation of phenylhydrazine and carbon disulfide yields I, the phenylhydrazine salt of β-phenyldithiocarbazic acid, which on heating forms diphenylthiocarbazide (II). This substance in the presence of alcoholic sodium hydroxide undergoes mutual oxidation-reduction, yielding diphenylthiocarbazone (III).

Experimental

Fifty-four grams (50 cc., 0.5 mole) of freshly distilled phenylhydrazine and 200 cc. of benzene are mixed in a 500-cc. three-necked round-bottomed flask fitted with an efficient Nichrome wire stirrer (*7*), reflux condenser, and dropping funnel. From the funnel 20 grams (16 cc., 0.27 mole) of carbon disulfide are added with vigorous stirring in the course of 15 minutes. The mixture of the salt (I) and benzene is then heated on the steam bath with stirring at gentle reflux either under the hood or with the condenser connected to a gas trap (*8*) until the evolution of hydrogen sulfide practically ceases (about 3.5 hours). Near the end of this heating period the evolved gas should be tested frequently with moist lead acetate paper. The reaction may be considered complete when the test paper does not turn dark until exposed for several seconds. (Overheating is indicated by the formation of a very dark color and the rapid evolution of ammonia must be avoided. Ammonia is slowly evolved during heating and this side reaction reduces the yield somewhat.) At this point the benzene layer is usually green in color and there is a heavy crystalline precipitate. The mixture is thoroughly cooled at 0° to 10° C. and suction-filtered, and the solid is washed with two 15-cc. portions of benzene. The yield of crude diphenylthiocarbazide is 48 to 50 grams, 80 to 83 per cent of the theoretical.

If diphenylthiocarbazone is the desired product, the crude diphenylthiocarbazide may be used without further purification. However, if the diphenylthiocarbazide is to be used as a reagent, it must be crystallized from 900 cc. of 95 per cent ethanol. As the alcoholic solution decomposes slowly at its boiling point, it should be boiled no longer than necessary to dissolve practically all of the solid. The solution is filtered hot, thoroughly cooled at 0° to 10°, and suction-filtered, and the fine needlelike crystals of diphenylthiocarbazide are washed with three 20-cc. portions of benzene. The yield of almost colorless product is 28 to 30 grams, 47 to 50 per cent of the theoretical; melting point about 145–150° C. with decomposition. No additional product of suitable purity can be obtained from the filtrate from this crystallization.

To prepare diphenylthiocarbazone the crude diphenylthiocarbazide is dissolved in a solution of 200 cc. of methanol and 80 cc. of 25 per cent sodium hydroxide. [In the mutual oxidation-reduction of diphenylcarbazide to diphenylcarbazone Slotta and Jacobi, (*9*), obtained improved yields by adding a small amount of dilute hydrogen peroxide to the alcoholic alkaline solution. In the case of diphenylthiocarbazone added hydrogen peroxide has no effect.] This solution is refluxed on the steam bath for 5 minutes (longer heating will materially reduce the yield), poured into 1 liter of water, and filtered. The filtrate is acidified with dilute sulfuric acid (1 volume of concentrated acid to 4 volumes of water); approximately 120 cc. of acid are required. The black precipitate of crude diphenylthiocarbazone is removed by suction filtration and then dissolved in an ammonia solution made from 100 cc. of concentrated ammonium hydroxide and 250 cc. of water. This dark red solution of the ammonium salt of diphenylthiocarbazone is allowed to stand in a stoppered flask overnight. (If the solution is not allowed to stand 8 to 10 hours, the diphenylthiocarbazone will not be pure.) This solution is filtered, diluted with 500 cc. of water, and then acidified with dilute sulfuric acid (same concentration as before). The blue-black precipitate of diphenylthiocarbazone is removed by suction filtration, washed with warm water until the filtrate is substantially free of sulfate ions, and dried in a vacuum desiccator over concentrated sulfuric acid. The yield is about 15 grams, 5 per cent of the theoretical based on the phenylhydrazine taken.

On standing, diphenylthiocarbazone undergoes some oxidative deterioration which may interfere with its use in analysis. A satisfactory purification method is described by the Association of Official Agricultural Chemists (*1*).

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Automatic Leveling Bulb Lifter for Butadiene Analysis

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IN THE gasometric determination of butadiene in gas mixtures by the method of Tropsch and Mattox (*2*), the sample is passed back and forth through a U-tube maleic anhydride absorber, from a gas buret into a gas reservoir. The routine analysis of a large number of samples is tedious and time-consuming, unless an automatic device for raising and lowering the leveling bulb is used. A semiautomatic hydraulic lift has been suggested (*1*).

The automatic device consists of a wheel mounted on a support, designed to translate circular motion into linear simple harmonic motion. The driving power is supplied by a 1725 r. p. m. motor, which is geared and belted down to a speed of 0.92 r. p. m. If mercury is used as confining fluid, its weight must be supported by a steel chain, which is fastened to a ring, that is free to rotate on a pin, near the rim of the wheel and run over a pulley, and attached to the top of the leveling bulb by a brace. As the wheel revolves, the bulb is raised to its highest position when the pin is at the bottom of the wheel, and to its lowest position when the pin is at the top of the wheel.

The diameter of the wheel is equal to the lift, which is the linear distance the leveling bulb travels to move the unabsorbed gases out of the buret. For a 100-cc. gas buret and a 50-cc. sample containing approximately 15 cc. of butadiene, a wheel with a diameter of 45 cm. (18 inches) is used. To prevent drawing mercury into the absorber, an iron ring is placed under the leveling bulb to act as a safety stop. The above sample requires the ring to be set at the 35-cc. buret graduation.

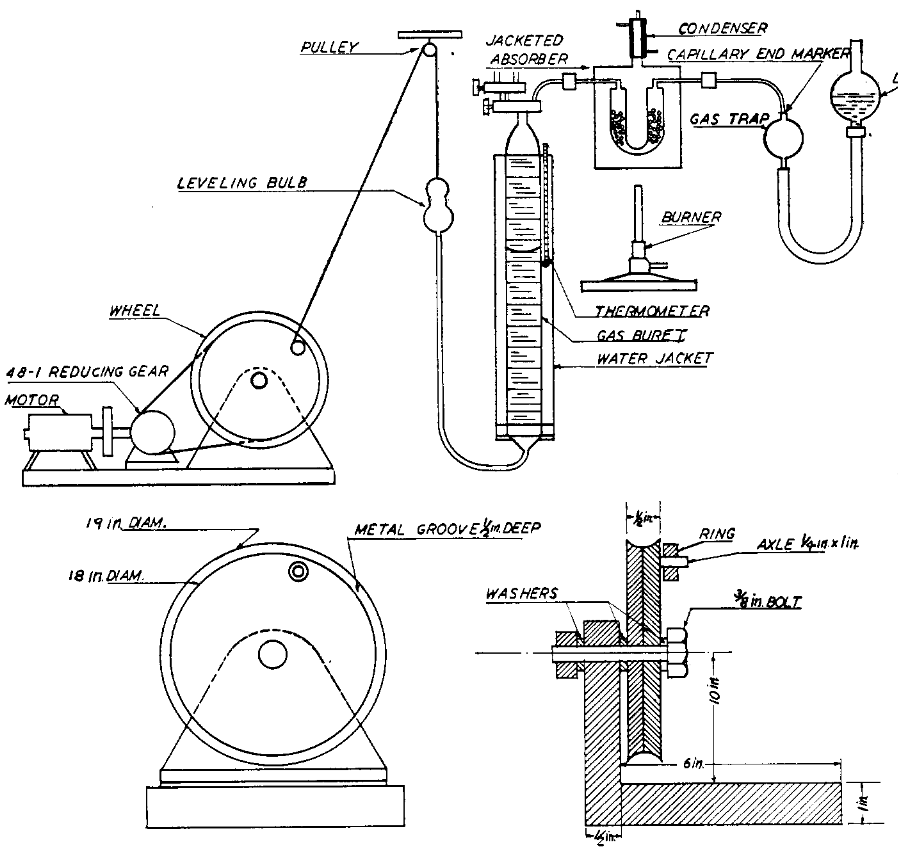

FIGURE 1. APPARATUS FOR DETERMINATION OF BUTADIENE

Samples up to 30 per cent butadiene require only filling the buret with a gas sample, recording initial volume, starting the device, and recording final volume after 20 minutes. Samples rich in butadiene can be handled by dilution of a 50-cc. sample with air to leave a 35-cc. residue. Samples absorbing more than anticipated can best be handled by raising the iron ring during the run to shorten the lift. No harm results from those absorbing less, except the minor disadvantage of the fact that all the gas is not circulated, and only a few more automatic cycles are required.

One device may run two or more burets, by using a longer pin, with parallel chains. For compactness, two burets are placed at opposite ends of a small table, and the wheel is set between them at right angles to each, so as to drive both simultaneously, the intervening space being used for outlets and sampling bottles.

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