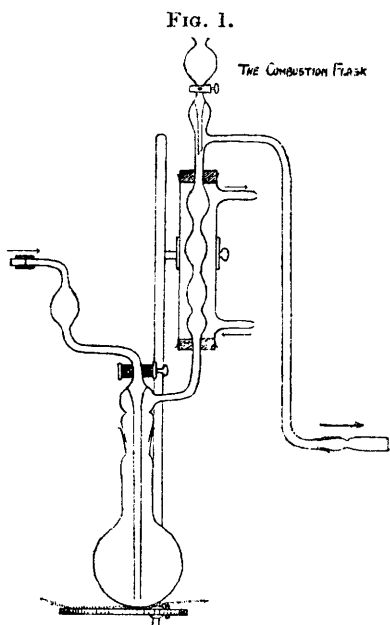


CCCXCV.—*The Determination of Total Carbon and Carbon Dioxide in Small Quantities of Soil Solutions.*

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DURING the course of a research on the ultimate composition of the soil solution, a method was needed for the determination of total carbon, which was present to the extent of 100—1000 parts per million parts whilst the quantity available for a determination was usually less than 10 c.c. The ordinary permanganate oxidation method used in water analysis did not yield concordant results.

The wet combustion method used in steel analysis (see Corleis, *Stahl u. Eisen*, 1894, **14**, 581; Treadwell-Hall, "Analytical Chemistry," vol. 2, 5th ed., p. 399, New York, 1919) was adapted to the routine examination of soil solutions containing nitrate and chloride as high as 3000 parts of NO_3 and 800 parts of Cl per million. This was achieved by using in the combustion-furnace tube a 6-inch cylinder of reduced copper gauze together with either copper oxide and a spiral of silver gauze or an 8-inch cartridge of lead chromate (see Thorpe and Whiteley, "Manual of Organic Chemical Analysis," London, 1926). The method was then used in the routine examination of a large number of soil solutions for total carbon, and a part of the apparatus was further adapted to the determination of carbon dioxide.



EXPERIMENTAL.

(1) *Total Carbon.*—The train of apparatus employed was as follows, in the order indicated: A soda-lime tower, a set of 3 potash bubblers, the combustion flask (Fig. 1) attached through a ground joint to the hard glass combustion tube heated in a light Dennstedt furnace, a sulphuric acid bubbler, a glass-stoppered U-tube containing pumice soaked in sulphuric acid, and glass-stoppered absorption and trap tubes, charged with "Sofnolite" or soda-lime and

topped with calcium chloride. Proper attention was directed to sieving the charges for these tubes and to regulating the speed of the air current; otherwise, fine dust was swept out, causing serious losses. A current of 4 bubbles a second in the bubbler was the fastest consistent with safety, and was used throughout, being regulated by a screw clip before the pumice tube.

50 C.c. of water, 15 c.c. of saturated pure chromic acid solution, and 120 c.c. of pure sulphuric acid were boiled gently in the combustion flask for 10 minutes with the tap-funnel open. The chromate cartridge was then heated to dull redness while a current of purified air was drawn through the apparatus for 20 minutes, the flask being allowed to cool. Next, the tap on the pumice tube was closed, the freshly reduced copper spiral was inserted and heated over a faintly luminous flame that just touched the trough, and the absorption and guard tubes were placed in position. The soil solution was placed in the tap-funnel and drawn into the system, admission of air being avoided, and the funnel was rinsed with a few drops of water. The air current was started again, and the flask boiled over a small flame for $1\frac{1}{2}$ hours. The pumice tube was then closed, the tap-funnel opened, and the absorption tube removed and weighed.

If the initial boiling-out had not been carefully performed, the evolution of gas from the combustion mixture was frequently so rapid as to blow the mixture back into the potash bulbs; this could be controlled to some extent by removing the burner and fanning the flask.

The following figures for blank determination and determinations of total carbon in a standard sugar solution and a soil extract are typical of the results obtained.

The method was tested on sucrose in an apparatus having rubber connexions to the furnace, instead of ground glass joints, and both with and without a reflux condenser. 10 C.c. of sugar solution, containing carbon equivalent to 27.7 mg. of carbon dioxide, and 5 mg. each of NO_3 and Cl , gave 27.2 mg. of carbon dioxide (without reflux) and 28.0 mg. (with reflux); 20 c.c. of liquid gave 55.6 mg. of carbon dioxide. This apparatus, as well as that shown in Fig. 1, gave less than 0.1 mg. increase in weight in blank determinations with the reagents when as much as 0.1 g. of potassium nitrate and 0.05 g. of potassium chloride were used. With the apparatus figured, 5 c.c. of a certain soil solution gave 1.6 mg. of carbon dioxide consistently.

Good agreement was obtained in repeated tests. The errors did not exceed 0.3 mg. with the largest quantities of carbon, which in general yielded 1—30 mg. of carbon dioxide.

(2) *Carbon Dioxide*.—The apparatus was adapted to the deter-

mination of carbon dioxide by cutting the horizontal delivery tube about 1 inch from the reflux condenser and connecting it to the drying and absorption train by means of a rubber joint. To prevent bumping in the solution on boiling, hydrogen was liberated by the action on aluminium of the hydrochloric acid with which the solution was acidified; this metal was chosen for its freedom from surface contamination of carbonate or sulphide. Very dilute acid was used in order to avoid a too rapid evolution of gas. The complete expulsion of carbon dioxide from the system was accelerated by the current of air and the generation of hydrogen, but boiling was continued for $1\frac{1}{2}$ hours as an additional precaution.

100 c.c. of water and 5 c.c. of hydrochloric acid were boiled for 20 minutes in the current of air after $\frac{1}{2}$ inch of 16-gauge aluminium wire had been placed in the exit tube from the reflux condenser; without stopping the boiling, the pumice tube was closed to allow the absorption and guard tube to be inserted; the sample of the soil solution was drawn into the system, and the wire was dislodged from its position and caused to fall into the mixture. (This procedure avoided all danger of "blowing back.") The boiling was continued for $1\frac{1}{2}$ hours, then the absorption tube was weighed.

Since blank determinations gave less than 0.1 mg. increase in weight of the absorption vessels, this method was applied to soil solutions, 10 c.c. being used for each test. With soil solutions of $p_H < 7$, the total carbon dioxide so found did not exceed a few parts per million.

During the publication of this work, a method was described (Nieloux, *Bull. Soc. Chim. biol.*, 1927, 9, 639) for the rapid and accurate determination of a maximum of 3 mg. of carbon present as organic matter in 1 c.c. of aqueous solution. The chromic-sulphuric acid oxidation takes place in a vacuum, and is catalysed by silver chromate. A method for the micro-determination of carbon dioxide was also described (*ibid.*, p. 758).

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