# ROYAL SWEDISH GEOTECHNICAL INSTITUTE PROCEEDINGS

No. 15

# CHEMICAL DETERMINATION OF SOIL ORGANIC MATTER

# A Critical Review of

# **Existing Methods**

By

LENNART SILFVERBERG

**STOCKHOLM 1957** 

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# Preface

The work described in this report was mainly performed during 1953-55 at the Physical Section of the undersigned Institute under direction of Mr. L. Silfverberg. Mr. J. Morath and Miss B. Gauffin assisted in the experimental work. The text of the report was worked out during 1956-57 and was kindly reviewed, from chemical point of view, by Dr. G. Assarsson, Geological Survey of Sweden, and, from linguistic point of view, by Mr. J. N. Hutchinson.

Stockholm, December, 1957

ROYAL SWEDISH GEOTECHNICAL INSTITUTE

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#### 1. Introduction

As the organic matter content of a soil has a marked influence on its geotechnical properties, especially on the compressibility and the shear strength, its determination is frequently a part of the routine investigations in a geotechnical laboratory. The different methods used for this determination however, give somewhat varying results even if applied to equivalent samples. It will be shown on the following pages that the organic content values frequently quoted in geotechnical publications are rather valueless unless precise information on the methods used for their determination is given at the same time.

For the determination of the content of organic matter many different analytical methods have been developed, mainly by agricultural scientists. In order to choose a suitable method for particular determination, it is first necessary to decide the purpose of the analysis as, for instance, the total organic carbon can be determined in quite a different manner from that in which the real "hnmus content" is found. The proper choice of method is also dependent upon whether a very accurate method for a few samples or a relatively inexpensive method, well fitted for routine tests, is required, while the need for the determination to be absolute or merely relative must also be settled. After consideration of such factors it is usually possible to facilitate the final choice by elimination of many of the analytical methods hitherto developed.

As far as is known, no complete investigation has been carried out on the influence of the contained organic matter upon the geotechnical properties of a soil; for example, it is not known exactly how the degree of humification can modify either the shear strength or its laboratory determination. In a geotechnical laboratory it seems natural to use an analytical method which excludes undestroyed plant remains as well as elemental carbon. Absolute values of the content of organic matter are valuable but not always necessary. For routine laboratory work a method is needed which is convenient for the analysis of large series of samples sufficiently accurate but not too expensive. This last condition is satisfied if the analysis can be performed rapidly with simple apparatus and inexpensive chemicals, and does not demand the attendance of highly qualified personnel.

The purpose of this paper is to review the methods for the determination of the organic matter content of a soil sample. Some experiments are also reported which were carried out to test the suitability of some methods for geotechnical purposes. It is not possible in this rather limited space to describe all the methods hitherto published and the reader is referred to the extensive bibliographies given by MAIWALD (1931 and 1939) and WRIGHT (1939). As the present report is written as a practical guide for non-specialists in this field, a chemist will probably find the descriptions overdetailed. The intention however is to give sufficient particulars of the various methods to get a general idea of the subject without having to work through the literature.

## 2. The Forms of Occurrence of Organic Matter in Soils

#### 2 a. General Aspects

The first chemical investigations of the composition of soil organic matter were undertaken more than 170 years ago. Since this time an immense number of facts have been gathered and to make a systematic collection of these is almost impracticable. In the previously cited works of MAIWALD (1931 and 1939) an attempt is made to systematize knowledge in this field by a subdivision based on the main lines of research on "the humus problem". A real obstacle to rapid progress in soil research is the fact that the fundamental organic chemistry of humified plant and animal remains is still largely unknown. A contributory cause of this is the difficulty of isolating material for chemical analysis. The extraction of the organic fraction from soils is complicated and laborious and is inseparable from the danger that the structure and properties of the compounds in question may be changed in the process.

There are also research workers, WAKSMAN (1929) for example, who do not look upon the humus problem as a mainly chemical one but emphasize more the microbiological aspects of the problem.

In this chapter it is intended to give only a schematic view of the chemical state of those types of organic matter in soils, which are well distinguished. It must be stressed that the organic matter in soils is not a homogeneous chemical compound but a large complex of compounds with a great variety of structures and therefore with very different affinities for the agents used in analysis.

Since the 19th century it has been usual to classify the different groups of organic compounds according to their solubility in alkali and alcohol. But as mentioned above there is a danger of chemical destruction occurring during the solution process, while the solubility is also a function of both the particle size and the time of solution. Freshly precipitated humie substances are for instance more easily dissolved than aged ones.

### 2 b. Different Types of Organic Matter

The total organic matter in the soil can first be divided in two main groups:

Soil organic matter = Undecomposed material (I) + Decomposition products (II and III).

I. The native material consists of dead, undestroyed debris and waste products of vegetable and animal origin, including living and dead micro-organisms. The ehemical substances in I are cellulose, pectine and other carbohydrates, lignine, proteins, fats, waxes, resins, *etc.*, which are mostly colourless or faintly coloured compounds. They are decomposed through the influence of water, oxygen and micro-organisms to II and III.

II. This group contains the smaller part of the decomposition products. It has been called "non-humus constituents of the humus extract", SHOREY (1928), or in German literature "Humusbegleitstoffe", MAIWALD (1931 and 1939). The chemical compounds in II are well-known, fairly simple substances such as amino acids, other organic acids, alcohols, aldehydes and organic bases, MAIWALD (1931 a).

III. The real humus substances, forming the main part of the decomposition products, in contrast to the two former groups, are fairly stable. Their mode of formation and chemical nature are not known in detail. III is mainly a dark coloured, amorphous substance of non-uniform composition. The chemical components of this amorphous mass seem to be physically and chemically similar but their solubility in alkaline solutions is unlike. Their separation from the soil without alteration of their natural state has probably not yet been successfully achieved.

Extraction with dilute alkali gives the following separation:

III A. Humines ("humus carbon"), insoluble in cold alkali. The carbon content in humine is high, about 65 per cent. Repeated extraction with alkali can dissolve part of fraction III A, and so can hot and more concentrated alkali. Thus there is no sharp boundary to the next fraction.

III B. Humic acids, alkali-soluble.

The extract can be separated from the lumines and mineral components of the soil through decantation, filtration or centrifugation. Some parts of I, for example alkali-soluble carbohydrates and pectin acids, can be included in III B. After making the extract acid this fraction can be divided into two parts.

III Ba. Humic acids, soluble in water.

These are not precipitated by making the extract acid. They have a yellowish colour and were named "Fulvosäuren" (fulvic acids) by ODÉN (1919). The carbon content is not so high as in III A.

III B b. Humic acids, insoluble in water.

A treatment with boiling alcohol can separate:

III B b 1. Hymatomelanic acids, soluble in alcohol, with a carbon content of a little more than 60 per cent.

III B b 2. Hnmic acids, insoluble in alcohol, with a carbon content of about 58 per cent.

The humic acids belonging to group III B b have been investigated the most fully. The proportions of the different chemical elements composing the alkalisoluble humus show great variations, on account of which it is impossible to get a gross formula for those compounds by means of elementary analysis. The amount of oxygen, varying betwen 30 and 40 per cent, is computed by subtraction, and for that reason it includes all the experimental errors from the other determinations.

HERMANN (1841-42) reported twelve different kinds of humus compounds, ranging from a nitrogen-free carbohydrate  $C_{12}H_6O_7$  to a high-molecular nitrogenous compound,  $C_{70}H_{70}O_{28}N_7$ .

ODÉN (1919) made a comprehensive investigation of the alkali-soluble but alcohol-insoluble fraction of humus substance (III B b 2). He found that a true salt was formed in the reaction between ammonia and humic acid. With aid of conductometric titration of humic acid with sodium hydroxide he determined the equivalent weight of humic acid to be about 340.

Odén used the following nomenclature: The alkali-insoluble humus fraction, "humus carbon" (III A) was subdivided in humine and ulmine, presumably humic acid anhydride and hymatomelanic acid anhydride, respectively. The alkali-soluble fraction was named hnmic acid, subdivided into alcohol-soluble hymatomelanic acid, alcohol-insoluble humic acid and water-soluble fulvic acid, as mentioned above.

The humus groups separated by means of their solubilities are not unchangeable substances but can be transformed directly or indirectly into each other and they can all be present at the same time in the soil. The mechanism of the transformation process is not known in detail.

If ultrafiltered fulvic acid solutions are allowed to stand, after some months, a mixture of humic acid and hymatomelanic acid is precipitated. If an alcoholic solution of hymatomelanic acid is left, a precipitate of humic acid can form. By heating humic acid to 100° C, water is driven off and a hard mass is produced similar to "humus carbon" and no longer soluble in alkali.

Odén characterizes humic acid as a fourbasic acid of medium strength with the formula  $H_4R_{IIum}$ , where the radical  $R_{IIum}$  is something like  $C_{64}H_{52}O_{32}$ .

As only a small part of the natural humus is alcohol-soluble, it seems probable that hymatomelanic acid is formed (at least partly) through hydrolysis of humic acid during the treatment with alkali. The equivalent weight of the hymatomelanic acid is, according to Odén, about 250 (compared with about 340 for humic acid) and the carbon content is 62 per cent (compared with 58 per cent for humic acid).

#### 2 c. A Simplified Classification of Organic Substance Groups

The subdivision according to the solubility of the organic matter has nowadays been abandoned by some scientists for the reason that the borderlines between the fractions are insufficiently precise.

In the following table the signs used in the previous subdivision are placed in parentheses.

One fraction of the non-humic matter, "Rotteprodukte", has not been mentioned previously. SIMON (1936) has drawn attention to these almost undecom-

Description	Equivalent terms				
	English	German	French		
Total amount of soil organic matter in the soil $(I + II + III)$	Soil organic matter	Gesamthumus	Matières orga- niques du sol		
Partly decomposed material not yet humified (colourless or faintly coloured)	Remains of native material (I) Non-humic matter	Humusbegleit- stoffe (II) "Rotteprodukte"			
Dark, coloured, colloidal humifica- tion products (III)	Humic matter	Eehte Humus- stoffe	Matière noire		
Part of the humic matter separable by certain methods	Humic acids and salts thereof, humatcs (III B)	Huminsäuren			
Partly soluble remainder	Humine, Humus carbon (III A)				

Table 1. A simplified classification of soil organic matter.

Table 2. Soil organic matter and its behaviour in solvents.

	Non-humified material			Humif	ied material
	Nativa material	"Rotteprodukte" (Humolignine)		Real hun	us substances
	of biological origin			Humic aeids (or humates)	Humine
Colour	Usually light	Yellow t red-brow	o n	Brown to grey-black	Black
Behaviour in water	Solubility uneven, sometimes high		So	ome colloidal lubility	Insoluble
Behaviour in alkaline solvents	Insoluble	/	' So	luble	Insoluble
Behaviour in hydrogen peroxide	Non-oxidizable	/	Ox	idizable	Non-oxidizable
Behaviour in acetyl bromide	Soluble			In	soluble

posed products. The composition is of lignine-type and another name is "humolignine". In the first subdivision (§ 2 b) this fraction is included in (I).

In Table 2, cited from MAIWALD (1939 a), some physical and chemical properties of the different groups of organic matter are summarized. The fraction (II) comprising simple decomposition products (amino acids, organic acids, alcohols, aldehydes, and so on) has been omitted from this table, as these compounds are usually present only in minute amounts and rapidly become further decomposed.

As can be seen from the above table, acetyl bromide treatment gives a sharp boundary between humified and non-humified organic matter. This agent has not however been used to a great extent as it is expensive and rather unpleasant to handle and the method is a slow one. Some studies of the influence of acetyl bromide on the organic content of clays have been published by the present anthor (SILFVERBERG, 1955).

#### 3. Direct Methods for Determination of Organic Matter Content

The amount of organic matter in a soil can be determined either directly or indirectly. In the direct methods the soil is treated with an agent, which can in some way remove the organic compounds, the residue after the treatment being weighed. The weight loss gives the organic content.

#### 3 a. Extraction with Alkali

The soil is treated with ammonia or alkali hydroxide and the content of "humus" is determined by either colorimetric or gravimetric methods, in the latter case after evaporation of the ammonia or alternatively after neutralization by acid and subsequent crystallization.

As mentioned in the previous section these extraction methods can neither give the total amount or organic matter nor a definite fraction of it. Only a part is dissolved, its magnitude depending on, among other things, the concentration and temperature of the alkaline solvent and the duration of the treatment. Another disadvantage is the possibility of chemical destruction during the solution process.

For these reasons alkali extraction methods have been abandoned in most laboratories, though only a few years ago. THOENES and JOUSTRA (1949) proposed a modification of the method. In this the soil is boiled with 3 per cent sodium hydroxide solution and filtered, and afterwards the filtrate is treated with potassium permanganate. Oxalic acid is then added in excess and a backtitration made with permanganate. As the method has not been compared with any other analytic procedure the percentage yield is not known.

#### 3 b. Hydrogen Peroxide Method

A method for the direct determination of organic matter which has become very widely used is the hydrogen peroxide method. The following procedure has been proposed by ROBINSON (1927 and 1930). To a weighed quantity of non-dried soil are added equal amounts of water and 30 per cent hydrogen peroxide. A violent reaction with strong heat development shows the presence of manganese dioxide. At small concentrations (less than 0.25 per cent) manganese dioxide can be removed by heating with a small excess of oxalic acid. After this treatment or in the absence of manganese dioxide the mixture is placed on a steambath and allowed to stand until all gas development has stopped. The mixture is then filtered through a thick asbestos cushion in a glass filter crucible, and the retained material is washed, dried and weighed. The filtrate is then evaporated to dryness and the residue ignited and weighed. The moisture content in the original sample is determined separately. The weight of the dried material retained in the crucible and the weight of ash resulting from ignition of the filtrate residue together subtracted from the dry weight of the soil sample before treatment gives the weight of organic matter.

The method has the disadvantage of being directly applicable only to clays:

- 1. with a calcium carbonate content of less than 1 per cent.
- 2. with a very small percentage of manganese dioxide.

There are also some difficulties in bringing the material into good contact with the reacting liquid and in obtaining a clear filtrate. Furthermore, carbonates, carbon and graphite, which are not destroyed by hydrogen peroxide, often contain enclosed paraffin-like substances, which are not attacked.

#### 3 c. Loss-on-Ignition Method

To determine accurately the percentage of organic matter directly from the weight-loss on ignition is not possible because of the weight-loss resulting from the escape of constituent water and from the thermal decomposition of carbonates. A rough estimation however, can be made by this method on clays very rich in organic matter and on sandy clays. If carbonates are present, the carbon dioxide must be driven off before the ignition by treatment with hydrochloric acid, which should be evaporated before weighing.

#### 3 d. Rather's Method

RATHER (1918) suggested a method of removing the hydrated minerals (and the carbonates) by repeated treatment with a mixture of dilute hydrochloric and hydrofluoric acid and subsequent washing to remove these acids and their soluble salts. The residual organic matter is then determined by ignition. As can be seen from Table 2, part of the organic material is water-soluble while another part can be decomposed by the acids. However, by determining by a dry combustion method the total carbon before and after the extraction with acids, that part of the organic matter which is lost by these causes can be estimated. ALEXANDER and BYERS (1932) compared the hydrogen peroxide method and Rather's method with a dry combustion method (see § 4 d) and found that Rather's method gave higher values of the organic content than the other two methods. In the case of the dry combustion method however, the conventional factor used to transform the carbon content to the organic matter content was considered to be incorrect. The authors came to the conclusion that although Rather's method gave the highest values, it was too slow and expensive for use in routine analyses.

#### 4. Indirect Methods for Determination of Organic Matter Content

#### 4 a. Introduction

The indirect methods are based on the assumption that a particular element is present in the organic matter of the soil to such a constant degree that the percentage of organic matter can be obtained from the amount of this element by use of a conversion factor. For such methods to be useful this factor must be known or at least easily determined and should not vary for clays of the same general character.

The elements chosen for this method are either nitrogen or carbon. READ and RIDGELL (1922) recommended the use of the nitrogen content as a measure of the organic matter in a soil. They found the nitrogen content of 37 samples to be 6.24 per cent, with a probable mean error of  $\pm$  0.63 per cent. The majority of the indirect methods are nevertheless founded upon the *carbon content*.

#### 4 b. The Carbon Content of Soil Organic Matter

The indirect methods can give the organic matter content (h) from the carbon content (c) of the sample only if the carbon content (p) of the organic matter is known. The following relation is valid:

$$h = \frac{100}{p} \cdot c = k \cdot c.$$

Much effort has been devoted to the determination of the "carbon factor" k. The most usual value is 1.724, which is based on the assumption that p is 58 per cent. Many investigators have adopted the factor 1.724 (with all decimals) very uncritically but other scientists have raised serious objections against the use of this conventional carbon factor.

The value of 58 per cent for the carbon content of "humus" seems first to have been stated as long ago as 1826 in the work of SPRENGEL (1826). This work was strongly criticized by BERZELIUS (1828). SCHULZE (1849) quoted that the carbon content of the *total organic matter* was 58 per cent and that the carbon content of *humus* was 60 per cent. WOLFF (1864) stated, without giving any analytical data, that the amount of humus in a soil could be obtained by multiplying the carbon content by 1.724 or the carbon dioxide content by 0.471. The work of Wolff seems to have been the foundation for the use of the conventional carbon factor, and is most generally known through VAN BEMMELEN (1891).

However, it has been shown repeatedly that the carbon content of soil organic matter can differ considerably from 58 per cent and several investigators have found a figure nearer to 50 per cent. CAMERON and BREAZEALE (1904) obtained carbon contents varying between 33.3 and 49.2 with a mean value of 41.8 per cent for humus extracted with 3 per cent ammonia from cultivated soils but unaccountably they recommended continued use of the factor 1.724. The reason given for this was that the part of the organic matter not extracted with ammonia contained cellulose and celluloselike substances, the carbon contents of which were said to lie "nearer to the value of van Bemmelen". This statement is surprising as the carbon content of cellulose is only 44.4 per cent!

READ and RIDGELL (1922) applied Rather's method to 37 clays of different types and found the carbon content of the organic matter to vary from 30.2 to 56.3 per cent with a mean value of 49.3 per cent for surface soils (0 to 0.5 m.), and from 13.3 to 56.6 per cent with a mean value of 39.2 per cent for sub-surface soils (0.5 to 1 m.). They suggested a carbon factor derived from a carbon content of 50 to 52 per cent but questioned whether a carbon factor could in fact be recommended at all.

ROBINSON (1927) arrived at quite different results. He found that organic matter decomposed by means of hydrogen peroxide contained from 37.5 to 70.1 per cent of carbon with a mean value of 54.8 per cent. Assuming the remainder after treatment with hydrogen peroxide to be carbon, he computed the average carbon content of the total amounts of organic substance to be 58.6 per cent. It should be noted that the maximum values were obtained with a soil which was known to contain free charcoal particles.

The International Committee for Mechanical and Physical Soil Investigation, (see SCHUCHT, 1914) recommended that the humus content should be determined by elemental analysis of organic carbon and multiplication of the carbon dioxide content by 0.5. (This means that 1 gm. carbon is equivalent to 1.8 gm. humus.)

Several other investigations of the carbon factor have been reported and most of them reveal the great uncertainty of the "Wolff-factor".

However accurately the carbon content in a soil may be determined, the error introduced by using a conventional factor is very great, because of the great variation of the carbon content in soil organic matter. It is possible of course, to base the comparison between different soils on the carbon values alone, but while this is analytically correct it is not really satisfactory as different contents of organic matter can exist for the same carbon content. Furthermore if the combined water of a soil is determined as the difference between the loss on ignition and the organic content (and sometimes the loss of inorganic carbon dioxide), the water content determination is also influenced by the error in the carbon factor.

#### 4 c. The Principles for Indirect Determination of Organic Carbon

Among the many methods published, four main groups can be distinguished, namely the dry and wet combustion methods, the Kjeldahl or Bangor method, and the rapid titration methods.

The dry combustion method is performed by heating the sample in a stream of oxygen or air, usually after the admixture of an oxidizing agent. The carbon dioxide developed is determined by means of gravimetric, titrimetric or gasometric methods. In the wet combustion methods the oxidation is achieved by boiling in an oxidizing liquid. In the Kjeldahl or Bangor method the oxidizing agent consists of sulphuric acid, potassium sulphate and copper sulphate, and the amount of sulphur dioxide produced is determined. In the rapid titration methods the soil is treated with a known quantity of oxidizing agent and the amount of the latter not consumed is determined by titration.

If the organic substance is assumed to have the general formula  $C_nH_{2m}O_m$ , the reaction for complete combustion would be:

$$C_n H_{2m} O_m + 2nO = nCO_2 + mH_2O.$$

Thus the equivalent weight of carbon in this reaction is 3. SCHOLLENBERGER (1927) found by analysis, that in titration 0.32 oxidation equivalents correspond to 1 gm. carbon, which gives an equivalent weight of 3.1. It is now generally accepted that in titration the oxidation of soil organic matter follows the empirical formula above and thus 1 milliequivalent corresponds to 0.3 per cent organic carbon.

#### 4 d. Dry Combustion Methods

Some investigators, for example CROWTHER (1935), consider the method using dry combustion to be the most accurate of the standard methods, though others do not favour it because of its relatively high costs. The most common alternative is wet combustion with chromic and sulphuric acid and determination of the carbon dioxide produced.

Many different procedures are used in dry combustion at present. In general all of them give satisfactory results and the choice between them is to a great extent a matter of personal preference and of the laboratory resources available.

In a determination of organic carbon through dry combustion and determination of the carbon dioxide, the carbonate present in the sample must first be destroyed or estimated by analysis and the amount of carbon dioxide produced in the combustion reduced in corresponding degree. The combustion must in this latter case be continued until all carbonate is with certainty decomposed. The heating of the sample is carried out in a stream of air or oxygen with sometimes the addition of further oxidizing agents or catalysts. If air is used it must first be freed from carbon dioxide; with oxygen however no purification is generally necessary. The reaction chamber is usually a cylindrical porcelain or quartz tube in an electric or gas furnace. The clay sample, contained in a "boat", is not inserted into the combustion tube until this has been ignited and the whole system freed from any carbon dioxide which may be present. The boat can be made of nickel (low in carbon), copper, vitrified clay, alundum, quartz or porcelain. If a nickel boat is used, it must previously have been heated to 1 000° C. After the reaction tube a wash bottle of sulphuric acid is then placed. The sulphuric acid can be saturated with chromic acid in order to oxidize to trioxide any sulphur dioxide that is formed, the trioxide being absorbed in the acid or in a following drying tube. The latter may be filled with anhydrone (anhydrous magnesium perchlorate) or dehydrite (magnesium perchlorate trihydrate). Calcium chloride is not satisfactory because it can retain carbon dioxide. The carbon dioxide can conveniently be absorbed in ascarite (sodium hydroxide—asbestos) in a Nesbitt or Fleming bulb (Fig. 1).



Fig. 1. Nesbitt and Fleming bulbs.

The exit of the absorption vessel must be filled with a desiccant to prevent loss or gain of moisture as the ascarite alone cannot completely retain water formed in the absorption process. Instead of ascarite, soda-lime may be used as an absorbent.

In order to illustrate the practical performance of dry combustion and to show how the procedure can be varied, four of the most common dry combustion methods will be described. They are:

- I. Determination of total carbon according to KOLTHOFF and SANDELL (1950);
- II. The method of U.S. DEPARTMENT OF AGRICULTURE (1930);
- III. The method of the AMER. Association of Official Agricultural Chemists (1930);
- IV. The method of Ter Meulen, see Spithost (1933).

Fig. 2 shows the apparatus for method I, originally applied to the determination of carbon in steel but is also applicable to the determination of organic carbon in soils. The differences of apparatus in the four methods will be discussed in parallel with the help of Fig. 2.



Fig. 2. Apparatus for determination of carbon according to Kolthoff and Sandell.

Furnace and combustion tube. In method IV a gas heated furnace is used, in the three other methods electrical furnaces. In method II the furnace is of multiple type, its length being about 30 cm. In Fig. 2, H is the regulation rheostat for the current through the furnace F. In methods I-III the combustion tube is made of quartz and has a length of 50-60 cm. and an inner diameter of 2.2-2.5 cm. In method IV the tube is of quartz or glass and has a length of 32 cm. and an inner diameter of 1-1.5 cm.

Reaction atmosphere. In I-III the combustion gas is oxygen from a tank (A in Fig. 2). In method I the oxygen is freed from carbon dioxide in a tower C, containing ascarite, and the water liberated in the absorption process is absorbed in sulphuric acid in the wash bottle D. In method III the oxygen passes through two wash bottles containing a 2 per cent potassium hydroxide. M in Fig. 2 acts both as a mercury manometer and a safety valve. In Ter Meulen's method the combustion atmosphere is air, passed through a wash bottle containing concentrated potassium hydroxide and a tower with strong potassium hydroxide in the lower and soda-lime in the upper part.

Loading of the reaction tube. In method I the boat is made of nickel, bnrnt clay, porcelain or quartz, sometimes with a lining of alundum. The sample is packed in a groove made in the alundum without admixture of any oxidizing agent. In method II the platinum or porcelain boat, containing 0.1-5 gm. soil is placed in the central part of the tube, and the end part of the tube is filled with finely divided asbestos. In method III, 2 gm. of the sample is mixed with 2 gm. of finely divided copper oxide in an alundum boat. In the end of the tube is placed a plug of platinum-asbestos. In method IV the fore part of the tube is filled with a catalytic mixture of lead peroxide and an active form of manganese dioxide. Reaction temperature. In methods I and II the reaction temperature is 1 000° C and 900° C respectively, and in method III, 900-950° C. In method IV the first part of the tube, containing the boat, is heated with a strong burner. The part

containing the catalyst is surrounded by an asbestos box divided in two parts. The first part is covered and heated by a burner to about  $400^{\circ}$  C, the second part is open and heated only indirectly to about  $100^{\circ}$  C. The temperature in this part must not exceed  $150^{\circ}$  C.

#### Wash vessels after the furnace

Method I: 1. U-tube or tower with asbestos. 2. Wash bottle containing concentrated sulphuric acid saturated with chromic acid. 3. Tower with anhydrone or dehydrite (I, J and K in Fig. 2).

Method II: 1. Wash bottle containing sulphuric acid. 2. Absorption tube with phosphorus pentoxide.

Method III: 1. Wash bottle of sulphuric acid. 2. Tube with granulated zinc. 3. Tube with phosphorus pentoxide.

Method IV: 1. Spherical widening of the glass tube for condensation of the main part of the water. 2. and 3. Two tubes containing calcium chloride.

#### Absorption of carbon dioxide

Method I: Nesbitt or Fleming bulb with ascarite or soda-lime. On the outlet side anhydrone or dehydrite.

Method II: Fleming bulb with soda-lime and phosphorus pentoxide.

Method III: Nesbitt bulb containing glass-wool and asearite.

Method IV: Two U-tubes in series, containing soda-lime. The absorbent should be renewed if the second tube increases in weight more than 10-20 mg.

#### Vessels following the absorption vessel

Method I and II: Usually no protecting vessels.

Method III: Fisher's bubble counter with concentrated sulphuric acid.

Method IV: Bubble counter containing silver ammonia nitrate that turns black in the presence of carbon monoxide. The absorption train in this method ends in a suction arrangement.

#### Procedure

Method I: A blank is run until the absorption vessel reaches a constant weight. Then a weighed sample is inserted and the combustion takes place with a gas velocity of 300-400 ml./min. After the reaction is finished (in 2 to 3 minutes) the velocity is lowered to 200 ml./min. for a further 5 minutes.

Method II: The absorption train is disconnected and the furnace is heated to 900° C for a short time. The absorption vessels are connected to the combustion tube and ignited in an oxygen stream for about 30 minutes until the Fleming bulb has reached constant weight. The soil sample is then inserted. The combustion in oxygen is continued until the absorption vessel has again attained constant weight (after an air volume of about 4-6 times the volume of the reaction vessel has been passed through). Method III: After the furnace is heated to the correct temperature the absorption train is connected to the tube and oxygen is passed through, the Nesbitt bulb is weighed and the soil sample inserted in the tube. Ignition in the oxygen stream is run for at least 30 minutes until constant weight of the absorption vessel is reached.

Method IV: The velocity of the air stream is about  $1\frac{1}{2}$  to 2 litres per hour. An active form of the manganese dioxide to be used as a catalyst in Ter Meulen's method can be prepared if fine-grained potassium permanganate or a concentrated solution of it is added to an equivalent amount of manganese sulphate (MnSO<sub>4</sub>). The precipitate is washed several times with hot distilled water, dried and heated on a sand bath to 250-300° C. The catalyst can be used as many as 50 times, SAUERBIER (1926).

Many other modifications of the dry combustion method are described. In one method the catalyst consists of granulated copper oxide, platinated asbestos and lead chromate and the oxidation is run in air at a temperature of 700° C. In another method the clay sample is mixed with sulphur and is burnt together with oxygen under pressure in a bomb containing sodium hydroxide. The sulphite formed is oxidized with hydrogen peroxide.

#### 4 e. Wet Combustion Methods

In the wet combustion methods oxidation takes place in the liquid phase. The oxidizing agent used is almost exclusively chromic acid in strong sulphuric acid. The soil is boiled in the oxidizing liquid under back flow, and the carbon dioxide formed is purified and absorbed in the usual manner. To ensure complete oxidation of all the carbon to the dioxide, the reaction in the liquid phase is often supplemented by oxidation in a combustion tube with a catalyst, for example, lead and silver chromate, copper oxide or mercury salts. Two methods of wet combustion will be described in detail.

ROBERTSON and SHEWAN (1935) used as reaction vessel a 300 ml. Kjeldahl flask, supplied with a combined dropping funnel and air intake tube and an Allihn condenser fitted with an outlet tube. The latter is connected to a combustion tube containing pulverized lead chromate and copper oxide. After the combustion or catalyst tube are connected a wash bottle containing sulphuric acid and a calcium chloride tube. For the absorption of carbon dioxide two tubes with soda-lime are provided, the first also containing calcium chloride.

The following procedure is employed. A quantity of soil, sufficient to give 0.5 to 1.0 gm. of carbon dioxide is mixed with 5 gm. of pulverized potassium dichromate. Carbon dioxide-free air is blown through the apparatus and a mixture of sulphuric acid and water (4:1) added. The mixture is then heated to the boiling point in 5 to 10 minutes and boiled for 15 to 20 minutes. Robertson and Shewan reported from the determination of carbon in 9 clays a yield of  $100 \pm 1$  per cent in comparison with a dry combustion method.

Van SLYKE and FOLCH (1940) used an oxidizing mixture consisting of phosphoric, chromic and iodic acids in fuming sulphuric acid. The method was improved and transformed to a semi-micro-method by McCREADY and HASSID (1942) (see Fig. 3). The latter investigators used a reaction flask with a capacity



Fig. 3. The wet combustion apparatus according to McCready and Hassid.

of 15 ml., the air inlet to which is protected by tubes designed to absorb carbon dioxide. The flask is supplied with a reflux condenser of Allihn type, modified by the provision of a long "cold finger" in the centre of the condenser to increase its efficiency. The outlet tube is connected to a bubble counter containing 0.5 ml. concentrated sulphuric acid, which is followed by a tube containing granulated zinc and a further one with anhydrone. Then follows the absorption U-tube containing mainly ascarite but with some anhydrone in each end. Finally a tube filled with granulated calcium chloride prevents backward diffusion of moisture and air. The procedure is as follows: A soil sample of 5 to 30 mg. (depending upon the carbon content) is placed in the reaction flask and 300 mg. of potassium iodide are added. Carbon dioxide-free air is sucked through the apparatus, which is then evacuated. The combustion subsequently takes place in partial vacuum after 4 ml. of the oxidizing agent have been added. The reaction mixture is heated to the boiling point in 2 minutes by means of a microburner and is then boiled for 1 minute. After the reaction has taken place and normal air pressure has been established through careful admission of earbon dioxide-free air, such air is slowly drawn through the apparatus for 15 minutes. The authors report that their method gave theoretical yields with the organic substances that were investigated.

#### 4 f. The Kjeldahl or Bangor Method

The method is described by ROBINSON, MCLEAN and WILLIAMS (1929). The oxidation of the organic matter is performed by means of concentrated sulphuric acid and the formula for the oxidation of the carbon is:

$$C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2$$
.

The sulphur dioxide developed in this reaction is absorbed in a standard iodine solution and the excess iodine titrated with standard sodium thiosulphate solution.

The soil sample (sufficient to furnish 0.02 to 0.05 gm. of carbon) is placed in 9 long-necked Pyrex Kjeldahl flask of 30 cm. length. Then 25 ml. of sulphuric acid, 15 gm. of ignited potassium sulphate and 0.3 to 0.4 gm. of copper sulphate are added and the flask connected with the absorption apparatus. The absorption of the sulphur dioxide by the iodine solution is most conveniently carried out in a tube 50 cm. long and with an internal diameter of 2 cm., fitted with three platinum gauze grids in its lower half to break up the bubbles. The sulphur dioxide is forced through the apparatus by means of an air stream. About 3 litres of air were found sufficient. The absorption tower is washed with water before titration of the excess iodine.

The carbon recovery of the method is reported by the authors to be 89.6 per cent, taking the organic carbon content determined by a dry combustion method as 100 per cent.

#### 4 g. Rapid Titration Methods

SCHOLLENBERGER (1927) proposed a very simple method for determining the amount of organic matter in a soil with reasonable accuracy. His method seems to have inspired research workers in several countries to develop similar procedures which are characterized by their rapidity and by the fact that the amount of organic carbon is determined not by measurement of the carbon dioxide produced, but by titrimetric determination of the amount of oxidizing agent consumed during the reaction with the soil sample.

Three main variants of the rapid titration method are described in I to III below.

#### I. Schollenberger's method

Since his first communication (1927) SCHOLLENBERGER has developed the method further (1931 and 1945) and the procedure is now briefly as follows. A Pyrex test tube is fed with 0.5 gm. soil mixed with a weighed amount of powdered potassium dichromate to oxidize the organic matter and give an excess of 2 to 4 milli-equivalents. 10 ml. of concentrated sulphuric acid are added and the reaction mixture is heated to between 170 and 175° in 90 to 120 seconds, the mixture being stirred during the reaction with a thermometer. The tube is cooled in air for one minute and then in water after which the mixture is poured into 100 ml. of a cold solution of about 5 gm. of sodium fluorid in water and titrated with 0.2 N. ferrous ammonium sulphate using diphenylamine as indicator.

#### II. Tiurin's method

TIURIN (1931 and 1934) has developed the following procedure. 0.1 to 0.5 gm. of soil is boiled for 5 minutes with 10 ml. of 0.40 to 0.45 N. of potassium dichromate or chrominm trioxide in sulphuric acid, diluted with an equal volume of water (S.G. 1.525). The reaction vessel is a 100 ml. flask with a small funnel as a condenser. After reaction the mixture is diluted and 2.5 ml. phosphoric acid (S.G. 1.7) added and titrated with 0.1 N. ferrous ammonium sulphate with diphenylamine as indicator.

#### III. Walkley-Black's method

This method is described by WALKLEY and BLACK (1934) and WALKLEY (1935 and 1947). Soil passing a 100 mesh sieve and containing 10 to 25 mg. of organic carbon is placed in a 350 ml. conical flask and treated with 10 ml. of N. potassium dichromate from a burette, followed by 20 ml. of concentrated sulphuric acid from an automatic pipette. The mixture is shaken for oue minute, cooled, diluted to about 150 ml. and titrated with 0.4 N. ferrous ammonium sulphate after addition of 5 gm. of sodium fluoride or 10 ml. of 85 per cent phosphoric acid, using 1 ml. of 0.5 per cent diphenylamine in sulphuric acid as indicator. No external heating is needed in this method, the temperature raised by the heat of dilution being sufficient to induce a fairly substantial oxidation after a reaction time of only one minute.

These three main variants have been further modified by many investigators and some results are mentioned below.

#### IV. Craig's modification of Schollenberger's method

This modification is mentioned by CROWTHER (1935) as being put forward by Craig in a private communication to Walkley. 0.200 gm. of dry silver dichromate is used in place of the potassium dichromate. The silver ion serves as a catalyst and ensures that the carbon is completely oxidized.

#### V. A modified Walkley-Black method

In the above mentioned report by Crowther a modification of the ordinary Walkley-Black method is described. This modification involves heating for 5 minutes at 140° C with 10 ml. of N. potassium dichromate and 10 ml. of concentrated sulphuric acid.

#### VI. Walkley-Black method with silver ion

In another modification mentioned by Crowther the sulphuric acid used in the ordinary Walkley-Black method contained 10 per cent of silver sulphate.

#### VII. Tiurin's method with silver ion

Even Tiurin's method has been modified by adding 0.1 gm. silver sulphate according to Crowther's report. Soils with a high chloride content were allowed to stand with 5 ml. of sulphuric acid (diluted 1 : 1 with water) and silver sulphate for one hour, with occasional shaking.

#### VIII. Degtjareff's method

In order to obtain better oxidation of the organic matter, DEGTJAREFF (1930) suggested the use of a mixture of dichronuate-sulphuric acid and hydrogen peroxide as the oxidizing agent. To 0.15 to 0.20 gm. of soil are added firstly 10 to 15 ml. of 0.3 per cent hydrogen peroxide and then an equal volume of a 1.6 percent solution of chromic acid in concentrated sulphuric acid. The mixture is shaken for a minute and the oxidation of the organic matter is assumed to take place in this short interval because of the considerable heat developed during the mixing. The mixture is poured into a beaker, diluted to 200 ml. and the excess chromic acid titrated with ferrous ammonium sulphate. A blank is run and the difference in chromic acid consumed is assumed to be caused by the reducing effect of organic compounds. Degtjareff supposed the following reaction to take place between chromic acid and hydrogen peroxide in strong sulphuric acid:

$$2\operatorname{CrO}_3 + 3\operatorname{H}_2\operatorname{O}_2 + 3\operatorname{H}_2\operatorname{SO}_4 = \operatorname{Cr}_2(\operatorname{SO}_4)_3 + 6\operatorname{H}_2\operatorname{O}_4 + 6\operatorname{O}_4$$

According to this formula the chromic acid molecule should be equivalent to 6 oxygen atoms in an oxidation reaction. Whether this assumption is correct or not, will be discussed further in a following section.

#### IX. Potassium permanganate methods

Potassium permanganate has been used to some extent as an oxidizing agent in rapid titration methods. See for example VAGELER and ALTEN (1931). In Spain this seems to be a commonly recognized method and is described in works by RUBIA PACHECO and LOPEZ-RUBIO (1950). The procedure described in the last mentioned reference is the following. 0.1 gm. of soil is boiled with 25 ml. of 9 per cent sulphuric acid for 3 minutes. After addition of 0.5 ml. of concentrated nitric acid the boiling is continued for another 3 minutes, the mixture diluted with 125 ml. of distilled water, 25 ml. of 0.1 N. potassium permanganate is added and the boiling continued for another 5 minutes. After addition of 25 ml. of 0.1 N. oxalic acid the excess of this is determined by titration with permanganate.

#### X. Ceriometric methods

The use of cerium salts as oxidation agents has been proposed by RUBIA PACHECO and LOPEZ-RUBIO (1950) and by NAJMR (1952). The redox potential of the cerium salts, the stability of their solutions even at the boiling point, and their non-interference with moderate amounts of hydrochloric acid are facts which argue in favour of the ceriometric methods. The following procedure is recommended by Rubia Pacheco and Lopez-Rubio. A finely divided sample of soil is boiled for 3 minutes with 10 per cent sulphuric acid. A small quantity of nitric acid is then added and the mixture boiled for another 3 minutes. The mixture is next diluted with 5 per cent sulphuric acid and a measured volume of 0.1 N. ammonium-ceric sulphate in N. sulphuric acid or 0.1 N. ammonium hexanitrocerate in N. nitric acid, is added. The boiling is continued for 60 minutes in the first case and 5 to 10 minutes in the second. After cooling and dilution, potassium iodide is added and 0.1 N. thiosulphate is used for titration of the iodine released. The instability of ceric sulphate was regarded as a drawback of the method because of the long boiling time needed for complete oxidation and the authors tried the addition of salts of molybdenum, vanadium and wolfram as catalysts in attempts to shorten this period.

GLEU (1933) recommended osmium tetroxide as catalyst in oxidation processes with cerium salts. Rubia Pacheco and Lopez-Rubio compared the results obtained with cerium oxidations with those obtained with the permanganate method, which in itself is rather uncertain, as will be discussed later.

#### 4 h. The Tinsley Method

An inconvenience of the rapid titration methods with dichromate-sulphuric acid mixtures is the instability of the dichromate at high concentrations and in strongly acid solutions. This instability is further increased through catalysis by certain inorganic soil constituents, as will be discussed later. A long boiling time is desirable to bring about as complete an oxidation of the organic matter as possible. Under the conditions in practice there is a strong tendency for chromium trioxide to distil over with the water vapour, and additional effects are the increase of concentration and boiling temperature through the evaporation of water. The desirability of reflux cooling is thus evident. Difficulties of this kind have given an impetus to search for a new titration method. TINSLEY (1950) has worked out a method that cannot be classified as a rapid titration method but is reported to give a very good recovery of the organic carbon. In this perchloric acid is added to the oxidizing mixture and sodium dichromate is used instead of the potassium salt in order to avoid the precipitation of the almost insoluble potassium perchlorate. The following procedure was developed by Tinsley. A 0.4 N. sodium dichromate solution, containing 40 per cent by volume sulphuric acid (S.G. 1.84) and 14 per cent perchloric acid (S.G. 1.70) is prepared. About 2 gm. of soil is boiled gently under reflux cooling with 25 ml. of the oxidizing mixture for 2 to 3 hours. The arrangement for the boiling and reflux cooling by means of a "cold finger" is shown in Fig. 4. After the mixture has been boiled and cooled it is dilnted with 100 ml. of saturated sodium fluoride solution, and titrated with 0.4 N. ferrous ammonium sulphate, using 10 drops of a 0.5 per cent solution of diphenylamine in sulphuric acid as an indicator. An alternative indicator is a solution in water of barium chloride and barium diphenylamine sulphonate. The fine suspension of barinm sulphate formed serves as a background for the colour change from blue to green.



Fig. 4. The cooling arrangement according to Tinsley.

To investigate the thermal decomposition of the dichromate solution, Tinsley boiled his oxidizing mixture together with acid-washed sand firstly in open flasks and secondly with reflux cooling and with varying boiling times. The same investigations were then made with 0.4 N. potassium dichromate solution in 50 per cent by volume sulphuric acid and finally with a 0.4 N. potassium dichromate solution with 40 per cent sulphuric acid and 20 per cent phosphoric acid (S.G. 1.75). He found that the two last-mentioned solutions, when boiled in open vessels, were decomposed noticeably after the first five minutes giving off white fumes and water vapour. In the oxidizing mixture containing perchloric acid the decomposition was delayed. The dichromate found by titration to remain after 15 minutes boiling was respectively 79.9 and 71.1 per cent in the first two mixtures but 96.2 per cent in the perchloric acid solution. During boiling for up to 3 hours with a cold finger condenser as in Fig. 4 the decomposition was found to be very slight because of the constant concentration and the constant boiling point. Recovery of the dichromate was best in the perchloric acid solution (99.s per cent).

#### 5. Discussion of Direct and Indirect Methods

#### 5 a. General Comparisons

As can be seen from § 3 the direct methods for the determination of organic substance in a soil are rather uncertain since the usual agents used for extraction or oxidation affect neither the total amount of organic matter nor a constant percentage of it. The most unreliable method seems to be the loss-on-ignition method for the reasons mentioned in § 3 c. A combination of hydrogen peroxide treatment and ignition is possible and will be discussed in the experimental part of this paper, § 7 a.

Among the indirect methods, the dry combustion is the most accurate. The main source of error lies in the effect of the carbonates which may be present in the sample. In the separate determination of the carbonate by treatment with acid there is the risk that part of the organic matter will also be affected while in the combustion process there is the possibility that not all the carbonate will be decomposed. The latter risk is greater in the methods where the reaction temperature is relatively low and the reaction time is short. The reaction between the acid and the organic matter in the determination of carbonate seems to be catalysed by manganese dioxide and can be prevented by the use of a reducing acid or reducing agents dissolved in the acid, such as ferrous or stannous chloride. The last-mentioned compound cannot however be recommended, since a white coating is formed which is very difficult to remove from the vessel.

The wet combustion methods in general give lower values of the carbon content than do the dry combustion methods. This is because free carbon, as graphite, and certain scarcely oxidizable parts of the organic matter, including non-humified soil material remain unaffected. The wet method, according to Slyke-Folch, is likely to give higher carbon values than the dichromatesulphuric acid methods. That all the carbon is not recovered by these methods is not necessarily a drawback, as much of the unrecovered carbon (elemental or organically combined) is not in fact a part of the humus and ought not to enter into the analysis.

In the wet combustion method also, the carbonate must be determined separately but here the risk of its incomplete decomposition in the oxidation process does not exist. The oxidation of soil organic substances to carbon dioxide and water does not take place directly, but by way of intermediate products, which must also be oxidized by means of appropriate agents. Thus, in general, small amounts of carbon monoxide and acetic acid can be produced. The rapidity of the "rapid" titration method lies mainly in the short reaction time needed. This advantage however is to some extent offset by the lower carbon recovery obtained compared with that from combustion methods. The results from titration must thus be multiplied by a "recovery factor", which can vary noticeably even for the same method. It is therefore necessary to check this factor now and then against a more accurate method and to standardize the procedure as far as possible. It should be possible to get a carbon recovery as high as in the wet combustion methods, if the reaction time is long enough, reflux cooling is arranged and the stability of the oxidizing agents is secured.

The principal difference between the titration and wet combustion methods is the question of what is measured. In the first case the carbon dioxide produced is measured in some way, while in the second case the consumption of oxidation equivalents is determined. Incomplete oxidation, as mentioned in connection with the wet combustion method, naturally gives rise to low values of the carbon content in the titration methods also, but the consumption of oxidizing agents for reasons other than the oxidation of organic carbon will tend to give a higher carbon content value than that actually present. That this lastmentioned source of error can under certain circumstances be very important and in special cases even invalidate a method, will be discussed in the following.

#### 5 b. Sampling and Accuracy

A study of the organic matter content of a soil must be based upon a correct analytical method as well as upon a representative sampling procedure. The local variation in organic content within the same stratum can be much greater than the experimental error in the analysis, so that it is inappropriate to strive after an accuracy of analysis that cannot be reached in the sampling if the object is to determine the organic content of a certain soil layer.

On the other hand, if the intention is to find a correlation between the content of organic matter and a certain geotechnical property, such as the shear strength or the compressibility, it is necessary to be able to obtain as accurate a value of the organic content as possible of the very sample for which the geotechnical data have been determined.

ALLISON (1935) reports an interesting investigation comparing the errors caused by sampling with those caused experimentally. Despite using a very large number of parallel samples, he found that the standard deviations for these were larger than the deviations caused by errors in analysis. Allison's investigation was made for agricultural purposes.

#### 5 c. Remarks on Degtjareff's Method

The value of Degtjareff's method (§ 4 g. VIII) would appear to lie in the rapidity of the procedure. No external heating is used, the heat of mixing alone being relied upon to achieve the complete oxidation of the organic substance.

The theoretical basis of the method however seems to be nnreliable, as has been pointed out by WALKLEY and BLACK (1934). It has been found that the reaction between chromic acid and hydrogen peroxide does not in all cases occur in accordance with the formula in § 4 g. VIII.

An alternative reaction

$$2$$
CrO<sub>3</sub> + 4H<sub>2</sub>O<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> = Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 7H<sub>2</sub>O + 7O

has been shown to take place in the absence of soil whereas the reaction mentioned by Degtjareff predominates if soil is present. Thus the blank and the true determinations are not commensurable in this respect. It is also unlikely that complete oxidation can take place in the short time available. In addition, nascent oxygen is liberated from the hydrogen peroxide in both of the reactions previously mentioned. This is itself capable of oxidizing part of the organic matter and thus, by reducing the quantity of chromic acid used, introduces a further element of uncertainty into the determination.

Thus it is clear that the addition of hydrogen peroxide to the chromic acid reaction mixture in a "rapid titration" introduces complications which can invalidate the method. In this paper this question is discussed in some detail, mainly because of the interesting fact that the presence of soil material can act catalytically and cause a reaction in an oxidizing mixture that does not occur in the absence of soil. A related effect will be discussed more closely in the following.

### 5 d. The Influence of Certain Inorganic Soil Constituents on the Titration Methods

The decomposition of chromic acid for other causes than the reducing by organic substances seems to be catalyzed by certain inorganic substances in the clay and this catalytic effect differs from clay to clay. To be able to correct for decomposition of chromic acid in the rapid titration process it is not sufficient to run a blank without the addition of some clay substance. Some research workers have used well-washed sand in the blank determination bnt the catalytic effect seems to be greater with elay. Naturally the clay must be well ignited to destroy all contained organic material. One consequence of this ignition is that one cannot be sure that the catalytic effect in the blank is the same as in the actual determination. If a series of analyses of clay samples of similar character is made, such a control determination need only be carried out on a few of the samples.

#### The influence of chlorine

Clays containing considerable amounts of chloride give abnormally high carbon values with the dichromate reduction methods (this is another term for the titration methods, whereby the effect upon the dichromate is marked). Dark vapours are given off and condense on the colder surfaces of the vessel as a heavy red liquid. This is chromyl chloride,  $CrO_2Cl_2$ , boiling at 118° C and is formed according to the equation

$$Cr_2O_7^{2-} + 4Cl^- + 6H_3O^+ = 2CrO_2Cl_2 + 9H_2O$$

One way to avoid errors from this source is to wash away the chloride from the sample before commencing the determination. However, in the washing a loss of water-soluble organic substance can occur and it is thus better to employ a correction founded on the chloride content as discussed below.

SCHOLLENBERGER (1931) proposed a correction based on the above equation, according to which 1 mol of chloride should give a carbon value that is <sup>3</sup>/s mol too high. WALKLEY (1935) showed however by experiments with sodium chloride that the dichromate is reduced quantitatively according to the equation:

 $Cr_2O_7^{2-} + 6Cl^- + 14H_3O^+ = 2Cr^{3+} + 6Cl + 21H_2O.$ 

Thus the chromyl chloride is an intermediate product in the reaction. Each mol of chloride therefore corresponds to 1/4 mol of carbon and for each gram of chloride in the soil the apparent amount of carbon ought to be diminished by 0.085 gm. (12 gm. of carbon being equivalent with 141.8 gm. of chloride). This correction is satisfactory up to a Cl: C ratio of 5. According to Walkley, if the chlorine content of the soil is unknown, its disturbing effect can be at least partly eliminated by precipitating the chlorine as silver chloride. Walkley found that concentrated sulphuric acid can dissolve up to 150 gm. of silver sulphate per litre. With sulphuric acid containing 100 gm. of silver sulphate per litre he obtained an apparent recovery of S5 per cent with Walkley-Black's method applied to a soil with more than 4 per cent Cl, whereas for the same sample, without using silver sulphate, he got an apparent recovery of 150 per cent. Normally Walkley-Black's method gives a recovery of 75 per cent. As mentioned formerly, the silver ion can serve as a catalyst for more complete oxidation of the organic carbon. In the case of soils poor in salt the effect of silver sulphate is of no importance. If the Cl: C ratio does not exceed unity, 25 gm. of silver sulphate per litre are sufficient to precipitate the chlorine. For soils richer in chlorides the salt content is a very important factor and must be controlled in the humus analysis. Mercuric oxide and sulphate have the same influence as silver sulphate.

#### The influence of nitrate and carbonate

Walkley found further, that a carbonate content up to at least 50 per cent of the soil weight and nitrate up to 5 per cent of the carbon content did not interfere with the carbon determination by the Walkley-Black rapid titration method.

#### The influence of manganese

The form of manganese in the soil is not known exactly. According to WALKLEY (1947) X-ray analysis has shown that 4 or 5 modifications of the oxide  $MnO_n$ 

exist, where n is a value in the neighbourhood of 2. It has been stated, that n may be as low as 1.7 or 1.8, though the oxide retains the same structure as an oxide for which n = 1.97. Walkley states that the "active oxygen" probably amounts to n = 1 atoms of oxygen per atom of manganese. Remarkable differences in reactivity seem to exist between different manganese oxides, which cannot be explained by differences in the amount of active oxygen. The ratio between the greatest and least activity of some natural manganese oxide minerals was found to be as high as 30:1, and for a chemically prepared oxide still higher reactivity values were reported. It seems quite possible, that manganese dioxides, very different in reactivity, can be present in natural soil samples.

If manganese dioxide and potassium dichromate in the presence of a strong acid are heated together with an oxidizable material, the resulting oxidation is caused partly by the manganese dioxide and partly by the dichromate. The proportion of oxidation caused by the first agent is entirely dependent on its reactivity and the chemical environment in the reaction vessel. Thus, even if the amount and structure of the manganese dioxide is known, it is not possible to correct for its influence. The effect of manganese dioxide in the sample is a carbon content which is too low.

WALKLEY (1947) proposes to annul the effect of the most reactive oxides, if they are present in large amounts, by adding cold acidified ferrous sulphate solution the required amount of which can be determined by a preliminary titration. Together with the sulphate is added some phosphoric acid. After five minutes the reactive manganese dioxide is dissolved and the treatment with the chromic acid performed in the usual manner.

#### The influence of ferrous iron

If soluble ferrous compounds are present in a soil to which a rapid titration method is applied they unavoidably give rise to carbon values that are too high. WALKLEY (1947) expressed the opinion that air-drying for a day or two would be enough to oxidize the iron to the ferric state to such an extent, that the amounts of soluble ferrous compounds would be trifiing compared with the content of organic carbon. However, it might be possible (at least at low carbon conteuts) that the ferrous compounds, and not only the easily soluble ones, can interfere with the determination of organic matter in the dichromate reduction methods.

#### The influence of sulphide

Clays rich in organic matter often contain sulphur in the sulphide state and they sometimes smell strongly of hydrogen sulphide. In this case also the greatest part may be oxidized in the drying process, but the reducing effect of sulphides which may possibly be present must not be neglected.

### 6. Earlier Investigations of Various Titrimetric Methods

Several comparative investigations have been undertaken of the reliability and usefulness of different analytical methods.

The Third International Congress of Soil Science set up a committee, the purpose of which was to study 1) the degree of accuracy attained in different laboratories by "recognized combustion methods", and 2) the merit of certain approximate rapid methods. Nine different soils were distributed to each of fourteen different laboratories for determination of the organic carbon by various methods. The first report of the committee was published by CROWTHER (1935). The dry combustion values were all in very good agreement and the mean values for each soil were used as standard when computing the percentage recovery of the other methods. The wet combustion methods gave recoveries which varied for different laboratories from 77 to 99.6 per cent with a mean value of 91 per cent. The best result was obtained with silver sulphate as catalyst in the oxidizing liquid. The "rapid titration methods", used in this comparative investigation, were Schollenberger's, Tiurin's and Walkley-Black's methods and some modifications of them. One of the samples was very rich in salt (4.6 per cent chloride) and this was enough to invalidate completely the rapid combustion values (recoveries from 70 to 168 per cent were found). For the remaining eight samples the individual recovery values for Schollenberger's method varied from 86.5 to 105 per cent with a mean of 91.5 per cent. For Tiurin's and Walkley-Black's methods the corresponding figures were 82.5, 108 and 92.5 per cent and 70.0, 93.4 and 80.0 per cent respectively. The highest recovery values in Schollenberger's and Tiurin's methods were obtained when silver ion was added as catalyst. Crowther describes some variants of Walkley-Black's method, one with external heating at 140° C for 5 minutes. The method seems to be very sensitive to varying experimental factors; the vessels, time for heating and cooling and so on must be standardized.

SMITH and WELDON (1940) made a comparison between the hydrogen peroxide method (modified Robinson method), a wet combustion method with absorption of carbon dioxide in barium hydroxide, Schollenberger's and Walkley-Black's methods. The last-mentioned method was somewhat modified in that after oxidation and dilution of the sample a known amount of ferrous ammonium sulphate was added, the mixture heated to 85 to 90° C and the excess of ferrous ammonium sulphate titrated with permanganate. The wet combustion values were taken as standard (equal to 100 per cent recovery), and the values found by the other methods showed very great variations from these. The recovery values for the Schollenberger's method varied from 55 to 212 per cent for 69 samples representing very different compositions and origins. The mean value happened to be 100 per cent but naturally with wide limits of error.

ALLISON (1935) compared Schollenberger's method with the dry combustion method. With 5 carbonate-free soil samples he obtained a recovery of 86.50

per cent. Allison considered Walkley-Black's method unsatisfactory because the carbon fraction could not be defined. He obtained recovery values between 60 and 80 per cent and thought the reaction rate at the temperature of  $124^{\circ}$  C to be too low for the attainment of equilibrium.

Walkley and Black applying their titration method to 20 soil samples of various origin obtained carbon recoveries of 60 to 86 per cent with a mean value of 76 per cent. The authors doubted whether the organic matter oxidizable by the chromic acid constituted a definite fraction of the total organic content.

BROWNING (1938) compared Walkley-Black's method with the dry combustion method, according to A.O.A.C. (method III in § 4 d) and found a mean recovery of 84.7 per cent. With a correction factor of 1.18 computed from this value, he applied the method to 50 samples of differing origin aud arrived at variations in recovery values from 92.9 to 110.1 per cent. Browning considered the time necessary for a double determination by dry combustion of both organic and inorganic carbon to be two hours, while the Walkley-Black determination could be performed on 4 to 5 samples in an hour.

Two variations in the method of determining the reduced dichronate may be mentioned. PAVEL (1952) made use of potentiometric titration and considered this method to be both more rapid than an indicator method and free from the risk of overtitrating. SCHOLLENBERGER (1945) suggested replacing the titration by a rapid colorimetric or photoelectric measurement since the reduction of chromic acid involves a strong and continuous colour change from orange to green.

TINSLEY (1950) compared his method (§ 4 h) with the wet combustion method according to Robertson and Shewan, and with the method of Walkley and Black. The recovery values of the Tinsley method, after different boiling times, and Walkley-Black's method arc found in Table 3. The wet combustion values were taken as 100 per cent. The analyses were performed on 10 samples and the standard deviations computed. The values are here given to only 1 decimal place, and the individual mean errors and the correction factors are derived.

Method					Recovery	Ind. mean	Corr.	
					p. c.	error	factor	
Walkley method Tinsley method, * * * * * *	boiling » » »	time » »	10 30 60 120 180	min. » » »		$\begin{array}{c} 83.6 \pm 1.3 \\ 89.9 \pm 1.2 \\ 94.3 \pm 1.2 \\ 96.4 \pm 1.2 \\ 98.3 \pm 1.3 \\ 99.1 \pm 1.3 \end{array}$	4.3 3.9 3.6 3.9 4.0 4.8	1.20 1.11 1.06 1.04 1.02 1.01

Table 3.

Thus 2 to 3 hours boiling is necessary for almost complete recovery (with wet combustion taken as standard), so the Tinsley method cannot be looked upon as a rapid method, even if the *effective* working time is not much longer than for the "rapid titration methods". The method has been subjected to an experimental investigation by the present author which is described in the next section.

#### 7. Experimental Investigations

In order to test their value and to find a relatively rapid and simple determination of soil organic matter, three methods, one direct and two indirect, were investigated by the Author. The results found were compared with the organic carbon values determined by means of dry combustion<sup>1</sup>.

#### 7 a. A Modified Hydrogen Peroxide Method

A combination of the extraction method by means of hydrogen peroxide and the loss-on-ignition method has been proposed by ROSENQUIST and was chosen for a closer study because of its simplicity and other apparent advantages. The method consists of a comparison between the ignition-losses for two parts of the same sample, one part merely dried at 105° C and weighed and the other part treated with hydrogen peroxide, dried and weighed. The ignition-loss should be smaller for the peroxide-treated than for the untreated part and the difference should constitute the weight of the organic matter removed by the hydrogen peroxide.

- If X = humus content in per cent by weight of dried and nutreated sample;
  - A = weight of dried and hydrogen peroxide-treated sample before ignition;
  - A' = the same after ignition;
  - B = weight of dried and untreated sample before ignition; and

B' = the same after ignition,

the following formula then applies:

$$X = \left(1 - \frac{A B'}{A' B}\right) \cdot 100 \tag{1}$$

If the "blank" determination of B and B' is made in n parallel determinations, the formula becomes:

$$X = \left(1 - \frac{A}{nA'} \cdot \sum_{i=1}^{n} \frac{B'_i}{B_i}\right) \cdot 100$$
(2)

<sup>1</sup> The determinations of organic carbon by means of dry combustion were made by Mr. A. Aaremäe at the Chemical Laboratory of the Geological Survey of Sweden.

As has been pointed out above (§ 3 c) the usual loss-on-ignition method is very uncertain because of the unknown loss of constituent water and the thermal decomposition of carbonates and other substances. In the modification mentioned above these sonrces of error are eliminated.

In the Robinson gravimetric method (§ 3 b) a disadvantage is the difficulty of transferring the treated soil substance to the filter crucible without losses. In the modified hydrogen peroxide method however it is not necessary either to know the weight of the sample or to dry it before the hydrogen peroxide treatment. Nevertheless this method has serious disadvantages as will be seen from the following.

Procedure: An amount of soil, either air-dried or wet, but corresponding to a dry weight of about 5 gm. is placed in a 800 ml. beaker. 25 ml. of 15 per cent hydrogen peroxide are added and the soil is mixed with the liquid by means of a glass rod. The beaker is placed on a hot plate and a strong foaming generally begins after a few minutes. If the foam tends to rise over the rim of the beaker it is necessary to slow down the reaction by cooling in water. When the reaction has almost stopped, more hydrogen peroxide is added and the procedure is continued nntil a fresh addition does not cause any noteworthy gas development. The beaker is allowed to remain on the hot plate until most of the water has been evaporated. The mixture is then transferred to a porcelain crucible (previously ignited at 800° C to constant weight) and the final drying takes place in an oven at 105° C. At the same time an untreated sample, the blank, is dried. After weighing, both the samples are ignited at 800° C. In the first experiments the drying to constant weight (less than 0.5 mg. difference between two successive weighings) occupied 48 hours and the ignition time was 5 to 6 hours. If the sample is ground in a mortar after drying overnight the drying and ignition times can be shortened. The effective working time per sample is quite short as many parallel samples can be treated at once.

Results: The results obtained with the method were very irregular. Firstly a series of determinations were made on samples from a clay core of 40 m length taken in Gothenburg in the southwest of Sweden. The organic carbon content varied between 0.5 and 1.6 per cent when determined by means of dry combustion. By taking the carbon content of organic matter to be 58 per cent (for the reservations on the reliability of this value, see § 4 b) the percentage recovery of the hydrogen peroxide determinations could be computed. The mean recovery of the carbon content in 16 samples was 44.2 per cent with a standard deviation as great as 17.8 per cent. In three cases an apparently negative value of the carbon content was obtained and these were naturally excluded from the computation of mean value. The results are shown graphically in Fig. 5. As the individual recovery values varied from 15 to 93 per cent, it was decided to undertake a thorough study of the method eliminating as far as possible all experimental errors and using a sufficient number of parallel determinations.

For control determinations with the hydrogen peroxide-ignition method, and for use in following determinations with two other methods, six clay samples



Fig. 5. Results of organic carbon determinations by means of the modified hydrogen peroxide method compared with those of dry combustion.

having varying values of organic and inorganic carbon content were chosen as "standard samples". Each of these was dried, finely powdered and made homogeneous and stored in quantities sufficient for many determinations. All the standard samples were of post-glacial origin<sup>1</sup>.

Standard sample No.	Type of soil and origin	Organic carbon content per cent of dry weight	Inorganic carbon content per cent of dry weight
Ť	Clay Stockholm	0.48	0.01
п	Clay, Kyidinge, Scania, S. Sweden	0.67	1.24
ш	Clayey mud from lake bottom, Stockholm	10.00	0.02
IV	Clay, Lilla Mällösa, 30 km. N. of Stock-		
	holm	1.36	U.09
v	Muddy clay, Stoekholm	3.19	0.03
VI	Clay, Stockholm	0.37	1.11

Table 4. Standard samples.

<sup>1</sup> The carbon contents quoted in Table 4 are the dry combustion values.

Standard sample No.	Organic carbon found per cent	Standard deviation per cent	Recovery per cent	Total number of determinations	Usable determinations
I	0.085	0.035	18	17	13
п	0.282	0.045	42	12	12
III	7.40	1.9	74	6	6
IV	0.202	0.078	15	17	13
v	0.667		21	12	3
VI	0.13		35	9	1

Table 5. Organic carbon content of standard samples by means of the  $H_2O_2$ -ignition-method.

The procedure for examination of the standard samples was as described above, but in addition some control determinations were made with 30 per cent hydrogen peroxide. The results are given in Table 5.

The individual values for parallel determinations on the same sample showed great variations as can be seen from the standard deviations. The carbon recovery with the dry combustion values as standard varied from 15 to 74 per cent, the highest value being obtained for the claycy mud with a high organic carbon content. For computation of the mean values some results were rejected as they indicated carbon contents to be about zero or in many cases even *negative*. Samples V and VI especially showed a pronounced tendency to give negative values. The only three positive values for sample V were obtained after a treatment with two to three 25 ml. portions of 30 per cent hydrogen peroxide. Of the nine determinations of the carbon content of sample VI only one gave a positive result. In this case a repeated treatment with 30 per cent hydrogen peroxide was quite ineffective.

From these results it can be concluded that the method of determination of soil organic matter by means of combined hydrogen peroxide treatment and ignition cannot be recommended even for routine work in spite of its theoretical and practical simplicity. It was expected that the degree of oxidation by hydrogen peroxide would vary for different kinds of organic matter, but the great variability in recovery values actually found cannot be fully accounted for by incomplete oxidation, while the negative carbon content values cannot be explained at all in this way. The highest carbon recovery was obtained for sample III, a clayey mud from a lake bottom. The method might be applicable to soils with very high organic contents if a constant recovery factor could be established.

The high standard deviation values show that even on the same sample the method gives considerably varying results. The formula (1), § 7 a, shows that the percentage of organic matter is expressed as 100 times the difference between

1 and a figure  $\frac{B'}{B} / \frac{A'}{A}$  which is not far from nnity. Thus a small error in the

weighing has a great influence on the result. Experimental methods leading to computations of this type are generally not well suited to accurate determinations.

In order to discuss why apparently negative organic content values can arise, formula (1) is rewritten as follows:

Let  $\triangle A = A - A'$  and  $\triangle B = B - B'$  be the weight losses of the hydrogen peroxide-treated sample and the untreated sample respectively. Then formula (1) becomes:

$$X = 100 \cdot \frac{\frac{\bigtriangleup B}{B} - \frac{\bigtriangleup A}{A}}{1 - \frac{\bigtriangleup A}{A}} \tag{3}$$

or if terms with higher degrees than one are neglected

$$X = 100 \left(\frac{\triangle B}{B} - \frac{\triangle A}{A}\right) \tag{4}$$

A negative value of the organic content X thus means that the relative weight loss during ignition is greater for the treated sample than for the untreated one and during the investigations for the present study it was found repeatedly that this astonishing phenomenon can in fact occur. It is beyond the scope of this paper to explain why the hydrogen peroxide method fails to give reliable results if performed in the way described above, but there seem to be complications in the reactions between the organic material and the peroxide, possibly caused by the formation of intermediate products during the oxidation, as for example peroxycarbonates. Thus a certain increase in weight might result from the use of the peroxide-treatment in certain cases. It is much less probable that the water-retaining capacity at 105° C would be greater for the treated sample than for the untreated one.

#### 7 b. The Tinsley Titration Method

The modified titration method reported by TINSLEY (1950) has been mentioned in § 4 h. It was chosen for experimental investigation as it was regarded as a good representative of the many methods developed from SCHOLLEN-BERGER'S (1927) first proposal of a "rapid titration method".

The oxidizing mixture used in the experiments described below is prepared as follows: 39.s gm. of sodium dichromate  $(Na_2Cr_2O_7, 2H_2O)$  are dissolved in 904 ml. of water, and 280 ml. of 70 per cent perchloric acid (S.G. 1.57) are added. 800 ml. of 96 per cent sulphuric acid (S.G. 1.84) are next added in small portions while the mixture is shaken and cooled. The mixture is then 0.4 N. in respect to sodium dichromate and contains 40 per cent by volume sulphuric acid and 14 per cent perchloric acid, just as did the oxidation mixture III used by Tinsley.



Fig. 6. A set of four modified apparatuses for organic carbon determination according to Tinsley.

The apparatus used by Tinsley is here modified in order to get better reflux cooling. The reaction vessel is a 500 ml. Erlenmeyer flask with a ground neck which is fitted to a vertical bulb condenser in whose upper end a "cold finger" is inserted. A set of apparatuses is shown in Fig. 6 in which four determinations could be made in the same time.

*Procedure:* The following procedure was developed. The soil sample for humus determination is pulverized, dried at  $105^{\circ}$  C and an amount of soil containing about 10 mg. of organic carbon is analytically weighed. After the powder has been transferred to the flask, 25 ml. of the oxidizing mixture are added by means of a calibrated pipette, the flask is attached to the condenser system and heating is begun. The contents of the flask are heated to boiling in 2 to 5 minutes and the flame is then adjusted so that the mixture boils very gently for one hour. It seems of considerable importance for the stability of the dichromate to heat very cautiously, so that the risk of thermal dissociation is eliminated as far as possible. Sometimes when irregular results were obtained they could be attributed to insufficient cooling or to vigorous boiling when often white fumes of perchloric acid were produced. If the colour of the boiling mixture should change to green after a few minutes' boiling, further oxidation mixture is added through the condenser.

After the boiling and a few minutes' cooling, the "cold finger" is removed and rinsed with distilled water that is allowed to flow through the condenser into the reaction vessel. 100 ml. of saturated sodium fluoride solution is then added through the condenser in such a manner that the inside of the condenser is well rinsed by the solution. Finally the ground joint between the condenser and the flask is rinsed by distilled water which also is allowed to flow into the flask. After cooling, the reaction mixture is then ready for titration.

The titrator nsed is 0.4 N. ferrous ammonium sulphate in sulphuric acid and the indicator a solution in water of the barium salt of diphenylamine sulphonic acid. The colour of the solution before the titration is orange to olive green. After addition of the indicator the colour becomes blue-violet but this colour often does not appear until some of the reducing solution has been added. Just before the equivalence point the colour changes to dark blue-violet and at the equivalence point to dirty blue-green. The colour change is not quite instantaneous and therefore the titration in the neighbourhood of the equivalence point must be performed very slowly. The correct colour change is best seen against the light if the liquid is shaken np onto the walls of the flask. Often a foam is formed on the surface of the liquid during the shaking. The foam is distinctly blue before the equivalence point and green after it is passed. (In this titration it is sufficiently exact to equate the colour change and the equivalence point.)

*Results:* The analyses were undertaken on the six standard samples, mentioned in Table 4. The results are given in Table 6.

The values in this table are the result of a total of 169 analyses. The individual variations for each sample were not very great as can be seen from the values of standard deviation. The apparent recoveries in per cent of the dry combustion values however, are varying and dependent on the kind of clay under investigation.

The main conclusion is that the recovery values are too high. The increase in apparent recovery values caused by certain inorganic soil constituents has

Standard sample No.	Organic carbon content found by dry combustion per cent of dry weight	Organic carbon content found by Tinsley method	Standard deviation	Apparent recovery per cent of dry combustion value
I	0.48	0.57	0.01	119
п	0.67	0.82	0.005	127
III	10.00	11.9	0.27	119
IV	1.86	1.87	0.025	137
v	3.19	4 60	0.075	144
VI	0.37	0,52	0.035	139
	131			

 Table 6. Organic carbon content of standard samples by means
 of the Tinsley titration method.

been discussed in § 5 d, and it is clear that certain of these, chlorine, ferrous iron and sulphur, for instance, were present in the standard samples. It has not been possible to study in detail how these substances have interfered with the organic carbon determinations. Instead, special attention has been devoted to the catalytic effect of the minerals themselves on the decomposition of the oxidizing mixture. As mentioned in § 4 h, Tinsley made his blank determinations with acid-washed sand and had very little thermal decomposition. As the present author found that the blank determinations, if performed on ignited clay samples instead of sand, gave considerably higher decomposition values, it was decided to run control experiments on fine powders of quartz, kaolinite and bentonite without ignition before the boiling. It was supposed that the catalytic effect would be greater if the minerals were not heated above the temperature of lattice-breakdown. 25 ml, of the oxidizing mixture were boiled for I hour with 0, 1, 2, 3, and 4 gm. of quartz, kaolinite and bentonite in turn and the remaining oxidation equivalents determined by means of titration in the usual manner. The result is shown in Fig. 7, where the percentage destruction of the oxidizing mixture is plotted against the amount of mineral powder. The destructive effect is seen to be an almost rectilinear function of the powder weight, most pronounced for bentonite and kaolinite but perceptible even for quartz. But it is quite clear that the decomposition when boiling with a few grams of coarse grained quartz sand is not very much more than when none is added.

The fourth curve in Fig. 7 is a purely hypothetical correction curve based on the assumption that the clay material in the standard samples would cause a catalytic decomposition of the oxidizing mixture to a degree somewhere between



Fig. 7. Reducing effect of three mineral powders upon the oxidizing mixture in the Tinsley method and a hypothetical correction curve.

that caused by bentonite and kaolinite. If the results of the analyses given in Table 6 are recalculated in accordance with this hypothetical correction curve, the apparent recovery values are reduced as shown in Table 7.

Standard sample No.	Recovery (uncorr.) per cent	Recovery (corr.) per cent
I II III IV V VI	$     119 \\     127 \\     119 \\     137 \\     144 \\     139     $	90 107 115 118 135 100
Mean value	131	111

 Table 7. Recovery values if corrected for catalytic decomposition

 of the oxidizing mixture.

It is not asserted that this correction is justified. It is very uncertain for several reasons. Corrections obtained from the curve in Fig. 7 are probably too high, as the clay sample does not consist exclusively of catalytically active clay minerals, but the total correction, including also the chemical reducing effects mentioned in § 5 d, would possibly be even higher. The intention of Fig. 7 and Table 7 is merely to draw attention to the influence of the sample weight on the oxidizing mixture. It is of special importance to take account of this influence if the analytical procedure is such that the sample weights are chosen to give the same weight of organic carbon even when the carbon contents vary.

Finally it can be said that the likelihood of errors in this method when used in the determination of carbon in clay sediments with low carbon contents is much greater than for carbon-rich soils.

#### 7 c. A Rapid Wet Combustion Method

Two wet combustion methods hitherto used in determination of soil organic matter have been reviewed in § 4 e. Both methods are gravimetric. Methods have also been developed in which the carbon dioxide formed during the boiling is measured manometrically or volumetrically. *Manometry*, see for example van SLYKE and FOLCH (1940), gives good results, but the complexity of the method is a serious disadvantage. *Gravimetric* determination of carbon dioxide by means of quantitative isolation of precipitated barium carbonate involves difficulties if the amount of precipitate is small. Some volumetric methods have the disadvantage that the liquid in the carbon dioxide absorption flask has to be transferred to a special titration vessel. The earbon dioxide is generally transported to the absorption vessel by means of a stream of air, but this can be avoided by evacuating the whole apparatus before the boiling and allowing the carbon dioxide to be transferred to the absorption liquid by diffnsion.

An apparatus of the last-mentioned type has been designed by THORN and SHU (1951) for biochemical purposes and is shown in Fig. 8.

In this method the combustion fluid is prepared from chromium trioxide, syrupy phosphoric acid and fnming sulphuric acid. (For details, see THORN and SHU, 1951.) The joints E, F and G and the stopcock Q are lubricated with ordinary stopcock grease. The moisture and carbon dioxide trap D seems to be dispensable and can be substituted by a wad of cotton. The trap M is filled with zinc turnings and granulated potassinm iodide.

Thorn and Shu used sodium hydroxide solution as the absorption fluid and added barium chloride before the titratiou. In the experiments described below the absorption fluid is barium hydroxide.

*Procedure:* 0.2 to 1.5 gm. of the sample are weighed out, put into the combustion flask and mixed with 0.3 gm. of potassium iodate. 25 ml. of 0.1 N. barium hydroxide are then pipetted into the absorption flask. The apparatus is assembled, the stopcock P is closed, the stopcock Q is opened and the apparatus is evacuated through the tube C by means of a water pump. When vacuum is attained



Fig. 8. Wet combustion apparatus according to Thorn and Shu.

#### Lcgend

A. Combustion flask (30 ml.). B. Combustion fluid reservoir (25 ml.). C. Evacuation tube. D. Moisture and carbon dioxide trap. E-K. Ground joints. L. Thermometer. M. Acid and iodine trap. N. Carbon dioxide absorption flask (125 ml.). O. Magnetic stirrer. P-Q. Stop-cocks.

the stopcock Q is closed and the combustion fluid is allowed to enter the combustion flask, care being taken to exclude air. The magnetic stirrer is started and the bottom of the combustion flask is heated by means of a microburner. When after 10 to 15 minutes the temperature reaches 210° C, the burner is extinguished and a period of at least 10 minutes is allowed for absorption of carbon dioxide by the stirred barium hydroxide. The vacuum is then released, the stirring stopped and the excess hydroxide titrated with 0.1 N. hydrochloric acid using phenolphtalein as indicator.

The titration result is used for computation of the total carbon content of the sample. For determination of inorganic carbon the same apparatus can be used. The sample is then not mixed with iodate and the combustion fluid is replaced by 15 per cent sulphuric acid. If the amount of carbonate is considerable the acid must be admitted very carefully to avoid too strong a foaming. Acid is added until the gas development ceases and the mixture of clay powder and acid is heated for a short while. After a diffusion period of 10 to 15 minutes the titration is performed in the same manner as before. The organic carbon content is the difference between the total and the inorganic carbon content.

*Results:* In Table 8 are quoted the total carbon content values found by means of the procedure just described in analyses of the six standard samples mentioned in Table 4. The total carbon content values are compared with those found by dry combustion and the recoveries in per cent are computed.

Standard sample No.	Total carbon content found by dry combustion per cent of dry weight	Total carbon content found by wei combustion per cent of dry weight	Standard deviation per cent	Recovery per cent of dry combustion value
Ι	0.49	0.40	0.01	82
II	1.91	1.82	0.02	95
пі	10.02	9.91		99
IV	1.45	1,21	0.08	83
v	3.22	3.85	0.04	103
VI	1.48	1.32	0.03	89
	92			

 Table 8. Total carbon content of standard samples by means
 of the Thorn-Shu wet combustion method.

For sample III no standard deviation is computed since the carbon content value is a mean of only two analysis results. In total 31 analyses were made. As may be seen from the standard deviations, the variations of the individual results were not great for each type of sample.

#### 7 d. Discussion of Results

Almost all the methods for determination of soil organic matter have been developed for agricultural purposes. Difficulties arise when trying to apply these methods to clay soils with low amounts of organic matter, and there is a real need for a method accurate enough for the correct classification of a soil sample for geotechnical purposes. The several methods now in use, as for example the "loss-on-ignition" method, are more truly qualitative than quantitative. For reasons mentioned in § 3 c this method cannot be recommended.

The hydrogen peroxide method is rather time-consuming and has the disadvantages already discussed in § 3 b. The modification of the peroxide method by combination with ignition has not given good results, as shown in § 7 a.

The "rapid titration methods" may be of some value for certain purposes if

the risks of incomplete oxidation and the sensitivity of these methods to small alterations in test procedure are realized.

The modification of the dichromate-reducing method, here described as the Tinsley method, seems to be accompanied by some complications. In a letter to the present author Dr. Tinsley has stated that a dichromate solution with 40 per cent sulphuric and 20 per cent phosphoric acid and no perchloric acid has been convenient for routine purposes and that this oxidizing mixture does not give too high recoveries when manganese oxides are present in the sample. The question of the high results obtained with fine grained materials withont any organic carbon is not fully solved. Dr. Tinsley agrees with the present author in concluding that the sources of error in applying the method to clay sediments with low carbon contents are probably much greater than when using it with soils.

It is beyond all doubt that the dry combustion method is the most accurate method available for determination of the total carbon content. It seems necessary for each laboratory working on the determination of organic matter to have access to a dry combustion apparatus, at least for the standardization of other methods.

The wet combustion method of Thorn and Shu appears to be rather more convenient than dry combustion for routine tests. The apparatus is simple and inexpensive and one person can run 2 to 3 determinatious almost at the same time. The recovery of carbon is good and is a measure of the "degree of humification" of the organic parts of the sample. The method of using diffusion instead of an air stream for the transport of the carbon dioxide from the reaction vessel to the absorbent is a great advantage and contributes much to the simplicity of the apparatus. It seems possible to modify the apparatus somewhat in order to improve its mechanical strength.

#### Summary

As an introduction an outline is given of the complexity of the chemical constitution of soil organic matter. Attention is drawn to the different stages of destruction of the organic material, starting with fresh waste products of vegetable and animal origin and ending with real humus substances of varying composition.

Of the large number of methods developed by agricultural chemists some typical methods are briefly reviewed. Both direct and indirect methods are described and critically examined, especially with regard to the difficulties in determining relatively small amounts of organic matter in clays and other fine-grained soils. Special difficulties arise from the interference of some inorganic soil constituents and from the catalytical effect of the small mineral particles themselves.

In the experimental part of the paper are given the results of testing one direct, and two indirect methods, on their usefulness for geotechnical purposes. The necessity is shown of observing the catalytical effects of the clay minerals on the chemical agents used in the analysis. A method developed by two biochemists for the determination of the carbon content of organic compounds is introduced as being a useful method also in soil chemistry.

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#### Meddelanden

No.	1.	Kortfattat kompendium i geoteknik 1946 (utgånget)	1946
	2.	Redogörelse för Statens geotekniska instituts verksamhet under åren 1944—1948	1949
	3.	»Bra borrat — bättre byggt». Meddelande utgivet till institutets deltagande i utställningen »Bygg bättre», Nordisk Byggnadsdag V	1950