

The solubility of ester-hydrolyzing material of the castor bean in water and in sodium chloride solution was confirmed. The action of the extracts and of the residue were studied under various conditions. The statement of Willstätter and Waldschmidt-Leitz with reference to the insolubility of the ester-hydrolyzing material of the castor bean was shown to be incorrect.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BIOCHEMICAL DEPARTMENT, STATE SCHOOL OF HYGIENE OF
WARSAW]

IMPROVEMENTS IN ELEMENTARY MICRO-ANALYSIS. DETERMINATION OF SULFUR AND HALOGENS

BY CASIMIR FUNK AND STANISLAS KON

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In continuation of our study of micro methods¹ we have arrived at certain useful modifications of the sulfur and halogen analysis of the classical and epoch-making methods of Pregl.

We have found first that the so-called "Perlenrohr's" supplied to us were of porous porcelain and therefore retained considerable amounts of material used for cleaning the combustion tube as well as of the material to be determined. To improve this condition we have adapted a different model of combustion tube (Fig. 1) which consists of a Jena glass tube with a capillary tube attached at right angles. The end of the tube is filled with glass beads made of Pyrex glass and carries a constriction to hold the beads in place. The capillary tube reaches to the bottom of a wide Pyrex test-tube in which the precipitation and from which later the filtration on a small Pregl's asbestos filter is effected. Pregl in his book² claims that the precipitate of barium sulfate, on account of its high specific gravity, cannot be transferred by vacuum filtration. By diminishing the bore of the filtering tube to a capillary size (about 1 mm.) the filtration is accomplished without difficulty. To avoid the occlusion of barium chloride which leads Pregl to adopt a rather complicated procedure, we have diminished the concentration of barium chloride solution from 10 to 1% and therefore diminished the possible error ten times. The procedure as modified by us renders the sulfur analysis simpler and speedier and, as a matter of fact much better, than the macro-analysis. We have convinced ourselves that the tube used by us can be used with equal success for the halogen determination. For determination of halogens in substances free from sulfur (and probably phosphorus) we have adapted the excellent procedure

¹ Casimir Funk, "Mikroanalyse nach der Mikro-Dennstedt Methode." Bergmann, Munich, 1925. Funk and Kon, *J. Chem. Soc.*, 127, 1754 (1925).

² Pregl, "Die quant. organische Mikroanalyse," 2nd ed., Springer, Berlin, 1923.

of Dennstedt.³ This consists of leading the combustion vapors over a weighed and heated boat containing molecular silver. Increase in weight of the boat gave us the correct value for the halogen content in the substances analyzed. As most substances are free from sulfur, this represents a very simple and expedient method for micro determinations of halogens. The details of our procedure are described in the experimental part.

Determination of Sulfur

For this analysis the equipment as represented in Fig. 1 is used. This consists of a Jena glass tube 46 cm. long with part of it, about 8–9 cm., filled with Pyrex glass beads, kept in place by constriction made by drawing in the softened glass.

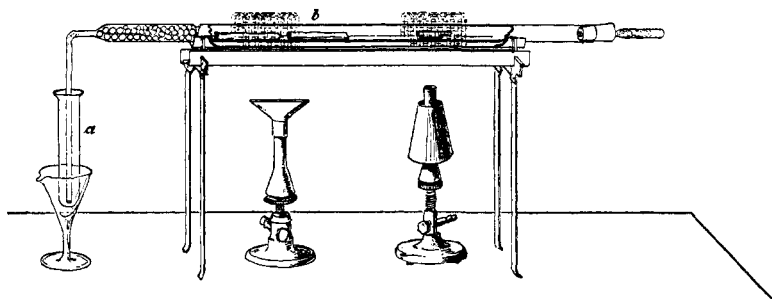


Fig. 1.

Before analysis a five-times diluted Perhydrol (30% hydrogen peroxide) solution is partly drawn into the beads so that, after blowing the remainder out, about 1 cc. remains in the test-tube *a*. The two platinum contacts *b* are ignited in the blast flame and placed in the tube. Finally, the boat with the substance is placed at least 5 cm. away from the platinum contact. A stream of oxygen is started at a speed of three bubbles a second. The burner under the platinum is lighted and when the latter is glowing red a slow combustion of the substance is started. After the completed combustion the tube is cooled in an oxygen stream and the beads are washed four times with water, the washings being collected in the test-tube. The latter is covered and heated in a water-bath. After cooling, hydrochloric acid and 20–40 drops (according to the content of sulfur) of a 1% barium chloride solution are added and the test-tube is heated again until the precipitate collects well at the bottom. After cooling, the precipitate is transferred by means of a capillary tube of 1 mm. bore to the Pregl's filter, previously weighed, as represented in Fig. 2. After three washings with water, the remainder of the precipitate is transferred with alcohol and the help of a small feather mounted on a glass

³ Dennstedt, "Anleitung zur vereinfachten Elementaranalyse," 4th ed., Otto Meissner, Hamburg, 1919.

capillary (as suggested by Pregl). Finally, the test-tube is washed with distilled water, alcohol and ether and the filter dried in a drying block in a vacuum. After being cleaned, the tube is weighed again after half an hour on the microbalance. The transfer of the barium sulfate precipitate needs a little care but can be effected without difficulty. Some of our test analyses follow.

Anal. NAPHTHALENE SULFOCHLORIDE. Subs., 9.856 mg.: BaSO_4 , 10.079 mg. Calcd.: S, 14.1. Found: 14.0.

CYSTINE. Subs., 5.226 mg.: BaSO_4 , 10.07 mg. Calcd.: S, 26.5. Found: 26.5.

COMBINATION OF NAPHTHOL YELLOW S WITH 2 MOLECULAR PROPORTIONS OF NITRON. Subs., 10.838 mg.: BaSO_4 , 2.53 mg. Calcd.: S, 3.4. Found: 3.2.

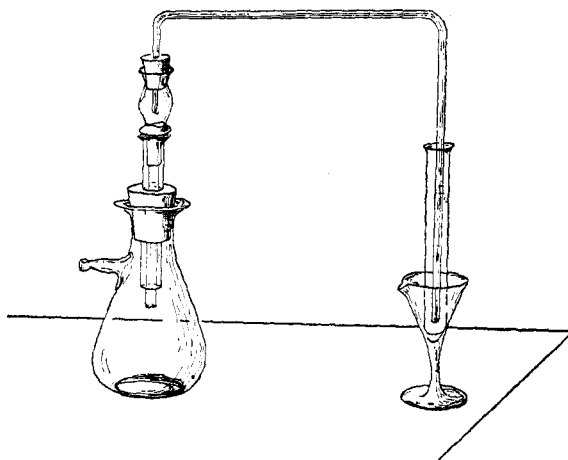


Fig. 2.

Determination of Halogens

We have convinced ourselves that the combustion tube devised by us can be used equally well for the determination of halogens, the only difference being that the glass beads and the test-tube are filled with an alkaline sodium bisulfite solution instead of with Perhydrol. To illustrate the adequacy of the method one example may suffice.

GLYCINE ESTER HYDROCHLORIDE. Subs., 8.095 mg.: AgCl , 8.341 mg. Calcd.: Cl, 25.4. Found: 25.5.

From our preliminary experiments it seems probable, and this happened to be important for our work, that a simultaneous determination of sulfur and halogens can be effected on a single sample of the substance. Our procedure in this case is somewhat modified. We use as an absorbing fluid an alkaline formaldehyde solution instead of sodium bisulfite. After the combustion is completed, the tube is washed out as usual, the solution acidified with acetic acid and the formaldehyde reacted with Perhydrol

by heating the mixture in a water-bath. After the reaction is completed, the sulfuric acid formed is precipitated with a 1% barium acetate solution, which gives a better precipitate than barium chloride. The precipitation is completed by heating and the barium sulfate is transferred by suction to a filter; the test-tube is washed out three or four times and the filtrate collected in a wide test-tube placed in a suction flask. The test-tube is then removed and the silver chloride precipitated in the usual way, while the quantitative transfer of barium sulfate precipitate is continued.

Determination of Halogens by the Micro-Dennstedt Method

In substances free from sulfur and other elements which combine with metallic silver the simple method of Dennstedt for the determination of halogens can be adapted. For this purpose we use an arrangement represented in Fig. 3, namely, a combustion tube of a Pregl's pattern closed at one end with a rubber stopper fitted with a capillary tube.

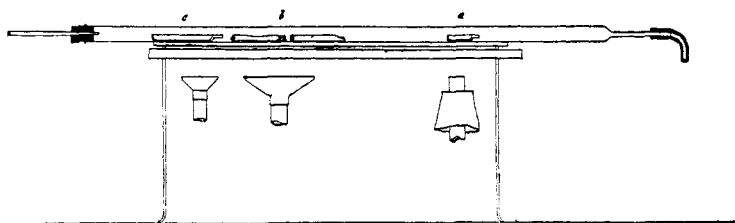


Fig. 3.

For substances which are not volatile a combustion tube fitted with rubber stoppers at both ends may be used. The filling of the combustion tube is very simple. A porcelain boat 5.6 cm. long and 5 mm. wide is filled with molecular silver powder, heated in oxygen and weighed after being cooled in a closed weighing tube. In fitting the combustion tube, first the platinum boat with the substance is placed in Position *a*, the two platinum contacts in Position *b* and finally the boat with the silver powder in Position *c*. Then a current of oxygen is started, the platinum contact heated to redness and the boat with silver heated to the temperature of 500–600° with a special burner, in order to avoid absorption of nitric oxides. After the combustion is completed and the tube cooled, the boat with the silver is taken out and weighed in the weighing tube previously described. The difference in weight found represents the absorbed halogen. To illustrate the merit of the method a few examples may suffice.

Anal. GLYCINE ESTER HYDROCHLORIDE. Subs., 7.218 mg.: Cl, 1.848 mg. Calcd.: Cl, 25.4. Found: 25.6.

BROMO-ACETANILIDE. Subs., 8.557 mg.: Br, 3.207 mg. Calcd.: Br, 37.3. Found: 37.4.

DI-IODOBENZENE. Subs., 7.797 mg.: I, 5.925 mg. Calcd.: I, 76.9. Found: 76.7.

Conclusions

Simplified and accurate modified methods for micro-determination of sulfur and halogens in organic substances are described.

WARSAW, POLAND

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTIONS OF THE ALCOHOLS OVER ZINC OXIDE CATALYSTS

BY HOMER ADKINS AND WILBUR A. LAZIER

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The attention of most investigators of catalytic reactions has been directed towards the study of the factors determining the amount of substance reacting rather than towards those which determine the ratio of the reaction products. It was first pointed out in this series of papers¹ that there were two phases to the problem and that there was apparently little relationship between the factors determining the amount of material undergoing reaction and those determining the path or paths followed by the reaction.

This paper is concerned with the variation in the proportion of the two simultaneous reactions of dehydrogenation and dehydration of alcohols over zinc oxide and with the significance of the experimental results in elucidating the mechanism of the reactions at the surface of solid catalysts. Six of the simpler alcohols and three zinc oxide catalysts have been used at temperatures of from 337° to 438°. A summary of the experimental results is presented in the figure.

The experimental methods were the same as those previously described. They involved the passage^{1h} of 40 g. of the alcohols, per hour, over 1 g. of the catalyst held at a constant temperature. The temperatures recorded in the figure are those indicated by a thermocouple placed in the catalyst mass. All of the data are for catalysts that had been in use for at least an hour and so had reached a rather constant condition of activity. The alkene dissolved in the distillate during an hour's run was boiled out and mixed with the gases collected during the hour, and the whole analyzed. There were always small amounts of carbon dioxide and air in the gas collected but these were calculated out of the analyses and the alkene and hydrogen reported as though they represented 100% of the gas. The preparation of the catalysts has been previously described.^{1e} Catalyst A was from the zinc hydroxide precipitated from a solution of zinc sul-

¹ Earlier papers of this series by Adkins, Lazier, Bischoff and Nissen, *THIS JOURNAL*, (a) **44**, 386 (1922); (b) **44**, 2175 (1922); (c) **45**, 809 (1923); (d) **46**, 130 (1924); (e) **46**, 2291 (1924); (f) **47**, 808 (1925); (g) **47**, 1163 (1925); (h) **47**, 1719 (1925).