

with other starches. It is claimed by the manufacturer, as indicated on the label of the carton of his package product, that "you do not get that starchy taste by using Florida Arrowroot."

Designation of the Product.—*Zamia* starch has been marketed under the designation "Florida Arrowroot." True arrowroot starch is obtained from *Maranta* root. This double use of the term arrowroot has led to confusion in the trade which will become greater if *Maranta* starch is manufactured in Florida, as now seems possible. It is of interest that *Maranta arundinacea*, the plant yielding the product generally referred to as arrowroot starch, is cultivated to a limited extent in some localities in southern Florida.

The names "Koonti," "Coontie," or "Comptie," used by the Seminoles, refer not only to the *Zamia* plant and its products, but have the general significance of the word "bread," "grits," or "grub."¹ Since differences in the spelling as well as in the pronunciation of these terms also occur, it is evident that none of them would be a well-chosen name. The names "Florida arrowroot starch" or "Florida arrowroot flour" should not be used for the reasons already given. The designation "flour" is distinctly objectionable, since during the process of manufacture tissue elements are practically eliminated.

In conclusion, the specific name *Zamia* starch should be applied only to the product obtained from *Zamia* plants.

NOTE: After completion of the manuscript, an article by J. K. Small appeared in the *Journal of the New York Botanical Garden*, Vol. 22, pages 121 to 137, 1921. It is entitled "Seminoles Bread—The Conti; a History of the Genus *Zamia* in Florida." The reader will find here interesting additional information on the subject of *Zamia* and its products.

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THE ESTIMATION OF NITROGLYCERIN IN TABLETS OF NITROGLYCERIN AND SPIRIT OF NITROGLYCERIN.*

BY R. I. GRANTHAM.

Several methods have been proposed for the estimation of nitroglycerin but, up to the present time, none of these have proved to be quite satisfactory. The method to be proposed here is essentially the Devarda method for the estimation of nitrogen in inorganic nitrates. However, the details of the method have been so modified that its practicable application to nitroglycerin has been made possible in the average laboratory. The results obtainable are quite satisfactory.

Of the various methods which have been proposed for the estimation of nitroglycerin the following may be mentioned:

I. Saponification Method.—This method depends upon the saponification of

¹ Clay MacCauley, "Seminoles Indians of Florida," Fifth Annual Report Bureau of Ethnology, 1883-4, p. 513.

Gifford, *Loc. cit.*, p. 170.

* Read before Scientific Section A. PH. A., New Orleans meeting, 1921.

the nitroglycerin with alcoholic caustic alkali. It is a well-known fact that this method is essentially unsound, because the reaction is indefinite. While it is based on the quite simple theory that when the ester is brought in contact with potassium hydroxide there will be produced potassium nitrate, potassium nitrite, glycerin and water; whereas the chemical reaction is really quite uncertain and variable. One author claims that one molecule of nitroglycerin requires three molecules of potassium hydroxide, another one molecule of nitroglycerin five molecules potassium hydroxide. On the other hand, it is claimed by different chemical writers that the resulting products of the reaction are potassium nitrate, potassium nitrite, potassium acetate, oxalate and formate, with glycerin, aldehyde and perhaps other substances as well; also that the several products resulting from this reaction will vary in accordance with the proportion of alkali present, the temperature, the degree of concentration and, perhaps, other factors.

II. Direct Extraction Method (for tablets).—This method involves the powdering of the necessary number of tablets, direct extraction with pure ether, the evaporation of the ether at room temperature, drying the residue in a desiccator and weighing it as nitroglycerin. It is obvious that in dealing with tablets containing no substance other than nitroglycerin, soluble in ether, this is an ideal method. It is well known, however, that the majority of commercial tablets of nitroglycerin do contain other substances which are soluble in ether. Hence this method is applicable to only a very limited number of commercial tablets.

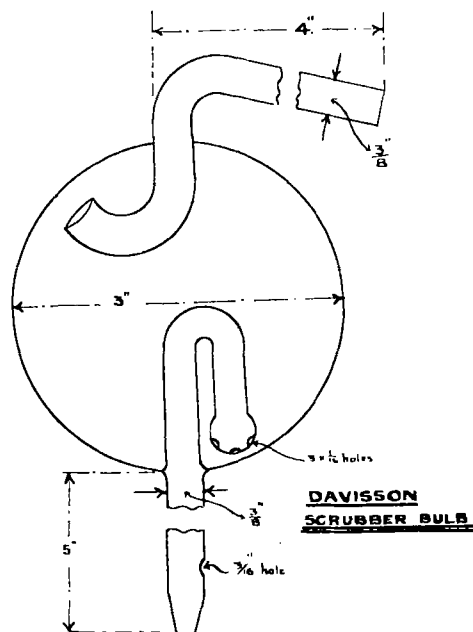
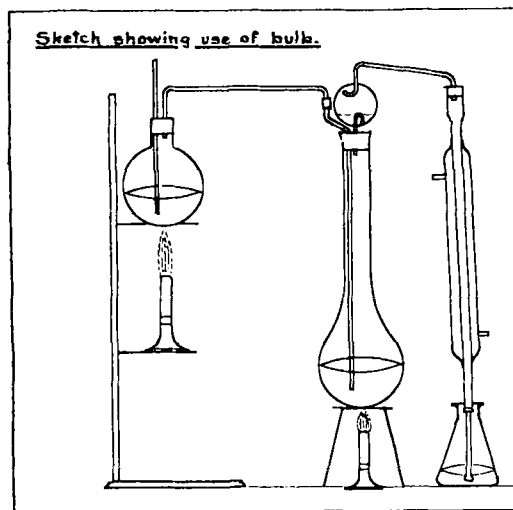
III. Scoville Method (for tablets).—This method is based on the well-known method for the estimation of nitrate nitrogen in water analysis. It depends upon the extraction of the nitroglycerin with ether, the evaporation of the ether at room temperature, the treating of the residue with phenoldisulphonic acid reagent and the addition of potassium hydroxide solution, under prescribed conditions—thus converting the nitrate radical into picric acid and the formation of the soluble potassium salt. In this way the nitroglycerin is estimated colorimetrically, using pure potassium nitrate to produce the standard color for comparison.

Considerable experience by the writer has shown that, fundamentally, this method is without a doubt correct; but owing to the disadvantage of the personal equation, *i. e.*, the difficulty of judging just what degree of color concentration is required to match another color concentration—which accompanies all colorimetric methods of analysis—it is impossible for any two analysts to agree, even when working on identically the same sample of material and under the same conditions.

IV. Hay Method (for tablets).—This method is based on the well-known method for the estimation of nitrite nitrogen in water analysis. It depends upon the extraction of the nitroglycerin with ether and the saponification with potassium hydroxide, assuming that the reaction takes place according to the following equation: $C_3H_5(NO_2)_3 + 5KOH = KNO_3 + 2KNO_2 + CH_3COOK + HCOOK + 3H_2O$. The nitrite thus formed is estimated by treating the residue, under prescribed conditions, with sulphanilic acid and combining the resulting diazobenzene-sulphonic acid with alphanaphthylamine hydrochloride. The azo-dye obtained in the reaction is estimated colorimetrically, using pure silver nitrite to produce the standard color for comparison.

As pointed out under the saponification method the assumed reaction here is essentially incorrect, because the quantity of potassium nitrite obtainable from a given quantity of nitroglycerin is subject to considerable variation, depending upon various conditions. Obviously the results obtainable from this reaction will vary in proportion to the amount of potassium nitrite formed. It also has the same serious objection that the results are greatly influenced by the "personal factor."

V. Devarda Method (for the estimation of nitrogen in nitrates).—This method is based on the quantitative reduction of nitrogen in inorganic nitrates to ammonia in alkaline solution by an alloy consisting of 45 parts of aluminum, 50 parts of copper and 5 parts of zinc. The ammonia evolved is distilled into standard sulphuric acid and thus estimated. The apparatus designed by Devarda and modified by W. S. Allen¹ is quite intricate and would hardly be found in the average laboratory unless its frequent use was required. However, there has been an improved form of a scrubber bulb designed by Davisson² which makes it possible to do away with most of the complicated parts recommended by Devarda.



Kohler, Marqueral, and Javinet³ undertook to apply the Devarda method for the estimation of nitrogen in nitroglycerin. They state that their results were erratic at first, but that it was found by saponifying the nitroglycerin with caustic soda solution (sp. gr. 1.40), at a temperature below 40° C. in the presence of hydrogen peroxide solution, with constant stirring, that the nitroglycerin could be estimated by this method. The details which they outline for the saponification

¹ Scott's "Standard Methods of Chemical Analysis," 2nd Edition, 301.

² *Journal Industrial and Engineering Chemistry*, 11, 485, 1919.

³ "Annales de Chimie Analytique," II, 271, 1920; abstract; *Pharm. Zentralhalle*, 61, 740, 1920.

are cumbersome, and as stated before, in the Devarda method, while not cumbersome, the use of specially constructed apparatus is required. Consequently, it was thought that if the method could be simplified in such a way that it could be used in the average laboratory, it would be superior to any of the methods hitherto proposed for the estimation of nitroglycerin in medicinal products.

The apparatus used in this investigation is shown in the accompanying illustration. The main feature of the apparatus is the Davisson scrubber bulb. The use of it is very important to prevent traces of caustic alkali from being carried over into the receiving flask.

It was first thought that by taking a known quantity of nitroglycerin and treating this directly with alkali and Devarda's alloy the ester could be estimated.

A number of experiments, however, showed that the results obtained by this procedure were about 10 percent too low.

METHOD.

Tablets of Nitroglycerin.—Tablets, the equivalent of one grain of nitroglycerin, are powdered in a mortar and transferred to a 3-oz. bottle, 50 Cc. of ether are added and the bottle is stoppered and shaken continuously for one hour. An aliquot part of the ether is filtered through a small plug of cotton and transferred to a 250 Cc. beaker, 15 Cc. of $\frac{N}{10}$ alcoholic potassium hydroxide solution are added and the mixture is allowed to stand for 10 minutes. After the addition of 10 Cc. of hydrogen peroxide solution the beaker is covered with a watch glass and heated on a water-bath, slowly at first, until the greater part of the ether is expelled; then the heat is increased until the greater part of the alcohol is removed, which requires about 20 minutes. The residue in the beaker is transferred to a 800-Cc. Kjeldahl flask and the beaker is washed with sufficient distilled water, adding the washings to the Kjeldahl flask, to make a total dilution of about 250 Cc. Two grammes of Devarda alloy powder are added and the flask is immediately connected with the scrubber (into which have been drawn 20-30 Cc. of water), the condenser and the receiving flask, containing 15 Cc. of $\frac{N}{10}$ acid, diluted with about 25 Cc. of water; then 5-6 Cc. of sodium hydroxide solution (sp. gr. 1.30) are added through the side tube, using a small funnel, and are washed down with 50 Cc. of water. Then connection is made with the steam generator. The contents of the Kjeldahl flask are heated, slowly at first until the greater part of the alkali is used up, which requires about 30 minutes. Heat is then applied to the steam generator, the ammonia distilled and received in the standard acid, which also requires about 30 minutes. About 300 Cc. of liquid should be distilled. The excess of acid is titrated back with $\frac{N}{10}$ potassium hydroxide solution, using methyl red as indicator. Each Cc. $\frac{N}{10}$ acid corresponds to 0.007569 Gm. nitroglycerin.

Spirit of nitroglycerin is assayed in the same way, using 10 Cc. of the spirits accurately weighed, adding the alcoholic potassium hydroxide solution and the hydrogen peroxide solution immediately.

I have made numerous experiments with this method, the details of which it is not necessary to record here. However, the following results obtained in analyzing tablets and spirit of nitroglycerin show the accuracy of the method. The tablets were supposed to contain $\frac{1}{100}$ grain. The spirit, when assayed by the U. S. P. method, left 1.02 percent of residue.

Tablets.	Spirit.
0.0102 grain	1.005 percent
0.0101 grain	1.00 percent
0.00997 grain	1.02 percent
0.00970 grain	1.01 percent
0.00970 grain	0.99 percent

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ABSTRACT OF DISCUSSION.

H. Engelhardt stated that one of the reasons for presenting this paper was to induce further research; it may be possible that the estimation is based on wrong fundamental principles.

Wilbur L. Scoville said he had tried the method of the paper, and that the reaction is faulty; in one trial with it on the same lot of tablets he obtained results corresponding to 100 percent, while another test only showed 60 percent; the reaction is not constant. He was asked by Mr. Engelhardt whether he had made use of hydrogen peroxide; in reply, he insisted that the reaction was fundamentally wrong. Mr. Engelhardt acknowledged this. Continuing, Mr. Scoville stated: that the objection to the colorimetric method is that the results of individuals differ; not as much difference in results of to-day as of a few years ago, because there is a better technique. The knowledge and experience of colorimetric methods, like anything else, must be learned. If better methods can be devised, let us have them.

It was voted that the paper be published.

THE INFLUENCE OF ACID IN THE EXTRACTION OF CINCHONA.*

BY WILBUR L. SCOVILLE.

Experiments on the extraction of cinchona with acidulated menstrua have been continued, the purpose being to secure, if possible, a more reliable menstruum or an improved method.

In the present series cinchona calisaya was used, 250 grammes being employed in each experiment. The usual mode of procedure was to moisten the drug with the menstruum in the standard way, pack in a percolator, flood with the menstruum, then macerate 48 hours. Percolation was then started, the first 200 Cc. reserved, then percolation was continued until 1000 to 1200 Cc. more of percolate had been collected. The first 200 Cc. were assayed, the weaker portion evaporated to a soft extract, this dissolved in the first reserve, and the final volume adjusted to 240 Cc. (190 + 50). The drug used assayed 5.30% of total alkaloids.

Experiment 1. Menstruum, alcohol 200, glycerin 15, hydrochloric acid 10, then alcohol 4, water 1. The first 200 Cc. showed 3.02% of alkaloids, equivalent to 57% of exhaustion. The finished product assayed 4.60% of alkaloids, indicating 86.8% exhaustion.

The residue in the percolator was dried and assayed, being found to contain 0.9% of alkaloids.

Experiment 2. The same menstruum was used, but the percolation was conducted with a hot menstruum. The apparatus used consisted of two copper percolators, the smaller being just large enough to hold the 250 grams of moistened drug and fitting into the larger so as to leave a space of about 10 millimeters between the two. A cover clamped to the top of the outer percolator provided for a reflux condenser, and to the lower end of this percolator was fitted a flask holding 1000 Cc. After macerating the drug for 48 hours in the inner percolator the neutral non-glycerinated menstruum was placed in the lower flask, the condenser attached, and heat applied. The hot vapors of the menstruum passed around the percolator containing the drug thus heating it, were then condensed and passed through the drug, then collected in a separate container by means of a side tubulure at the bottom of the percolator. In this way the heat was maintained during the percolation, independently of the rate of flow. The latter was regulated to correspond with the cold percolation—about 12 drops per minute.

The first 200 Cc. assayed 2.67% of alkaloids showing 50.4% of exhaustion, and the finished product 4.92% of alkaloids, showing 92.4% exhaustion.

This suggests a less rapid rate of exhaustion than the cold process, but more complete exhaustion with the same amount of menstruum. The residue in the percolator assayed 0.45% of alkaloids.

Experiment 3. Menstruum, alcohol 200 Cc., concentrated hydrochloric acid 10 Cc., water 15 Cc., then 76% alcohol.

* Read before Scientific Section A. P. H. A., New Orleans meeting, 1921.