A GUIDE

TO THE

Scientific Examination of Soils:

Comprising

Select Methods of Mechanical and Chemical Analysis and Physical Investigation.

Translated from the German of

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With additions by

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PREFACE.

This translation of Dr. Felix Wahnschaffe's *Anleitung zur wissenschaftlichen Bodenuntersuchung*, has been prepared in the belief that it will prove of interest to those engaged in scientific agriculture and the investigation of agricultural problems.

Some of the methods of analysis described are in use in the laboratory of the Royal Prussian Geological Institute, whilst others have been taken from approved text-books, but in many respects modified by Dr. Wahnschaffe. Only methods yielding scientifically useful results, and of comparatively easy and rapid execution, have been selected.
PREFACE.

The chapter on "The Definition of the Soil," being of interest only to German readers, has been omitted, and a few trifling changes and additions have been made.

WILLIAM T. BRANNT.

Philadelphia, December, 1891.
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THE EXAMINATION OF SOILS.

I.

DERIVATION AND FORMATION OF THE SOIL.

The superficial formation of the earth's crust, which serves as the bearer and nourisher of plants, is effected either by the loosening and decomposition of the exposed rocks, or by the transport of coarse and fine materials worn from other rocks, or, finally, by the transformation into humus of decayed vegetable remains piled up in large masses.

The forces active in the first-mentioned mode of soil-formation are partially of a physical and partially of a chemical nature. Their co-operation is called weathering, and will have to be considered somewhat more closely. First of all, it is heat which, by itself as well as in conjunction with water, prepares the rock for the further disintegrating process. In consequence of changes in temperature small cracks and fissures are gradually formed in the rock by the unequal expansion and contraction of the different minerals occurring in it. When it rains the water flows down through all these cracks and lodges in countless minute fissures in the face of the rock. After a heavy rain, when the rock is filled with water, it may clear away and a sharp frost set in.
Every drop of water freezes and expands and bursts open the rock, splitting off minute specks and scales or throwing down great lumps. In the summer there is no frost, and yet the rain may be at work washing moss and dust into the cracks already opened and forming a sponge ready to hold water that, freezing next winter, will act with still greater force. The dry dust sifted into the cracks and openings in the rock will also expand when wet and push off small pieces, or start a great mass that last winter's ice left just ready to fall. These disintegrating agencies are still further aided by the root-growth of plants, by the burrowing of worms and other earth-delving creatures, and in no small degree by the generation of organic acids—humic, crenic, etc.—by organic decay.

Furthermore, rocks containing decomposable minerals undergo a chemical process of transformation in which the oxygen of the atmospheric air and water, as well as the carbonic acid dissolved in the latter, are the chief agents. The oxygen converts the metallic protoxides in the rocks into oxides, and, since water is almost always present, into hydroxides. Ferrous oxide combined with silica is in this manner changed to ferric hydrate. By this process the texture of minerals containing ferrous silicate—as, for instance, many feldspars, certain micas, hornblende, and augite (pyroxene)—is loosened. Rocks distinguished by the occurrence in them of metallic sulphides, to which among the sedimentary rocks chiefly belong the clay-slates, bituminous marls, and clays, are decomposed by the conversion of their metallic sulphides, on coming in contact with moist air, into sulphates or vitriols. By the lixiviation of the latter by water, the
rock becomes porous and cellular, and finally breaks up into fragments.

The process of *kaolinization* is due to the action of waters containing carbonic acid upon silicious rocks rich in alkalies (potash and soda) and alkaline earths (calcareous earth, magnesia). By such waters, which acquire their carbonic acid, partially from the atmosphere, and partially from the organisms decaying upon the surface, the alkalies and alkaline earths are converted into carbonates and bicarbonates, while silica is separated. The carbonates and bicarbonates are soluble in water, and, together with the separated gelatinous silica, are carried away by the water, while a silicate of aluminium containing water—the kaolin—remains behind. For this theory of the formation of kaolin we are indebted to Forchhammer. It takes place, for instance, in orthoclase, which consists of one molecule potash, one molecule alumina, and six molecules silica, by the separation of four atoms silica and one atom potash, while the remaining alumina combines with two molecules silica and two molecules water to kaolin and clay.

*Denudation of the soil.*—The rain falling on the wasting rocks sweeps away the minute specks and grains chipped off by the weather and carries them down to the nearest streamlet and brook. These fine bits of rock do not float, but are suspended in the water or roll along the bed of the stream. The ragged flakes and scales of stone crash and grind against each other. Every rough corner is knocked off, and all the pieces become rolled into smooth round particles. The brook is a mill. It is making, from the chips brought down by the rain, sand. A flood comes with more water, and larger pieces
of rock are pushed into the rapidly moving water, and these knocking, tumbling, and grinding over each other, are soon ground into smooth round pebbles and gravel. Onward rolls the confused mass of gravel, sand, and finer bits of rocks, grinding and polishing each piece as it goes. In time the stream comes to more level ground and runs slower and slower. The current, not being able to push the larger stones any further, leaves them all by themselves. Thus the transported matter is gradually deposited as the current diminishes in velocity, the very finest particles being carried as long as the stream remains in motion. When the river reaches a flat or level tract, and over which its waters can flow in flood with a slow motion, the suspended matter, consisting principally of sand and mud, is deposited and constitutes the alluvium or new land, formed by such deposits at the river's mouth and along its banks. Though the soil is thus continuously washed away, still it remains nearly constant in quantity, since what is taken away by denudation is made up from other causes, and this augmentation can evidently proceed from nothing but the slow and constant disintegration of the rocks.

The rocks which weather most easily and rapidly do not always exhibit most soil; very often the reverse. A pure limestone would show hardly any weathered band or soil, because the carbonic acid of the rain would almost at once dissolve and remove the particles it acts upon. Even in the case of igneous rocks, their composition may be such that those which weather the most rapidly would, likewise, show little of a weathered band, owing to the same solvent action.
II.

CLASSIFICATION OF SOILS.

In conformity with Lorenz von Liburnau's system, soils may preferably be divided, according to their formation, into two large principal groups, viz., *primitive* soils and *derived* soils. Primitive or original soils may be called such as have been directly formed by the weathering of exposed rocks, or, like peat, by the decomposition of vegetable remains in their original place of location. According to the original structure, a distinction has to be made between primitive soils of the crystalline and of the sedimentary rocks, as well as of the peat formations. Derived soils (deposited or transported soils) are such as have been transported either in a solid or liquid form by water, or, also, by the wind.

For the further classification of soils it is preferable to make use of the physical system of soil classification proposed by Albrecht Thaer, the founder of scientific agriculture. He distinguishes the varieties of soil according to the predominance in them of the admixed parts of what may be called the principal soil constituents. From this result the following groups of soils: 1. Stony soils. 2. Sand soils. 3. Loam soils. 4. Clay soils. 5. Marl soils. 6. Lime soils. 7. Humus soils.

The same experience met everywhere in nature that sharp limits cannot be drawn in the classification of animate, as well as inanimate bodies, shows itself in the
division of soils, the above-mentioned groups exhibiting very gradual transitions into each other, and even, like the clay and marl soils, are already partially transition formations.

A single principal constituent, be it sand, clay, lime, or humus, cannot afford to cultivated plants an adequately fertile soil; the more uniformly all the constituents participate in the composition of the soil, the greater its value and yield will be. Hence, the quantitative determination of the principal constituents is an important task of scientific soil-analysis, since, on their proportions to each other, the value of the soil for cultivation depends. As is well known by a greater or smaller content of clay, a sand-soil gains essentially in the power of holding water and in absorbent capacity. But the physical properties of a clay-soil are also improved by a content of sand, it becoming thereby more friable, more permeable, and more easy to cultivate. Of still greater importance to agriculture is a lime soil combined with sand and clay—hence, the more it approaches a marl soil—while an extreme humus soil (peat) first requires special meliorations to make it fit for cultivation.

It is not to be understood that in naming the varieties of soils after the principal constituent, the admixed part reaching the highest number of per cent. furnishes the name, this being the case only with sand and lime soils. On the contrary, it is rather the physically most important admixed part, which has to be considered as the guide in this respect, even if it is not represented by a relatively high number of per cent. in the composition of the soil. Thus clay is the most important soil constituent so long as its physical properties are not covered or invalidated by
another admixed part. If, for instance, this is done by sand, a soil when no longer plastic, but only binding, has to be classed among the loam soils. With a still greater content of sand, the soil also loses its binding power, and we have then a sandy loam or a loamy sand.

Loams which may be considered as typical soils are a mixture of sand, clay, and humus, which are spoken of as light when the sand predominates, and as heavy when the clay is in excess. These terms, light and heavy, do not refer to the actual weight of the soil, but to its tenacity and the degree of resistance it offers to the implements used in cultivation. Sandy soils are, in the farmer's sense of the word, the lightest of all soils, because they are the easiest to work, whilst in actual weight they are the heaviest soils known. Clay, though hard to work on account of its tenacity, is comparatively a light soil in weight. Peaty soils are light in both senses of the word, they being loose or porous and having little actual weight.

Besides the soils proper which come immediately under cultivation, there are in most places a set of subsoils which differ from the true soils, and which cannot be ignored. The true soils, or, as they are sometimes called, the top soils, are usually of a darker color from the larger admixture of humus, whilst the subsoils are lighter in hue, yellow, red or bluish from the greater preponderance of the iron oxides. The soils are more or less friable in their texture, whilst the subsoils are tougher, more compact, and more largely commingled with rubbish and stone. The soils are usually a little more than mere surface coverings, whilst the subsoils may be many feet in thickness.
III.

THE OBJECT OF SOIL-ANALYSIS.

In the analysis of soils we may be guided by geological or agricultural considerations.

From a purely geological standpoint, the determination of the petrographic composition of the soil, as well as that of its relations to the mother rock—the weathering process—will chiefly be of interest. But, since the soil is of importance principally in an agricultural respect, it is also the object of most of the analyses of it to solve scientific and practical questions relating to agriculture as well as to a knowledge of the soil, and though the latter is an agronomic science, it must rest upon a geologico-petrographic basis.

Those times in which the soil was simply considered the bearer, but not the nourisher of plants, and when it was believed that only its physical properties exerted an influence upon vegetation, have long since passed. Today it is well known that, though the production of plants is materially influenced by these physical properties, it does not exclusively depend upon it.

One of its principal constituents—carbon—the plant absorbs directly from the atmospheric air, whilst all the remaining substances required for its nourishment and development, it obtains, partially directly and partially indirectly, from the soil. Since soil-analysis has for its object the determination of the nourishing matters of the
plant, the elementary substances of the latter shall be briefly discussed.

All the living parts of plants contain a large quantity of water, which not only forms a principal constituent of the juice, but also saturates all membranes and the protoplasm. In the substance of all organized vegetable structures small particles of water are stored. This water, which is absolutely necessary for vegetation, escapes on heating the parts of plants for some time to from 212° to 230° F. The content of water, which is to be calculated from the decrease in weight, varies very much in the different parts of plants, it amounting, for instance, in dry seeds to from 12 to 15 per cent., in juicy plants to from 60 to 80 per cent., and in aquatic plants and fungi up to 95 per cent. The plant obtains the water directly from the soil, since on account of its capillary structure it possesses, similar to a sponge, the capacity of absorbing and retaining, to a more or less degree, the water offered to it.

In the parts of plants dried at 230° F. a large number of chemical combinations are found, of which those representing chemical unions of carbon with other elements are designated as organic combinations. By incineration the organic combinations are destroyed, while the inorganic combinations of the plant substance remain behind as a white ash. It may here be mentioned that in the incineration of the plants, the sulphur, which forms a constituent of the organic combinations, also reaches, by chemical processes, the ash in which it is found as sulphate. Furthermore, the carbonic acid formed during incineration and which combines with the inorganic substances of the residue, must also be left out of con-
sideration in analyzing the ash. The organic combinations occurring in larger quantities in plants consist of carbon and hydrogen, or of carbon, hydrogen, and oxygen, or of carbon, hydrogen, nitrogen, and sulphur.

By experiments it has been determined that certain inorganic substances are not accidentally admixed parts of the plant, but are absolutely necessary for its life and growth, and consequently for the formation of the above-mentioned organic combinations.

The elements which are necessary for the nourishment of the plants may, according to their uses, be divided as follows:

*Elements for the formation of the organic combinations.*—Carbon, hydrogen, oxygen, nitrogen, sulphur, and

*Elements for the formation of the inorganic combinations.*—Phosphorus, chlorine, potassium, calcium, magnesium, and iron.

Besides these, some other elements are occasionally found in the plant-ash, as, for instance, sodium, lithium, manganese, silicium, iodine, bromine, and, very seldom, aluminium, copper, zinc, nickel, barium; but are of no importance in the nourishment of the plants.

From the above it follows, that in examining the soil as to its content of plant-nourishing substances, the eight following elements, independent of oxygen and hydrogen, have to be taken into consideration, namely: nitrogen, sulphur, phosphorus, chlorine, potassium, calcium, magnesium, and iron.

Since, as previously indicated, the thriving of the plant depends not only on the chemical composition of the soil, but also, in a high degree, on its mechanical mixture
and physical properties, a soil analysis which is to satisfy all demands of agriculture has to be executed as follows:

1. The *mechanical mixture* of the soil must be quantitatively determined. This examination may be designated *mechanical soil analysis*.

2. The *soil-constituents*, sand, clay, humus, lime, have to be quantitatively determined. This is partially affected by the mechanical analysis and partially by chemical methods of analysis executed on the one hand, independent of the mechanical analysis, and on the other, in connection with it.

3. The content of *plant-nourishing substances in the soil* has to be determined by chemical analysis.

4. The *substances injurious to the vegetable world* must be taken into consideration.

5. Experiments have to be made to gain direct information in regard to *certain properties of the soil*, which depend partially on physical and partially on chemical causes.

Such complete examinations are of great importance for judging the soil, but it must be borne in mind that by them alone its value cannot be determined. The greater or inferior fertility of a soil depends not only on its mechanical and chemical composition, but also on various conditions outside of them; for instance, the more or less inclined, as well as the higher or lower location of the soil, the condition of the subsoil, the underground water, exposure to the sun, climate, etc.
IV.

PREPARATORY LABORS FOR SOIL-ANALYSIS.

Before entering upon the methods of analysis it will be necessary to discuss the labors which must precede them. They consist in taking samples from the soil and storing and preparing them for analysis.

In the same field different varieties of soil often occur, and some recommend that in collecting a specimen for analysis, portions should be taken from different parts of the field and mixed together, by which an average quality of soil would be obtained. But this is bad advice when the soils in different parts of the field are really unlike. Suppose one part of a field to be clay and another sandy, as is often the case in most countries, and that an average mixture of the two varieties of soil is submitted to the analysis; the result obtained will apply neither to the one part of the field nor to the other, that is, it will be of little or no practical value. In taking samples it is, therefore, recommended not to select mixed average samples, but characteristic separate samples.

After selecting a proper spot, pull up the plants growing on it and scrape off the surface lightly with a sharp tool, to remove half-decayed vegetable matter not, as yet, forming part of the soil. Dig a vertical hole, like a post-hole, at least twenty inches deep. Scrape the sides clean, so as to see at what depth the change of tint occurs which marks the downward limit of the surface soil and record it. Take at least half a bushel of the
earth above this limit, and, on a cloth or paper, break it up and mix it thoroughly, and put up at least a quart of it in a sack or package for examination. This specimen will ordinarily constitute the "soil." Should the change of color occur at a less depth than six inches, the fact should be noted, but the specimen taken to that depth nevertheless, since it is the least to which rational culture can be supposed to reach.

In case the difference in the character of a shallow surface soil and its subsoil should be unusually great, as may be the case in tule or other alluvial lands or in rocky districts, a separate sample of that surface soil should be taken besides the one to the depth of six inches.

Specimens of salty or "alkali" soils should, as a rule, be taken only toward the end of the dry season, when they will contain the maximum amount of the injurious ingredients which it may be necessary to neutralize.

Whatever lies beneath the line of change, or below the minimum depth of six inches, will constitute the subsoil. But, should the change of color occur at a greater depth than twelve inches, the "soil" specimen should, nevertheless, be taken to the depth of twelve inches only, which is the limit of ordinary tillage; then another specimen from that depth down to the line of change, and the subsoil specimens beneath that line. The depth down to which the last should be taken will depend on circumstances. It is always desirable to know what constitutes the foundation of a soil down to the depth of three feet at least, since the question of drainage, resistance to draught, etc., will depend essentially upon the nature of the substratum. But in ordinary cases ten or twelve inches of subsoil will be sufficient for the purpose
of examination in the laboratory. The specimen should be taken in other respects precisely like that of the surface soil, while that of the material underlying this "subsoil" may be taken with less correctness, perhaps at some ditch or other easily accessible point, and should not be broken up like the other specimens.*

At the same time when taking samples, the general condition of the soil should be noted and accurate information gained chiefly in regard to the following points:—

1. The geological origin and petrographic nature of the soil.
2. The relations of the foundation of the soil to a depth of six feet if possible.
3. The thickness of the surface soil.
4. The location of the soil above the level of the sea.
5. The inclination of the soil.
6. The height of the underground water.
7. The climatic conditions of the region.
8. The judgment of a practical agriculturist residing in the neighborhood in regard to the quality and yielding capacity of the soil.
9. The manner and quantity of manuring the soil has received in the preceding years.
10. The meliorations (marling, draining, irrigation, etc.) which may have been made.
11. The lowest yields and rotation of crops.

In fact, every circumstance that can throw light on the agricultural qualities or peculiarities of soil and subsoil should be carefully noted.

It is recommended to immediately label each sample.

In summer, the sample is allowed to dry out slowly in the air, and in winter, in a moderately warm room until it shows a quite equal and constant weight. In this condition it is called air-dry soil. If the sample has to be kept any length of time, it is recommended to store it in wide-mouthed glass bottles hermetically closed, as otherwise it might undergo changes in the laboratory where vapors of ammonia and acids cannot always be avoided. Clayey and humus varieties of soils possess the property of absorbing ammoniacal vapors, and, hence, if the sample has for a long time remained unprotected in the laboratory, the analysis would show too high a content of nitrogen.

V.

MECHANICAL SOIL-ANALYSIS.

The object of mechanical soil-analysis is the quantitative determination of the proportional quantities of coarser and finer constituents composing the soil. To attain such a mechanical separation of the soil two mediums are employed—granulating with the sieve, and elutriating with water or silt analysis.

A. Granulating with the sieve.—For the examination of soils with coarser constituents, granulation with the sieve should always precede silt-analysis, since such soils cannot be well brought into the elutriating apparatus, and, even if this were possible, would clog it. Sieves
with round holes are to be preferred to square-meshed sieves, they permitting more accurate measurements.

In order to sufficiently characterize the mechanical composition of a soil, and to compare it with other varieties, the soil is divided into the following products:

1. Grains larger than 2 millimeters in diameter.
2. " from 2 to 1 " " "
3. " 1 to 0.5 " " "
4. " 0.5 to 0.2 " " "
5. " 0.2 to 0.1 " " "
6. " 0.1 to 0.05 " " "
7. " 0.05 to 0.01 " " "
8. " smaller than 0.01 " " "

The sizes of grains Nos. 1 to 3, i.e., to 0.5 millimeters in diameter, are obtained by sifting through sieves with holes 2, 1, and 0.5 millimeters in diameter; all other products of granulation are separated, as will be shown later on by silt analysis.

For the execution of the mechanical analysis, spread the air-dry soil out upon a sheet of paper or in a shallow dish, and, after finely dividing it by rubbing between the hands, or by means of a wooden pestle in a mortar, weigh out a good average sample of 500 to 100 grammes. For weighing all the products of granulation obtained by sifting and elutriating, as well as for the physical experiments, an accurate balance must, of course, be used. The quantity weighed out for granulation is then passed, in a dry state, through the 2-millimeter sieve.

Since the entire sample of soil has been weighed, it is only necessary to weigh the residue remaining in the 2-millimeter sieve. The quantity of soil which has passed through the sieve is then learned from the difference
resulting by deducting the product of granulation of over 2 millimeters from the total weight. With loamy soils the product of granulation of over 2 millimeters must always, before weighing, be rinsed off with distilled water to free it from adhering sand and loam, then dried at 212° F. upon the sand-bath, and weighed only when entirely cold.

The soil which has passed through the 2-millimeter sieve will be designated as fine soil. It forms the initial material to be employed in the silt analysis as well as in the chemical investigations in the execution of which products of elutriation are not to be used.

Emil Wolff and Schoene designate as fine earth the soil which has passed through a 3-millimeter sieve. Knop's conception is a still different one. He calls fine earth the soil which has passed through a ¼-millimeter sieve, and fine soil the residue resulting from igniting the fine earth. M. Fesca applies the term fine soil to soil less than 4 millimeters in diameter.

From what has been said it will be seen that there is a great difference in the ideas of agricultural chemists as to what constitutes fine soil and fine earth, and yet it is absolutely necessary to establish a definite limit of value for them, since, if every analyst selects another initial substance, all possibility of comparing the analytical results must of course cease. We therefore adhere throughout to the term fine soil as a designation for soil less than 2 millimeters in diameter, and take it as the initial material for analysis, as has for a number of years been customary in the laboratory for soil analysis in the Royal Prussian Geological Institute.
The fine soil which has passed through the 2-millimeter sieve is thoroughly mixed and 30 to 100 grammes of it taken for silt analysis.

The residue remaining after the silt analysis, with an elutriating velocity of 25 millimeters, is dried and weighed and then further granulated by passing through sieves with holes 1 and 0.5 millimeter in diameter.

B. Silt analysis.—The object of silt analysis is to separate the fine soil obtained in the above-described manner into still finer products of granulation.

The principle adopted in the apparatus used for this purpose is either to separate the coarser from the finer particles by their different subsiding velocities in water at rest (decanting apparatus), or to effect separation by an ascending jet of water (rinsing or elutriating apparatus).

To the former class of apparatus belong: 1. Bennigsen's elutriating flask; 2. Knop's elutriating cylinder; and 3. Julius Kuehn's elutriating cylinder; and to the latter class the elutriating apparatuses of Noebel, Schoene, and Hilgard.

Of these apparatuses only Schoene's and Hilgard's yield sufficiently reliable results. However, as Noebel's apparatus is occasionally used, it shall also be briefly described.

1. Noebel's elutriating apparatus.—This apparatus, Fig. 1, consists of a water reservoir of 10 liters' capacity and four pear-shaped vessels, whose volumes are as $1 : 8 : 27 : 64 = 1^3 : 2^3 : 3^3 : 4^3$, and which are connected with each other by knee-shaped tubes. The last small vessel is connected with the water reservoir by
means of a rubber tube provided with a clip. The largest vessel in front is provided with a discharge tube, the point of which is drawn out, so that when the apparatus is filled with water 9 liters run out in

Fig. 1.

40 minutes. The water reservoir is provided with a gauge, A, so that elutriation may be carried on with a constant pressure by connecting the tube, a, with a water reservoir located at a higher level.

Fifty grammes of the soil to be elutriated (which, by agreement, is to be less than 1 millimeter in diameter) are prepared by boiling with water, and are then rinsed into the second smallest vessel, b, the smallest vessel being filled with water only. The two larger vessels are then filled to the brim with water, and after connecting the entire system by the connecting tubes the clip is opened and the water allowed to flow for 40
minutes through the apparatus. The following products of elutriation are obtained by this operation:

1. The residue in vessel II.
2. The residue in vessel III.
3. The residue in vessel IV.
4. The particles of soil elutriated from vessel IV.

By now evaporating the residues in vessels II., III., and IV. in small, weighed porcelain dishes and then weighing them, the finest elutriated parts are obtained from the difference.

Noebel's apparatus, with its four vessels of ever-varying capacity and slope of sides and variable head of pressure, has many defects. Not one of the sediments obtainable by its use is ever of a character approaching uniformity, and even in one and the same instrument successive analyses of one and the same material differ widely in their results.

2. Schoene's elutriating apparatus.—Like Noebel's, this also is a rinsing apparatus, a current of water regulated by a stop-cock and rising vertically in the elutriating space being also used. The water comes from a reservoir standing at a higher level.

Whilst in the elutriating process, by means of decantation, the gravity retarded by the fall in water is made use of in Schoene's as well as in Noebel's apparatus, an impelling force of the waters upwards, acting counter to the gravity, is employed. Hence, in Schoene's apparatus, by velocity of elutriation is understood the space through which a particle of soil is lifted in one second. The length of this space is dependent on the volume-content of the elutriating vessel, the cross-section and
specific gravity of the particle of soil, as well as on the velocity of the ascending current of water.

Schoene's elutriator, Fig. 2, consists of a glass vessel, the upper portion, $B$, of which must be perfectly cylindrical and at least 10 centimeters long, so that during elutriation an entirely uniform velocity of current prevails, at least, in the upper portion. Its clear diameter should be, according to Schoene, 5 centimeters, as accurately as possible. In order to accurately fix still smaller velocities, this diameter should not be less than 4 centimeters. The cylindrical portion is joined by the very gradually tapering portion $C$, which is 50 centimeters long. Below the portion $C$ passes into a tube $D E$ the clear diameter of which should, under no conditions, be more than 5 millimeters, and not less than 4 millimeters. This tube is bent semicircularly and extended upwards in a vertical direction. Above the cylindrical space the apparatus has a shoulder, and passes into the neck $A$, which serves for the reception of a perforated rubber cork. The neck is 2 centimeters long, with a diameter of 1.5 to 2 centimeters.

A piezometer, which serves as an indicator of the current velocity, is pushed through the rubber cork. It has a clear diameter of 3 millimeters, and, at a point 8 centimeters above its lower end, is bent twice in the form of
a knee at an angle of 45°. In the zenith of the second
bend is a circular discharge-aperture, the edges of which
should be as smooth as possible. From 1 to 10 centi-
meters the piezometer is graduated into millimeters, from
10 to 15 centimeters into half centimeters, and above
that into whole centimeters.

In order that the current of water, which is regulated
by a stop-cock, may remain as constant as possible, it is
necessary to use as a reservoir a capacious shallow box
of zinc with a capacity of 50 liters, in which the level
undergoes but little change during elutriation.

The arrangement shown in Fig. 3 is very suitable
for the elutriating process.

The table C serves for securing the elutriators, and is
71 centimeters high, 50 centimeters wide, and 85 cen-
timeters long. Its top consists of lath-work. The
elutriators are inserted between the laths and screwed
into the joints of a stand provided with a heavy cast-
iron plate. To render it more secure the plate of the
stand is by means of a binding screw fastened to the
table. The latter also carries a wooden frame, G, 140
centimeters high, which, on the top, is provided with
two shiftable coupling boxes for the support of the
piezometer tubes. The water reservoir F is provided
with a glass gauge and stands upon a board secured by
cramp irons. The inlet pipes E, screwed in the bottom
of the reservoir and provided with brass cocks, D,
are connected by means of rubber tubing with the
elutriators.

The elutriating velocity in the cylindrical space of
Schoene's elutriator (Fig. 2 B) with a determined head
of pressure is dependent on the cross section of the
Fig. 3.
cylinder and the size of the discharge aperture on the piezometer. Hence it is necessary first accurately to determine the diameter of the cylindrical elutriating space. For this purpose graduate the cylinder by pasting strips of paper on the outside. A plane laid through the upper edge of the two strips of paper should stand as perpendicular as possible to the axis of the cylinder; the distance of the two strips of paper from each other should be 10 centimeters. Now fill the entire cylinder with water, close the end of the tube $E$ with a cork, so that no air-bubbles remain therein, and let the lower meniscus of the water in the cylindrical space sit upon the upper edge of the uppermost strip of paper, whereby the axis of the cylinder should stand as perpendicular as possible. Now, by means of a pipette, remove the water from the cylinder to the upper edge of the lower strip of paper, and bring it into a measuring vessel graduated into cubic millimeters.

The content of a cylinder ($J$), as is well known, is equal to the product of the base ($r^2 \pi$) and the altitude ($h$).

$$J = r^2 \pi \cdot h$$

$$r = \sqrt{\frac{\pi h}{J}}$$

Now since the cross section of the cylindrical portion of the elutriator is known, the water is put at a determined height into the piezometer and a measuring flask, for instance, a liter, is allowed to run full, the number of seconds, $t$, required to fill the flask being noted
by a stop-watch. The quantity \( (Q) \) which flows out in a second is then:

\[
Q = \frac{x \text{ mm}^3}{t}
\]

The elutriating velocity is obtained by dividing the number of cubic-millimeters, which have not run out in one second, by the cross section of the cylinder in square millimeters \( (K) \):

\[
\frac{x \text{ mm}^3}{t} = \frac{Q}{K}
\]

If a definitely determined elutriating velocity is desired, commence first at a higher point of the piezometer, calculate the velocity from the quantity discharged in one second, and note whether it approaches the desired velocity or not. According to the result, commence the next experiment at a higher or lower mark of the piezometer.

With the use of very slight elutriating velocities, the thread of water does not appear at a fixed mark, only a dripping of the fluid taking place on the discharge aperture of the piezometer. In this case, the point to which the meniscus of the thread of water in the piezometer sinks in dripping off is taken as the mark, the number of drops running off in one minute being also counted. For calculating the quantity discharged in one second, it suffices to allow a measuring flask of 100 cubic-centimeters capacity to run full. By a few experiments, in which the water-level in the piezometer is so regulated that the mean between the two last determined
limits is always taken, the water-level corresponding to the elutriating velocity sought is readily obtained.

Instead of this empirical manner of finding a determined elutriating velocity, it can also be calculated by taking the piezometer graduated into centimeters as a basis.

According to the theoretical law of discharge, the quantities of discharge with one and the same piezometer, and hence, for one and the same discharge aperture, are as the square roots from the heads of pressure in the piezometer. If, now, the heads of pressure are indicated by \( h_I \) and \( h_{II} \), and the quantities of discharge in one second by \( 2_I \) and \( 2_{II} \), the result will be the equation:

\[
\frac{h_I}{h_{II}} = \frac{2_I^2}{2_{II}^2} \quad (\text{No. 1.})
\]

In the case in question the law of discharge has to be somewhat modified, as the water-level in the piezometer is influenced by the capillary attraction in the narrow tube of the piezometer, as well as by the resistance the water meets with in running from the narrow discharge aperture. Hence to eliminate these influences, a constant magnitude, \( C \), to be empirically determined for all heads of pressure of the same piezometer, must, according to Schoene's experiments, be deducted from the observed head of water \( h \). Thereby, equation No. 1 is modified as follows:

\[
\frac{h_I - C}{h_{II} - C} = \frac{2_I^2}{2_{II}^2} \quad (\text{No. 2.})
\]

For the determination of the constant magnitude, \( C \), it suffices to execute two experiments by once allowing a
liter to run full at as low a head of pressure (2 to 3 centimeters), and then at as high a head of pressure (80 to 100 centimeters) as possible, noting the number of seconds and calculating the quantity discharged in one second. By inserting the data obtained in formula No. 2, the following formula results:

\[ C = \frac{2_1^2 h_{11} - 2_{1I} h_1}{2_1^2 - 2_{1I}^2} \text{ centimeters (No. 3.)} \]

The constant magnitude \( C \) having thus been found, the corresponding quantities of discharge, \( Qn \), can be calculated for all desired heads of pressure, or, also, the corresponding heads of pressure for all desired quantities of discharge.

From formula No. 3 result:

\[ Qn = \sqrt{h_n - C} \cdot \frac{Q}{\sqrt{h - C}} \text{ cubic-centimeters (No. 4.)} \]

\[ h_n = Qn^2 \cdot h - C + C \text{ centimeters (No. 5.)} \]

Since the quantities of discharge in one second \( Q \), also flow in the same time through any cross section of the elutriating space whose diameter is \( D \), it follows that if \( v \) designates the elutriating velocity in one second:

\[ Q = v \cdot \frac{\pi}{4} D^2 \text{ centimeters (No. 6.)} \]

\[ v = Q \cdot \frac{4}{\pi D^2} \text{ centimeters (No. 7.)} \]

Hence when the constant magnitude \( C \) has been determined by experiments and the velocity \( v \), in the elutriating space at a determined head of pressure \( h \) is
known, it can be readily calculated what head of water, $hn$, has to be used, in order to obtain the velocity, $vn$, sought. It is only necessary in this case to insert the value for $Q$ from formula No. 6, and the corresponding value for $Qn = vn \frac{\pi}{4} D^2$ in formula No. 5, whereby is obtained

$$hn = \left( \frac{vn \frac{\pi}{4} D^2}{\pi} \right)^2 \frac{h - C + C}{v} = v \frac{2}{n} \frac{h - C}{v^2} + C$$

(No. 8.)

With an approximately equal specific gravity and globular form of the material determined sizes of grains correspond to determined velocities. By experiments, Schoene has determined that with quartz sand in globular form and elutriating velocities of from 0.1 to 12 millimeters per second, the following relation exists between the diameter of the grains $d$ and the elutriating velocity $v$:

$$d = 0.0314 v \frac{7}{11} \text{ millimeters.}$$

From his calculations, controlled by microscopical measurements, it follows that starting from quartz in globular form, the annexed products of granulation correspond to the following elutriating velocities:

- 0.2 millimeter of elutriating velocity = grain less than 0.01 millim.
- 2.0 millimeters " " " = " from 0.05 to 0.01 "
- 7.0 " " " = " 0.1 to 0.05 "

Since, on account of the narrowness of the discharge aperture in the piezometer, a velocity of 7 millimeters can only be obtained by the introduction of a second
piezometer with a wider discharge aperture, Orth has proposed the insertion of a small auxiliary cylinder 2.5 centimeters in diameter. Its cylindrical portion should be 50 centimeters long, so that it can also be used for a velocity of 25 millimeters.

Since the production of an accurate sieve with holes 0.2 millimeter in diameter is very difficult and expensive, and the sifting of the soil through such a sieve does not yield good results on account of the holes readily clogging up, Laufer’s proposition to obtain the size of grains from 0.2 to 0.1 millimeter by elutriation may be recommended. For this purpose Orth’s auxiliary cylinder is used; a piezometer about 5 millimeters in diameter and with a discharge aperture of from 3 to 3.5 millimeters being placed upon it. The cross-section of the cylinder is determined in the previously described manner, and, in order to find the velocity of 25 millimeters which corresponds to the size of grains 0.2 to 0.1 millimeters in diameter, the quantities discharged at different marks of the piezometer are measured. When the desired velocities in the various elutriators have been determined, a table is made according to the following scheme, which is used for all analyses to be executed with the apparatus:
For the execution of an analysis, the air-dried fine soil passed through the 2-millimeter sieve is used. Spread the soil upon a sheet of paper and weigh out an average sample of exactly 100 grammes. Of very uniformly and finely divided soils, 30 to 40 grammes suffice for the analysis.

Bring the quantity of soil, weighed out, into a porcelain or enameled iron dish, pour distilled water over it and boil it, with constant stirring with a glass rod, until the clayey constituents are entirely dissolved. With tenacious clay soils, small nodules of clay frequently remain behind which do not dissolve even with continued boiling; and it is best to crush them with the index-finger, which for the purpose should be protected with a thick rubber coating. The material thus prepared is permitted to become cold, when, without stirring up the sediment, the supernatant turbid fluid is poured into the large elutriator of the apparatus. Now, by opening the stop-

<table>
<thead>
<tr>
<th>Large elutriator.</th>
<th>Small elutriator.</th>
</tr>
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<tbody>
<tr>
<td>Diameter : mm.</td>
<td>Diameter : mm.</td>
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<tr>
<td>Cross section : mm².</td>
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<tr>
<td>Head of water in the narrow piezometer, cm.</td>
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<tr>
<td>Velocity in one second.</td>
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<tr>
<td>0.2 mm.</td>
<td>7.0 mm.</td>
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<tr>
<td>2.0 mm.</td>
<td></td>
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<tr>
<td>Head of water in the wide piezometer, cm.</td>
<td>25.0 mm.</td>
</tr>
</tbody>
</table>
cock, fill the small elutriator before connecting it with the larger elutriator, with water up to above the semicircular lower bend. The purpose of this is, on the one hand, to prevent the apparatus from becoming clogged, when introducing the soil, by the latter ascending in the narrow tube, and, on the other, to avoid mistakes in the commencement of the elutriating process by ascending air bubbles. For the introduction of the soil into the small elutriator, it is best to place upon the latter a wide-mouthed funnel and inject the material with the assistance of a wash bottle. Detach any adhering particles by means of a glass rod, the lower end of which is covered with a piece of rubber tubing.

If it is intended to make further chemical investigations with the products of elutriation at 0.2 and 2 millimeters velocity, the soil has to be elutriated with distilled water. This is necessary, because in gaining the product of elutriation at 0.2 millimeter velocity, the elutriating water has to be evaporated, and, by the use of ordinary water, too many impurities would be introduced into the material under investigation. The product of elutriation at 0.2 millimeter velocity can only be elutriated with ordinary water, if it is not to be weighed, but to be calculated from the loss.

For elutriation with distilled water it is best to use the apparatus shown in Fig. 4. A glass tube, \(d\), reaching to the bottom of a glass balloon, \(A\), filled with distilled water, connects with a glass flask, \(B\), of about 10 liters capacity. Near the top of the tube \(d\) is inserted a glass tube provided with the glass stop-cock, \(a\). The rubber cork of the flask \(B\) is provided with two other perforations, in one of which is inserted, even with the under
side of the cork, the knee-shaped glass tube \( g \), which is connected by means of a rubber tube with the lead tube \( e \). The latter is connected with a small water air-pump so that a rarefied space can be created in \( B \). Through the third perforation in the rubber cork passes a siphon, \( h \), reaching to the bottom of the flask, the long leg of which is provided below with a glass stop-cock, \( b \). This

Fig. 4.

siphon \( h \) passes into one of the tubulures of the glass flask \( C \) standing at a lower level, while the other tubulure serves for the reception of the water-gauge \( D \), through the bottom of which passes the tube \( e \), which effects the constant level of the water. On each side, near the bottom, the gauge \( D \) is provided with a tubulure, one serv-
ing to connect the gauge with the flask $C$, while the other, by means of a rubber tube and an inserted tube provided with a glass stop-cock, $f$, communicates with the two elutriators. When the flask $B$ is to be filled, the stop-cocks $a$ and $b$ are closed, and after putting the air-pump in action, it is connected with the tube $c$. In consequence of this a rarefied space is formed in $B$, and the water will ascend from the balloon through the tube $d$ and fill $B$. Now, in order to have a constant level while elutriating, the flask $B$ is filled, the stop-cocks $a$ and $b$ are opened, and approximately as much water is allowed to flow into $C$ as in elutriating flows out of this vessel. The water discharged from the gauge-pipe $e$ may be caught and poured back into the balloon.

After the soil has, in the manner previously mentioned, been introduced into the small elutriator, the stop-cock, $f$, which serves for regulating the current of water, is opened a little and the operation commenced at the mark on the piezometer tube corresponding to the lowest elutriating velocity of 0.2 millimeters. Two or three liters are first allowed to run off, and, in case the product of elutriation is to be gained, evaporated in a large porcelain dish upon the water bath. In this manner one is sure to obtain all the soil constituents soluble in water. If, after running off two or three liters, the water in the elutriating space of the large elutriator has not become entirely clear, elutriation is continued at the same velocity, without interrupting the operation, until nearly complete clarification takes place in the upper portion of the elutriating space. The elutriating water thus obtained is brought into a large porcelain dish and heated to boiling. By continued boiling the suspended
particles of clay ball together and settle on the bottom, so that, after cooling and standing for some time, the supernatant, nearly clear water may be siphoned off and thrown away. The sediment is added to the product of elutriation first obtained.

In many cases the further elutriating process may be continued with ordinary water, the remaining products of elutriation depositing readily so that the supernatant water can almost be entirely siphoned off. The product of elutriation is then several times washed with distilled water, and, after allowing the sediment to settle, the water is siphoned off.

The velocity next to be used is dependent on the proportion of the cross-sections of the two elutriators. If the velocity of 7 millimeters appears in the small elutriator at a greater height of the piezometer than the velocity of 2 millimeters in the large elutriator, commence first at the height of the piezometer at which a velocity of 2 millimeters prevails in the large elutriator. In the reverse case, first elutriate with a velocity of 7 millimeters in the small elutriator, and, only after disengaging the latter, set the piezometer so as to obtain a velocity of 2 millimeters in the large elutriator.

The products of elutriation are caught in large cylindrical glass vessels (A, Fig. 3) having a capacity of from 10 to 15 liters. After, with a velocity of 7.0 millimeters, clarification has taken place in the small elutriator, the wide piezometer (compare p. 45) is placed upon the small elutriator and elutriation continued with 25 millimeters velocity until clarification is complete.

By the elutriating process the following products have
been obtained (compare the numbers in the table, p. 32):—

8. Product of elutriation at 0.2 millimeter velocity. Discharge.
7. " " 2.0 " " "
6. " " 7.0 " " " Residue in the large elutriator (eventually also partial discharge).

5. " " 25.0 " " " Discharge.
4. Residue " 25.0 " " " Residue in the small elutriator.

The two residues (6 and 4) are best removed from the elutriators by connecting the latter with the water reservoir, then inverting them in a large dish, and, after opening the cock, rinsing out their contents.

The supernatant clear water is next siphoned off, when the products of elutriation are brought into small previously weighed porcelain dishes with flat bottoms and for some time dried in a sand bath heated to about 212° F. After cooling, the dishes, before being weighed, are allowed to stand at least one or two days so that the products of elutriation may re-acquire the content of moisture of the air of the room.

The products obtained by granulation and elutriation are centesimally calculated for the entire soil, and the figures entered in the following scheme:—
Mistakes in elutriating with Schœne’s apparatus are avoided by executing the process as uninterruptedly and uniformly as possible. Numerous experiments have shown that the method yields sufficiently accurate results.

3. *Hilgard’s elutriating apparatus.*—To avoid mistakes arising from flocculent aggregates of the finest particles of soil, Prof. E. W. Hilgard has proposed* the elutriating apparatus shown at Fig. 5. He uses a cylindrical elutriating tube, $T$, of 34.8 millimeters inside diameter at its mouth, and 290 millimeters high. Attached to its base is a rotary churn, $P$, consisting of a porcelain beaker triply perforated, viz., at the bottom for connection with the relay reservoir, $R$; and at the sides for the passage of a horizontal axis, $A$, bearing four gratted wings. This axis, of course, passes through stuffing boxes firmly cemented to the roughened outside of the beaker and provided with good thick leather washers, saturated with tallow. These washers, if the axes run true, will bear a million or more of revolutions without

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material leakage. From 500 to 600 revolutions per minute is a proper velocity, which may be imparted by clock-work or a turbine.

As the whirling agitation caused by the rotation of the dasher would gradually communicate itself to the whole column of water, and cause irregularities, a (preferably concave) wire screen of 0.8 millimeter aperture is cemented to the lower end of the cylinder. No irregular currents are then observed beyond about 75 millimeters above the screen, whose meshes are yet sufficiently wide to allow any heavy particles or aggregates to sink down freely. Any grains too coarse to pass must, however, be previously sifted out.
Thus arranged, the instrument works quite satisfactorily; and by its aid, soils and clays may readily be separated into sediments of any hydraulic value desired. But in order to insure correct and concordant\(^*\) results, it is necessary to observe some precautions, to wit:

1. The tube of the instrument must be as nearly cylindrical as possible, and must be placed and maintained in a truly vertical position. A very slight deviation from the vertical at once causes the formation of return currents, and hence of molecular aggregates on the lower side.

2. Sunshine, or the proximity of any other source of heat, must be carefully excluded. The currents formed when the instrument is exposed to sunshine will completely vitiate the results.

3. The Mariotte's bottle should be frequently cleansed, and the water used be as free from foreign matters as possible. For ordinary purposes, it is scarcely necessary to use distilled water; the quantities used are so large as to render it difficult to maintain an adequate supply; and the errors resulting from the use of any water fit for drinking purposes are too slight to be perceptible, so long as no considerable development of the animal and vegetable germs is allowed. Water containing the slimy fibrils of fungoid and moss prothallia, vorticella, etc. will not only cause errors by obstructing the stop-cock at low velocities, but these organisms will cause a coalescence of sediments that defies any ordinary churning, and completely vitiates the operation.

4. The amount of sediment discharged at any one

\(^*\) Usually within 5 per cent. of the quantities found.
time must not exceed that producing a moderate turbidity. Whenever the discharge becomes so copious as to render the moving column opaque, the sediments assume a mixed character; coarse grains being, apparently, upborne by the multitude of light ones whose hydraulic value lies considerably below the velocity used; while the churner also fails to resolve the molecular aggregates which must be perpetually reforming, where contact is so close and frequent.

This difficulty is especially apt to occur when too large a quantity of material has been used for analysis, or when one sediment constitutes an unusually large portion of it. In either case, a portion of the substance may be allowed to settle into the relay reservoir until the part afloat in the churn and tube is partly exhausted; after which the rest can be gradually brought up and worked off. Or, the sediments shown by the microscope to be much mixed, may be worked over a second time. Either mode, however, involves so grievous a loss of time as to render it by far preferable to so regulate the amount employed, that even the most copious sediments can be worked off at once. Within certain limits, the smaller the quantity employed, the more concordant are the results. Between ten and fifteen grammes is the proper amount for an instrument of the dimensions given above.

It has been found that, practically, 0.25 millimeter per second is about the lowest velocity available within reasonable limits of time; and that by successively doubling the velocities up to 64 millimeters, a desirable ascending series of sediments is obtained, provided always that a proper previous preparation had been given to the soil or clay.
VI.

DETERMINATION OF THE SOIL–CONSTITUENTS.

A. Determination of the content of calcium carbonate or of magnesium carbonate.—With soils containing only small quantities of magnesium carbonate, it suffices to determine the carbonic acid expelled by stronger acids, and to calculate from it the equivalent quantity of calcium carbonate.

The content of calcium or magnesium carbonate in a soil is of double significance, for, on the one hand, they may be present in such large quantities as to form an important constituent of the soil, and, on the other, they play an important role in the nourishing of plants, even if present in such small quantities that they can no longer be classed as constituents.

According to the degree of accuracy aimed at, the carbonic acid may be determined by three different methods, viz: by volumetric measurement, by weighing from the loss, or by direct weighing a volumetric measurement of the carbonic acid with Scheibler’s apparatus.

a. Volumetric measurement of the carbonic acid is made use of for strongly calcareous soil; for instance, diluvial marls, meadow limes, and argillaceous marls, where the rapid determination of the approximative content of calcium carbonate in whole per cent. is sufficiently accurate. As the initial material for this purpose, fine soil dried at 212° F. is used, and if such is not at hand, the soil itself. The material is to be quite finely pulverized in a cast-steel mortar.
Scheibler's apparatus, Fig. 6, is arranged as follows:—

Two glass tubes 28 millimeters in diameter are vertically secured to a wooden frame. The tube to the right is graduated into half and whole centimeters and holds about 300 cubic centimeters. Below both the tubes are connected by a bent glass tube. The top of the tube to the left is closed by a cotton plug. Near the bottom of this tube is a glass tube which is bent upwards and connects, by means of a rubber tube provided with a clip, with an open flask tubulated near the bottom. The rubber tube must be of such a length that the flask may conveniently be placed upon a board located above the frame. The graduated tube is connected, by means of a tube provided on the side with a glass cock, having a glass bulb which receives the carbonic acid, so that the latter cannot be absorbed by the water in the graduated tube. With the lower end of this glass bulb is connected, by means of a rubber tube, the developing vessel, which consists of a glass flask with a wide neck, in which accurately fits a rubber cork provided with a tube.

In using the apparatus the glass flask filled with water is set upon the board above the frame, and the glass cock to the right being opened, both tubes are allowed to run full to above
the graduation. The flask is then taken down, and by carefully opening the clip, water is allowed to flow off until the lower meniscus of the water level in the graduated tube sits exactly upon the 0 mark. In both the communicating tubes the water will be at the same level. In order to have always approximately the same tension of aqueous vapor, the developing flask is, shortly before use, rinsed out with concentrated common salt solution. Then by means of a pipette 20 cubic centimeters of hydrochloric acid (1 part concentrated hydrochloric acid to 3 water) are introduced. Now place, with the assistance of straight crucible-tongs, a small porcelain crucible containing about four to eight grammes of the substance to be examined in the hydrochloric acid, and firmly put the rubber cork into the neck of the flask, without, however, touching the developing space with the warm hand. Now close the glass cock, and by opening the clip allow about 20 cubic centimeters of water to run off, as otherwise, in consequence of the violent evolution of carbonic acid in the beginning of the operation, water would be thrown from the tube to the right. After the discharge of the 20 cubic centimeters of water, the level in the tube to the right will be somewhat lower, but will remain constant at one point. Should this not be the case, the apparatus leaks somewhere. Now, grasp with the left hand the clip, and, with the right the developing flask so that the thumb lies on the left of the neck, the index-finger upon the top of the rubber cork, and the middle finger on the right of the neck. In this manner the vessel can be very firmly held, and heating by the hand is avoided. Incline the flask until the
porcelain crucible tumbles over and then impart a circular motion to the flask. During the evolution of carbonic acid a quantity of water, corresponding to the sinking of the level in the tube to the right, is discharged by opening the clip. Shaking of the developing vessel is continued until the level in the tube to the right remains constant. The apparatus is now allowed to stand quietly for ten minutes, then again shaken, and, when the water is at the same level in all the tubes, the number of centimeters of carbonic acid is read off. With due regard to the temperature and the height of the barometer, the weight of the carbonic acid or of the calcium carbonate corresponding to it, is calculated to R. Finkener’s tables (pp. 60 and 61), in which the weight of a cubic centimeter of carbonic acid at different temperatures and barometer heights is given in one-thousandths milligrams. In this figure is included the error arising from measuring the gas in a moist state, and from the absorption of a quantity of carbonic acid by the hydrochloric acid of the developing vessel.
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<tr>
<th>Thermometer (Centigrade)</th>
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I.—Table for calculating the carbonate acid for Scheibler's apparatus.

The figures indicate the weight of 1 cubic centimeter of carbonate acid in thousands of milligrammes.
### Determination of the Soil-Constituents

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The figures express thousandths of a millimeter.

The formula for calculating the carbonate acid found with Scheele's apparatus to calculate the carbonate acid is:

\[ \text{Carbonate Acid} = \frac{\text{Thermometer Reading}}{\text{Barometer Reading}} \times 1000 \]
b. Determination of the carbonic acid by weighing from the loss.—This method consists in expelling, in a weighed apparatus, the carbonic acid by dilute acids, again weighing the apparatus and calculating the content of carbonic acid in the substance from the loss in weight. An apparatus very suitable for this purpose is Mohr's, modified by Laufer and Wahnschaffe, Fig. 7. It consists of a small glass flask with a thin bottom and short wide neck, which serves for the reception of the sample of soil to be examined. The finely pulverized material is dried by spreading it out upon a watch crystal and placing it in a drying chamber heated to 212° F. for one hour. It is then brought hot into a small glass tube also dried out at 212° F., and the latter closed with a cork. After cooling, the tube together with the cork is weighed, two or three grammes of the substance are poured into the glass flask, and the tube is again weighed. The difference between the two weighings corresponds to the weight of the initial substance dried at 212° F. In the neck of the glass flask a hollow glass stopper provided with two tubulures is hermetically ground in. In the tubulures two glass tubes of different forms are also ground in. One tube is bent at a right angle, and then again upwards and widens above the second bend. It serves for the reception of calcium chloride, and is filled by first pushing in loosely a small cotton plug, placing upon the latter a layer of pieces of calcium chloride the size of pin-heads, then introducing
another cotton plug and finally closing it with the glass stopper provided with two tubulures. Over the end of the tube is drawn a small piece of rubber tube, in the top of which a small glass rod is pushed. The other tube reaches nearly to the bottom of the vessel, and near the top it is provided with a glass cock for the admission of the acid into the apparatus. Above, the tube expands pear-shaped for the reception of the acid, and is closed in the same manner as the other tube by a glass stopper, rubber tube, and glass rod. The filling with dilute acid (1 part concentrated acid and 10 parts water) is effected by immersing the pear-shaped tube inverted in the acid, and, with the glass cock open, sucking the acid up until the pear-shaped receptacle is nearly filled. The cock is then closed, the tubulure dried with blotting-paper, and the rubber tube placed over it. Some distilled water is poured over the material in the flask. When all the tubes have been firmly placed in position, the apparatus is wiped off with a dry piece of leather, and, after standing for half an hour, weighed. The rubber tubes are then removed, and the acid is allowed to run, drop by drop, into the flask. The carbonic acid having been expelled, the bottom of the flask is heated with a very small flame by placing the flask upon an asbestos plate, whereby the acid pipe must remain closed. After heating nearly to boiling, so that the carbonic acid absorbed by the water is expelled, allow the apparatus to cool, and then, in order to remove all the carbonic acid, draw a slow current of air through the apparatus by connecting the calcium chloride tube with an aspirator (E, Fig. 8). Now close the apparatus with the rubber tubes, let it stand for half an hour in the weighing-room, so that
it again acquires the temperature of the latter; lift, before weighing, the rubber tube on the calcium chloride tube for the equalization of the air pressure, and weigh after replacing the rubber tube. By duly observing all precautionary measures and paying special attention that in heating, the fluid is not brought to the boiling point, the carbonic acid can, by this method, be accurately determined to \( \frac{1}{10} \) per cent.

c. Determination of the carbonic acid by direct weighing.—This mode of determination consists in expelling the carbonic acid by hydrochloric acid and catching it in an absorption-apparatus which can be weighed. This method is used whenever the carbonic acid, even in very small quantities, is to be determined as accurately as possible.

R. Finkener's apparatus, shown at Fig. 8, is very suitable for the purpose. Of the substance dried at 212° F., 0.5 to 2 grammes are weighed out and brought into a flask upon the neck, \( a \), of which sits a tube secured to the flask by two copper wire rings connected by spirals. On one side the tube has an ascending joint, upon the end, \( e \), of which sits the calcium chloride tube. The latter is 93 centimeters long, and has an ascending and a descending leg, \( cd \) and \( de \), the latter of which is only filled with calcium chloride, while the former serves for the reception and condensation of the aqueous vapors escaping in boiling. The calcium chloride tube is also secured to the glass joint by means of rings and spirals. Above the glass joint is a glass stop-cock, \( B \), and over it a funnel in the bottom, \( b \), of which a knee-shaped tube is ground in. Below the glass stop-cock the funnel tube narrows and reaches nearly to the bottom of the
flask where it is bent upwards, so that during the evolution of carbonic acid no bubbles can ascend in it. The end of the calcium chloride tube is connected by means of rubber tubing with a small Geissler potash-apparatus,

Fig. 8.

Fig. 9.

\(D\), which is more plainly shown in Fig. 9. It is filled with caustic potash solution (1 part caustic potash to 2 parts water). The small wash bottles of this apparatus are filled three-quarters full by providing the upper end
of the tube with a rubber tubing dipping in the caustic potash solution, and sucking with the mouth on the tube end of the calcium chloride tube. The wash bottles having been filled, the rubber tubing is removed and the tube-end thoroughly cleansed with blotting-paper. The calcium chloride tube is then filled, and the apparatus, after having been wiped with a piece of leather and closed with rubber tubing, is placed for some time in the balance in order to acquire the temperature of the weighing-room.

Some distilled water is then poured over the material in the flask, and after inserting the glass tube bent at a right angle in the funnel, a current of air previously freed from its carbonic acid in a potash wash bottle (A, Fig. 8), is conducted through the apparatus. For the conduction of the air it is best to use a small Bunsen water air-pump, the current of air being regulated by inserting the apparatus, E, seen in the illustration. This apparatus consists of an ordinary glass flask with a doubly perforated rubber cork. In the cork sit two glass tubes, the lower end of one of which is drawn out to a fine point, and dips about two centimeters deep into the water in the flask. The other tube, which is even with the lower surface of the cork, is in direct communication with the air-pump, and is provided with a glass stop-cock, the boring on the mouth of which is laterally indented, so that, even with a strong air pressure, small air bubbles can, at determined intervals, be passed through the fluid in the flask. After sucking through about three times as much air as the apparatus contains, the tube is removed from the funnel, and, after closing the glass stop-cock, B, the funnel is filled with dilute
hydrochloric acid (1 part acid to 10 parts water). The weighed Geissler potash-apparatus is then connected with the long calcium chloride tube and the acid allowed to run, drop by drop, into the flask. When evolution has somewhat abated, a very small flame is brought under the apparatus, while a slow current of air is passed through it. The fluid is now heated to just below the boiling point, when the flame is removed and the current of air somewhat augmented. The operation is finished when three times the volume of air which the apparatus contains is sucked through it. The potash apparatus closed at both ends with rubber tubing is allowed to stand half an hour in the balance and is then weighed, after being wiped with a piece of leather and removing the frictional electricity thereby produced with a metallic brush.

If metallic sulphides are present in the soil, which are decomposed by the acid and yield sulphuretted hydrogen, add first some chloride of mercury to the fluid. If, with the use of hydrochloric acid, chlorine should be evolved, which may happen in the presence of oxides of manganese, first let some concentrated stannous chloride solution run into the flask.

After using the apparatus the condensed water in the ascending portion of the calcium chloride tube is removed by means of a flame, and the tube closed on both ends. By this means it can be used for a long time without the necessity of refilling it.

d. Determination of the carbonate of calcium and magnesium by boiling with ammonium nitrate.—If it is necessary to determine the proportion of the carbonates of calcium and magnesium, the following method, first
used by E. Laufer, can be recommended. Bring one or two grammes of the material, pulverized as finely as possible and dried at 212° F., into a beaker-glass and pour 20 cubic centimeters of completely saturated ammonium nitrate solution over them. After covering the beaker-glass with a watch crystal, boil the fluid for half an hour, and, in case the salt should separate by the evaporation of the water, add some hot water. Ammonium nitrate possesses the property of converting the carbonates of calcium and magnesium into soluble nitrates, while the ammonium carbonate formed thereby is decomposed by boiling and escapes.

\[ CaCO_3 + MgCO_3 + 4(NO_3NH_4) = Ca(NO_3)_2 + Mg(NO_3)_2 + 2(CO_3[NH_4]_2). \]

The soil is then allowed to settle, and the supernatant hot solution decanted off through a filter by placing the funnel in a copper hot-water funnel, Fig. 10, heated to 212° F., so that during filtration the ammonium nitrate cannot separate and clog up the funnel. The boiling with the solution is repeated twice; the material in the glass is then washed with somewhat more dilute ammonium nitrate solution and the washing fluid also poured through the filter. In case the material is not to be further used, it is unnecessary to bring it entirely upon the filter. Washing with pure distilled water cannot be done, as otherwise the fluid running off is rendered turbid by the fine particles of soil which pass through the filter. Washing is finished when a drop running off from the filter leaves no perceptible residue when evaporated upon a platinum sheet.

The filtrate strongly diluted with water is heated to
boiling, compounded with a few drops of ammonia and the lime precipitated with ammonium oxalate. After standing for twelve hours the white precipitate of calcium oxalate has completely settled. The supernatant fluid is then poured off through a filter; the precipitate is washed by several times decanting it with hot water in the beaker-glass and finally brought upon the filter. The portions of the precipitate adhering to the glass are removed with a glass rod over the lower end of which a piece of black rubber tubing has been drawn. The filter is now washed out with hot water, with the aid of the wash bottle. The operation is finished when a drop
running off leaves no perceptible residue when evaporated upon a platinum sheet.

The oxalate of lime is dried in the drying stove (Fig. 12), at 212° F., then detached from the filter and brought into a weighed platinum crucible, while the filter is Fig. 11.

folded together and incinerated upon the lid of the crucible. The ash is then brought into the platinum crucible, which is best effected with the aid of a pencil, and, after placing the lid upon the crucible, the latter is gradually brought to ignition. In order to completely convert the calcium carbonate formed by gentle igniting
into calcium oxide, it is necessary to subject the crucible for ten minutes to a strong heat over a blast-lamp (Fig. 11). Before weighing, cool the hot crucible and contents in a desiccator. Caustic lime being hygroscopic, weighing must be effected as rapidly as possible. Generally speaking, it is best to weigh all hygroscopic substances twice, by allowing the weights of the first weighing to remain in the pan of the balance, then again heating the crucible and its contents, and again weighing after cooling in the desiccator. Since the difference amounts at the utmost to from one to two milligrammes, the weight can very rapidly be determined by two or three oscillations of the beam of the balance. To find the corresponding quantity of calcium carbonate, multiply the number of weighed grammes of calcium oxide with the factor 1.786.

The filtrate from the lime-precipitate is evaporated to about half its volume in a platinum dish, then brought into a beaker-glass and solution of sodium phosphate added. Then add concentrated ammonia sufficient to amount to one-third of the entire solution. With a moderate heat (77° to 86° F.), a white crystalline precipitate consisting of ammonium magnesium phosphate $= PO_4 Mg NH_4 + 6 H_2 O$ is separated inside of twenty-four hours. The precipitate is filtered off and washed out with a cold mixture of one part of concentrated ammonia and three parts of water. Before igniting in a porcelain crucible, the dried precipitate is detached as much as possible from the filter, and the latter incinerated by itself. Then add the ash to the contents of the crucible and ignite over the blast-lamp. If, after igniting, the precipitate should be colored gray or black by unburnt
coal, moisten it by allowing a drop of nitric acid to fall upon it, place the lid upon the crucible and heat the latter gently at first, and, afterwards, over the blast-lamp. By the action of the heat the ammonium magnesium phosphate is transformed into magnesium pyrophosphate = Mg₃(PO₄)₂. Cool the crucible and contents in a desiccator and weigh. The increase in the weight of the crucible represents the weight of the magnesia pyrophosphate; this multiplied by 0.757 will give the equivalent quantity of magnesium carbonate.

B. Determination of the humus substances.—By humus are understood all the substances originating from the decomposition of plant-remains, in which carbon appears in organic combination.

With a full access of air and at an ordinary temperature, plant-remains are decomposed into a pale brown or dark brown substance, which dissolves with a brown color in alkalies and forms alkaline humates. The reaction of this humus is neutral.

If the decomposition of the plant-remains takes place under water, hence, without the access of air, a gray-black mass is formed, which in a fresh state is muddy, but in a dry state pulverulent. On account of its acid reaction this mass is called acid humus (gein).

If the decomposition of plant-remains begins at first with the full access of air and at an ordinary temperature, but is afterwards continued under water without the access of air, the humus substance richest in carbon, which is known as peat, is formed.

Between these different products of decomposition are found gradual transitions into each other, so that the humus substances represent no fixed chemical combina-
tions. For agriculture, it is first of all of importance to know the distribution of the humus substance in the soil and its reaction. The distribution and the degree of decomposition are learned from mechanical analysis by a microscopic examination of the various products of elutriation. The reaction is best learned by laying a moist sample of soil upon blue litmus-paper and observing whether the test paper is more or less strongly reddened. Since, however, the free carbonic acid present in the soil may also redden the paper, in making the experiment, the latter has to be dried and examined as to whether the reddening remains visible after drying. Sour humus soils are very detrimental to cultivation.

In regard to the quantitative determination of the humus substances, their content of carbon can, with approximate accuracy, be determined by Knop's method. If, however, it is to be determined with the greatest accuracy possible, combustion, customary in elementary analysis, has to be employed. With some soils a guide for judging the content of humus is already obtained by determining the loss in igniting.

a. Knop's method for the determination of humus.—Knop's method is based upon the conversion of the carbon contained in the humus by oxidation with chromic acid into carbonic acid, and collecting the latter in a weighable absorption-apparatus.

Spread about two to ten grammes of fine soil (less than two millimeters in diameter) of the substance to be examined upon a watch crystal and dry it for at least one hour at 212° F. in a drying chamber. The drying chamber shown at Fig. 12 has been devised by Dr. R. Muencke, of Berlin, and can be highly recommended
for drying at a constant temperature. The box of strong sheet-iron is provided with double walls, so that the hot gases of combustion in the interspace between

Fig. 12.

the walls surround the entire box on all sides, with the exception of the door, which is also double-walled. The outside of the box is surrounded with a jacket of asbestos card-board. The gases of combustion escape
through apertures in the top of the box, which can be more or less opened by a slide. The two tubes serve for the reception of a thermometer and a heat regulator. A glass plate provided with two holes is placed in the interior immediately under the top of the box. The heating which is very uniform is effected by means of a gas-spiral with twenty small flames, which can be regulated by two screws.

The temperature of 212° F. should never be exceeded since, already, at 230° F., the water distilling from the humus sometimes shows a brownish color which indicates decomposition. Together with the substance a weighing-flask is placed in the drying-chamber, the air-tight ground-in stopper of the flask being however first removed. When the substance is dry, it is brought hot into the weighing-flask, and, after closing the latter with the stopper, it is allowed to cool in the desiccator. It is then weighed, and one to ten grammes of the substance, according to its greater or smaller content of humus, are carefully, without scattering any dust, brought into a small glass flask with a wide neck, in which oxidation of the humus substance is to be carried on. For this purpose the apparatus for the determination of carbonic acid, Fig. 8, may be used. If, however, such an apparatus is not at hand, place in the glass flask a doubly perforated rubber cork. Through one of the perforations passes a glass tube somewhat bent on the bottom and closed above with a small piece of a glass rod in rubber tubing. Through the other perforation passes the calcium chloride tube which is bent above the cork and otherwise has the same shape as described under Fig. 8. In the beginning of the operation it is best not
to dip the straight tube into the fluid, as otherwise it may easily clog up below by the separated chromic acid.

Pour over the weighed substance in the flask 20 to 30 cubic centimeters of distilled water, and add 30 to 40 cubic centimeters of concentrated sulphuric acid, which is best gradually introduced through a funnel. On the acid mixing with the water strong heating takes place, so that the free carbonic acid present in the soil, as well as that fixed on lime, is completely expelled. If much calcium carbonate is present, as is, for instance, the case with moor-marls, the sulphuric acid must be very gradually introduced, with frequent cooling of the vessel, as otherwise the fluid might foam over. Before commencement of oxidation the flask is allowed to completely cool off and the air over the fluid sucked off to remove the last traces of carbonic acid.

Since plant-remains not entirely converted into humus frequently occur in soils, and cannot be well sorted out, the substance is allowed to remain in contact with the sulphuric acid for some days. Carbonization of the organic remains now takes place, and oxidation with chromic acid is effected more rapidly and uniformly.

After connecting the previously weighed Geissler absorption-apparatus (Fig. 9), with the calcium chloride tube, 10 to 15 grammes of pulverized potassium bichromate are quickly poured upon the substance through a paper tube inserted in the flask, and the apparatus is immediately closed. To avoid errors, which might originate from the fluid spurting against the rubber cork in case of a very violent evolution of carbonic acid, it is best to cover the lower side of the cork with thin
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platinum sheet. A very small flame is now brought under the flask and the evolution of carbonic acid beginning with the heating is so regulated that one bubble per second passes through the Geissler apparatus. If evolution becomes more vigorous, moderate the flame, and if it abates, heat more strongly.

By the sulphuric acid, the potassium bichromate is decomposed as follows: \( \text{Cr}_2\text{O}_7\text{K}_2 + \text{H}_2\text{SO}_4 = 2(\text{CrO}_3) + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \). By its oxygen the free chromic acid oxidizes the carbon of the humus substances to carbonic acid. An excess of sulphuric acid being always present, chrome-alum \((\text{SO}_4)_2\text{CrK} + 12\text{H}_2\text{O})\) is generally formed in the fluid. The heating is increased to boiling until a perceptible evolution of carbonic acid no longer takes place. Finally, the straight glass tube is dipped in the fluid and connected with a potash wash bottle, while a slow current of air is sucked through the entire apparatus. The flame is now removed, and, for the rest, the operation carried on as given under “determination of carbonic acid by direct weighing.”

To approximately calculate from the carbonic acid found, the quantity of humus free from water and nitrogen, it has been agreed to take 58 per cent. as the average content of carbon in the humus no matter in which form it may occur in the soil. Hence, in order to find the content of humus, the quantity of carbonic acid found need only be multiplied by the factor 0.471.

Since errors may originate in the presence of ferrous sulphide by the development of small quantities of sulphuretted hydrogen, or in the presence of chlorides, by escaping hydrochloric acid gas, it is recommended to insert between the calcium chloride tube and the Geissler
apparatus a U-tube. The latter is filled with pieces of pumice previously saturated with blue vitriol and heated until the latter is dehydrated. By this means the sulphurated hydrogen and hydrochloric acid gas are retained.

b. Determination of the carbon of the humus substances by elementary analysis.—The object of the method to be discussed here, which was first mentioned by Liebig, is to burn the carbon to carbonic acid by igniting together with cupric oxide. Since, however, the humus substances of the soil always contain nitrogen which, by this mode of combustion, is converted partially into nitrous gas and nitrous acid, the method is accordingly modified.

To effect this analysis by combustion, a hard Bohemian glass tube from 50 to 55 centimeters long is used. After being thoroughly cleansed, one end is drawn out and turned over in the shape of a beak, while the other end is fused together. The tube is heated upon the sand bath, and, after removing the air contained in it by sucking with a glass tube, it is filled half full with pure, freshly ignited and still warm cupric oxide, introduced through a previously heated metallic funnel, care being had that none of the cupric oxide reaches the beak-shaped portion. This is best prevented by loosely inserting, before filling, a cork of pure asbestos. Now pour some warm cupric oxide into a heated porcelain mortar and add 0.5 to 10 grammes of the finely pulverized fine soil, the quantity depending on the larger or smaller content of humus. The cupric oxide is intimately combined with the fine soil and the mixture also brought into the tube. Any particles adhering to the mortar are removed by rubbing them together with
some fresh cupric oxide and adding this mixture to the other in the tube. Suppose the whole occupies a space of 5 centimeters in the tube. Then add 5 centimeters more of cupric oxide; upon this follows a layer of 10 to 12 bright, fine copper wire shavings or a copper wire spiral of the same length. It is still better to use spirals of very fine silver wire, which, besides completely reducing the nitrous gas, also retain any chlorine present by the formation of silver chloride. The tube having been filled, rap repeatedly with it lengthwise upon a table so that a channel is formed on top of the contents through which the gases of combustion can escape. The tube thus filled is provided with a calcium chloride tube which is joined by a forked glass tube. One end of this tube is connected with a water air-pump and the other provided with rubber tubing and a clip. While the combustion tube is being pumped out, dried air is allowed to enter by means of the clip through the calcium chloride tube, so that all moisture is thereby removed.

The tube thus prepared is placed in a combustion furnace (Fig. 13), the empty space, about five centimeters long, being allowed to project from the furnace, while the perforated rubber cork closing the tube is protected by a piece of asbestos card-board. The tube is connected to a previously weighed calcium chloride tube and the latter to the weighed Geissler potash-apparatus also, provided with a calcium chloride tube.

Combustion should be conducted as slowly as possible. After the whole arrangement has been found perfectly air-tight, the front and back parts of the tube are heated, and, when red-hot, the portion of the tube containing the substance is gradually heated, the heat being so
regulated that one bubble per second passes through the potash-apparatus.

The operation is finished as soon as with strong heating the potash solution begins to pass back into the bulb nearest to the apparatus. The extreme point of the tube is then broken off and the main gas-cock closed. The bent-up portion of the tube must not be too strongly heated so that it can be connected by means of a rubber tube with a potash wash-bottle. A calcium chloride tube is inserted between the combustion tube and the potash wash-bottle, so that no moisture from the potash solution can reach the front calcium chloride tube. After connecting the calcium chloride tube of the Geissler potash-apparatus with the aspirator described under "determination of carbonic acid," a slow current of air is allowed
to pass through the combustion tube in order to expel all the carbonic acid from it.

After finishing the operation, the Geissler potash apparatus and the U-tube of the calcium chloride tube are brought into the weighing-room and allowed to stand for half an hour to acquire the temperature of the room before weighing them separately. The water weighed in the U-tube contains the entire hydrogen, that of the humus substances as well as that fixed to the other soil constituents.

To calculate, from the quantity of carbonic acid absorbed by the Geissler potash apparatus, the content of carbon in the soil, multiply it with the factor 0.273. If, however, the humus substance is to be determined, multiply the weighed carbonic acid by the factor 0.471.

**c. Determination of the loss by ignition.**—If the sample of soil to be examined contains no clay, or only a very small quantity of it, the humus can be approximately ascertained by determining the loss by ignition.

The fine soil dried continuously at 212° F. is poured into a previously weighed porcelain crucible, and the latter again weighed. Now heat the crucible very gradually by placing it obliquely upon a triangle and advancing it from the outer edge towards the small flame of a Bunsen burner. Then heat gradually after placing the lid upon the crucible, and regulate the combustion of the substance so that no small particles can be carried away by the draught. When combustion of the humus is complete, accelerate entire incineration by stirring with a stout platinum wire, the lower end of which has, by hammering upon an anvil, been given the shape of a spatula.
For the determination of loss by ignition Knop uses two grammes of fine earth, mixes the residue from ignition with pure pulverulent oxalic acid and gradually raises the temperature until the oxalic acid just begins to decompose. This operation is repeated with one-half the quantity of oxalic acid until the crucible, after cooling and weighing, shows a constant weight. The crucible must not be too strongly heated, as otherwise a portion of the carbonic acid regenerated by the oxalic acid is again expelled.

According to another method, the residue from ignition is repeatedly moistened with ammonium carbonate and slightly ignited to regenerate the alkaline earths present in small quantity, then dried at 302° F., and, after cooling in the desiccator, weighed.

If, however, larger quantities of the carbonates of calcium and magnesium are present, and heating has been carried on to a higher degree in order to destroy all organic substances, the oxides of calcium and magnesium cannot be regenerated, since, by the intimate mixture of the alkaline earths with dust-like silica, silicates are formed which cannot be reconverted into carbonates. In such a case, it is advisable to carefully bring the residue from ignition into a platinum crucible and heat the latter until all the carbonic acid is expelled and fusible calcium silicate has been formed. The carbonic acid of the initial substance is determined in a special sample and deducted from the loss by ignition. The vesicular slag is best removed from the platinum crucible by dissolving it in fluoric acid.

C. Determination of the content of clay.—Formerly the content of clay was frequently determined by elutriat-
ing the finest portion from the soil and designating this as clay. More accurate chemical investigations have, however, shown that a considerable quantity of quartz-flour is admixed with the finest portions, so that the content of clay determined by elutriation was always too high.

The object is better attained by combining for the determination of the clay, the silt-analysis with a chemical examination. It has been shown that with an elutriating velocity of 0.2 millimeter the greater quantity of clay contained in the soil is elutriated, and with a velocity of 2 millimeters, the entire quantity, provided the substance is previously thoroughly loosened by boiling. Hence, in investigating soils with the intention of simultaneously determining the clay, elutriation will have to be effected from the beginning with distilled water in order to obtain the products of elutriation at 0.2 and 2.0 millimeters per second as pure as possible. If the clay alone is to be determined, it is best to at once elutriate the soil at 2.0 millimeters velocity. Soils containing only small quantities of coarse material may be pulverized in an agate mortar, and, without previous elutriation, be directly used for the determination of clay. If, however, in the mechanical analysis, the products of elutriation at 0.2 and 2.0 millimeters' velocity have been separated, they are, after drying and weighing, again combined and very carefully mixed in a dish.

Disintegration with sulphuric acid in a closed tube.—This method of the determination of clay is based upon the property of pure clay or kaolin dissolving in hot sulphuric acid, while feldspars and quartz are not decomposed. In order that the action of the sulphuric
acid may be as uniform as possible, disintegration is best effected in a closed glass tube.

For this purpose a hard Bohemian glass tube about 30 centimeters long, without the neck, is used. One end of the tube is drawn out to a capillary which is thickened by fusion. The other end is also drawn out so that a neck is formed, which must, however, be wide enough for the convenient insertion of the weighing-tube. Before use, the tube is thoroughly boiled with aqua regia, rinsed with distilled water and dried.

For the execution of the analysis, 1 or 2 grammes of the finely pulverized substance are continuously dried at 212° F. and brought hot into a long thin weighing-tube closed with a cork. After cooling, the substance is poured into the Bohemian glass tube by pushing the weighing-tube down as far as possible so as to prevent any of the substance from adhering to the neck. The weighing-tube is then again weighed.

By means of a pipette 20 cubic centimeters of dilute sulphuric acid (1 volume of concentrated acid to 5 volumes of water) are now brought into the Bohemian glass tube and the latter closed by drawing out the neck.

If the substance contains carbonate of lime, the sulphuric acid has to be added very gradually, and the tube, before closing it, must be placed in boiling water, so that all the carbonic acid can escape.

The closed glass tubes are now placed in a tubular furnace (Fig. 14), so arranged that it will hold four tubes. They are heated for six hours at 248° F., and when perfectly cold, are opened by drawing a ring around them with a diamond, and holding the point of a
red-hot glass rod against the mark. The glass breaks off smoothly, and the contents can be conveniently emptied into a beaker-glass with the aid of a wash-bottle. The fluid is strongly diluted, and, in the presence of much calcium carbonate, compounded with some hydrochloric acid to dissolve the gypsum formed; it is then covered with a watch crystal and heated to boiling. After allowing the substance to settle, the fluid is decanted off through a filter. Finally, the undissolved substance is also brought upon the filter and the latter washed out with hot distilled water until a drop running off from the funnel shows no perceptible turbidity when compounded with barium chloride solution.

To oxidize the ferrous oxide the filtrate is compounded
with bromine water, and, after covering it with a watch crystal, boiled until the yellow coloring disappears and an odor of bromine is no longer perceptible.

The flame is now removed, and the fluid, being constantly stirred with a glass rod, is compounded with dilute ammonia until it shows a slight ammoniacal odor, and a piece of red litmus-paper thrown in acquires a permanent blue color. The precipitate formed consists of aluminium and ferric hydrate = Al(OH)$_3$ + Fe(OH)$_3$. If too much ammonia has been added, the larger portion of it has to be expelled by heating the fluid for some time, the aluminium hydrate being somewhat soluble in an excess of ammonia.

Now, pour the fluid boiling hot, and without allowing the precipitate to settle, through a filter so arranged that filtration will be rapidly effected. The filter should only be filled with fluid up to, at the utmost, one centimeter from the edge, as otherwise the washing out of the precipitate is very difficult. In filtering, the funnel should not be allowed to become entirely empty, as otherwise the gelatinous precipitate fixes itself firmly to the paper, clogging it up. After the precipitate has been transferred from the beaker-glass to the filter and the particles adhering to the glass removed with a feather, the precipitate is washed with hot water with the aid of a washbottle, until a drop running off shows no turbidity when compounded with barium chloride solution.

The precipitate of ferric oxide and aluminia is continuously dried in the drying-chamber at 212° F., whereby it shrinks together so much that it can be almost completely detached from the filter. Now lay a sheet of white paper upon the table, place upon it a
weighed platinum crucible and bring the precipitate into the latter by rubbing the interior sides of the paper against each other. Any scattering grains fall upon the paper and are also brought into the crucible. The precipitate being detached as much as possible from the filter, the latter is folded together, wrapped round with thin platinum wire and burnt in the point of the flame of a Bunsen burner. When the coal of the filter is completely burnt, add the ash to the precipitate in the crucible and strongly ignite the latter for some time, commencing however with a moderate heat, the crucible being covered with the lid. Then allow the crucible and its contents to cool in the desiccator, and weigh as rapidly as possible, since both the ferric oxide and alumina are quite hygroscopic. After deducting the filter-ash, the quantity of ferric oxide and alumina = $Al_2O_3 + Fe_2O_3$ dissolved by sulphuric acid is found.

Separation of the ferric oxide from the alumina. a. Determination of the iron as ferrous oxide by titration with potassium permanganate solution.—The ignited and weighed precipitate of ferric oxide and alumina is carefully, without scattering anything, poured from the platinum crucible into a small glass flask with a long neck. The particles adhering to the crucible are detached with a feather and washed by means of a washbottle into the flask. Add to the water about an equal volume of pure hydrochloric acid and place the flask obliquely inclined upon the sand bath, which is sufficiently heated to bring the fluid to boiling. The oblique inclination of the neck of the flask is necessary to avoid loss by squirting in consequence of the bumping of the fluid during boiling. If, inside of a few
hours, the precipitate is not entirely dissolved, add to the strongly evaporated fluid a mixture of hydrochloric acid and water, and heat again until the entire precipitate is dissolved. If a few white flakes should remain, they consist mostly of silica or titanic acid; the quantity is, however, generally so small that no notice need be taken of them. When the solution in the flask is cold, compound it with dilute sulphuric acid, again place the flask in an oblique position on the sand-bath and heat, in order to expel the hydrochloric acid, and convert the chlorides of iron and alumina into sulphates, until the fluid is quite evaporated and clear as water. Dilute the cold solution with water, and compound it again with pure dilute sulphuric acid.

In order to dissolve the iron in the ignited precipitate of iron and alumina, another method may be used, which, however, has the disadvantage that the substance has to be previously powdered in an agate mortar, whereby slight particles may readily be lost, again ignited in the platinum crucible and weighed. The powder is then compounded with ten times its quantity of previously fused potassium bisulphate and heated in the covered platinum crucible until the powder is completely dissolved. After cooling, the melt is dissolved with hot water and compounded in a boiling flask with pure dilute sulphuric acid.

Now add to the iron solution, obtained by either one of the two methods, pure granulated zinc, and place a small funnel upon the boiling flask. Should the evolution of hydrogen, which now takes place, be not sufficiently vigorous, it may be promoted by dipping the point of a glass rod in platinum chloride and after
allowing the drop adhering to it to drop off, injecting what remains on the rod into the flask by means of the wash-bottle. A vigorous evolution of hydrogen will at once commence. Hydrogen in a nascent state possesses, as is well known, the property of converting ferric oxides into ferrous oxides, or, according to the more modern conception, of transforming the trivalent into bivalent iron.

The reduction of the solution may also be promoted by placing the flask on a moderately heated sand-bath. When evolution of hydrogen has vigorously continued for about one hour, the solution is tested as to the complete reduction of the iron. This is effected by taking, by means of a glass rod, a drop of the fluid from the flask and allowing it to run upon a white porcelain plate into a drop of freshly prepared, not too concentrated potassium sulphocyanate solution. If the latter is reddened, reduction is not finished and has to be continued, with the addition of some zinc and sulphuric acid if necessary, until a repeated test shows no coloration of the potassium sulphocyanate solution. When the solution is completely reduced, pour it rapidly through a funnel in which a glass-wool cork has been loosely inserted. In doing this, a current of pure carbonic acid should be conducted above upon the funnel, as well as into the beaker-glass beneath it, so that during filtering no oxidation of the solution by the oxygen of the air can take place. The flask, together with the zinc remaining therein, is rinsed with distilled water, and the rinsing water also poured through the funnel. The filtrate, which should not be hot, is further compounded with some dilute sulphuric acid, and the
solution is then titrated with previously standardized potassium permanganate solution.

*Standardizing of the potassium permanganate solution.*—The potassium permanganate solution is prepared and standardized as follows:

Dissolve, with the assistance of heat, 1 gramme of pure crystallized potassium permanganate in distilled water, and add to the solution sufficient water to make 1 liter. The solution thus prepared will keep for some time in a glass-stoppered bottle, but should not be exposed to the direct light of the sun.

The solution is standardized by measuring in a burette with a glass stop-cock as many cubic centimeters of it as are required for just imparting to a ferrous oxide solution of known content a violet color. For preparing this iron solution iron-ammonium alum or ammonioferric sulphate is used. This salt, being seldom found pure in commerce, is purified by dissolving a quantity of it in hot distilled water to which a few drops of sulphuric acid have been added, until a film of salt commences to separate. The beaker-glass containing the concentrated solution is then placed in cold water and the solution constantly stirred with a glass rod, so that the salt separates as a fine crystalline powder. When the fluid is perfectly cold, it is separated from the salt by pouring it into a funnel provided with a platinum cone, which, by means of a doubly perforated rubber cork, is placed upon a glass flask. Through the other perforation of the cork passes a glass tube which is connected with a water air-pump. When nothing more drips off, the glass flask is exchanged for another, and the precipitate rinsed with a mixture of two parts absolute alcohol and
one part distilled water. The salt is pressed between blotting-paper until perfectly dry. A solution of it must be reddened by potassium sulphocyanate.

Of the perfectly dry ammonio-ferric sulphate, accurately weigh out two portions of 0.1 gramme each, and pour them into two beakers. Shortly before use, dissolve the salt in 200 cubic centimeters of water to which some dilute sulphuric acid has been added. The burette provided with a glass stop-cock should have a capacity of at least 30 cubic centimeters, and be graduated into tenths of a cubic centimeter. It is filled to the 0 point with potassium permanganate solution, and for more convenient reading a small float is put in it. The foot of the burette stand is best covered with a dead white glass plate, or, if such an arrangement cannot be had, a piece of white paper is placed under the beaker containing the ammonio-ferric sulphate solution. Now allow the potassium permanganate solution to flow slowly from the burette into the ammonio-ferric sulphate solution, stirring constantly with a glass rod. The red color of the potassium permanganate solution at first disappears very rapidly, but later on more slowly, so that in order to hit the exact point, the solution must finally be admitted only drop by drop. When finally all the iron is oxidized, one drop suffices to very slightly color the fluid. The operation is finished when this coloration lasts a few minutes after stirring. Now, after waiting a short time to allow the fluid from the walls of the burette to run together, read off the number of cubic centimeters of potassium permanganate solution used. To control the correctness of the first reading, the
experiment is repeated with the other quantity of salt weighed out.

Since the quantity of iron contained in the ammonio-ferric sulphate amounts to \( \frac{1}{7} \), or, to be more exact, to \( \frac{1}{7.0014} \), it is necessary, in order to find the iron in the quantity weighed off, to divide the latter by \( 7 \), or, what is the same, to multiply it by the factor 0.143. To calculate the quantity of ferrous oxide equivalent to the quantity of salt weighed out multiply by the factor 0.184, and to find the ferric oxide with the factor 0.204. With the assistance of the figure found, the effective value of the potassium permanganate solution is calculated according to the following proposition:

Cem. of potassium permanganate solution consumed:

\[
\begin{align*}
\text{g} \left( \frac{\text{Fe}}{\text{FeO}} = 100 \text{ cem} : xg. \right) \\
\text{g} \left( \frac{\text{Fe}_2\text{O}_3}{\text{FeO}} \right)
\end{align*}
\]

The titration of the ferric oxide solution reduced by hydrogen is effected in exactly the same manner as the standardizing of the potassium permanganate solution just described. However, to obtain a sharp final reaction, the potassium permanganate solution must, towards the last, be very carefully added drop by drop. From the quantity of potassium permanganate solution consumed, the equivalent quantity of ferric oxide is then calculated. The percentage of ferric oxide deducted from the total percentage of ferric oxide and alumina gives the percentage of alumina by difference.

6. Calculation of the content of clay in the total soil.—
To find the content of clay in the soil, calculate for the quantity of alumina found the equivalent quantity of clay containing water, according to Forchhammer's
DETERMINATION OF THE SOIL-CONSTITUENTS. 93

formula \((\text{Al}_2\text{O}_3\cdot2\text{[SiO}_2\text{]} + 2\text{H}_2\text{O})\), by multiplying the weighed quantity of alumina by the factor 2.5294. Since the quantity of clay in the argilliferous particles (less than 0.05 millimeters in diameter) has been determined, the percentage of clay in the total soil is calculated.

With very fine soils, especially loess and fat clammy soils, as well as such as, on account of their strongly humus nature, cannot be subjected to silt analysis, the disintegration with sulphuric acid in the tube will have to be at once executed with the total soil. With humus soils it will, however, be better to retain the method of disintegration with concentrated sulphuric acid by heating in an open platinum dish. It was formerly almost generally used for the determination of clay, though it does not yield as uniform results as disintegration in the tube in which the concentration of the sulphuric acid, its quantity, the temperature and time of action can be uniformly regulated.

Fesca and others have frequently drawn attention to the fact that a portion of the alumina contained in the soil is soluble in hydrochloric acid, and is not referable to clay according to Forchhammer’s formula. Fesca believes that this quantity of alumina soluble in hydrochloric acid indicates zeolitic silicates. Though the correctness of this opinion is by no means proved, in very accurate and comprehensive soil investigations, it will be of interest to treat the argilliferous portions (less than 0.05 millimeter in diameter), with hot concentrated hydrochloric acid and to disintegrate the residue remaining thereby with sulphuric acid in the tube.

However, for the approximate quantitative determina-
tion of clay as a soil constituent, it is better to calculate the total alumina in dust and finest disintegrable particles as clay for the entire soil. Most soils do not contain the clay in a pure form, as already shown by Forchhammer's clay formula, but it is rather a collective term for all silicates more or less in a state of decomposition or already decomposed. For agricultural purposes, it is of importance to be able to express the content of clay, as well as that of humus, in fixed numerical values, and it does not much matter whether in each separate case an exact petrographic equivalent is thereby designated, especially not, when still further experiments regarding the physical properties of the soil are to be made.

D. Determination of the content of sand.—According to its chemical composition, the soil-constituent, sand, may represent something of very dissimilar nature. Sand being a transported product of the disintegration and elutriation of heterogeneous minerals and rocks, it shows many variations in its perfected state. However, the minerals disintegrating with the greatest difficulty, especially quartz, will always preponderate in it. If the mechanical analysis is carefully executed, and with grains more than 0.05 millimeter in diameter, the sand can, with an elutriating velocity of 2.0 millimeters per second, be quite completely separated from the clayey particles, and, hence, by the mechanical analysis already described, the content of sand and its granulation are found.

Petrographic determination of the coarser admixed parts of the sand.—The petrographic determination of the coarser admixed parts of the sand is geologically of
importance, since it discloses the origin and formation of the soil. In an agricultural respect it is of value for judging the soil, as, for instance, in the presence of an abundance of feldspar, the soil possesses for the future a nearly inexhaustible reserve of plant-food, which becomes only gradually available by the progressing decomposition of the feldspar.

A certain amount of information regarding the nature of these admixtures is obtained by sorting out and testing the grains of sand of from 2 to 1 millimeters in diameter, and the gravel over 2 millimeters in diameter. For this purpose moisten the sample to be examined with water and test the grains, best by Mohr's scale of hardness, as to color, lustre, and hardness, and further, as to cleavage, fusibility, and magnetic properties. Small limestones are recognized by the evolution of carbonic acid when treated with dilute hydrochloric acid.

A further separation may be effected by bringing the admixed parts into specifically very heavy fluids.

For this purpose, Thoulet prepares a solution of 2.77 specific gravity (at from 52° to 59° F.) by alternately introducing iodide of mercury and potassium iodide in water, and effects with it the separation of all bodies of higher specific gravity. By diluting the solution, bodies of slighter specific gravity may also be separated from each other.

Goldschmidt dissolves 210 grammes of potassium iodide and 280 grammes of iodide of mercury in 25 cubic centimeters of distilled water and produces a solution of 3.196 specific gravity, upon which, for instance, fluor spar (specific gravity 3.1 to 3.2) floats.
Rohrbach takes 100 parts of barium iodide and 130 parts of iodide of mercury to 20 cubic centimeters of water, heats in the oil bath to from 302° to 360° F., and filters. The solution has a specific gravity of 3.39, and topaz floats upon it.

With the aid of such solutions and the following table of specific gravities, the distinct admixed parts of the sand obtained by sifting or elutriating can be separated and determined.

<table>
<thead>
<tr>
<th>Gypsum</th>
<th>2.2 to 2.4</th>
<th>Augite</th>
<th>2.88 to 3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthoclase</td>
<td>2.53 &quot; 2.58</td>
<td>Tourmaline</td>
<td>2.94 &quot; 3.24</td>
</tr>
<tr>
<td>Albite</td>
<td>2.62 &quot; 2.67</td>
<td>Amphibole</td>
<td>2.9 &quot; 3.3</td>
</tr>
<tr>
<td>Oligoclase</td>
<td>2.63 &quot; 2.68</td>
<td>Fluor spar</td>
<td>3.1 &quot; 3.2</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.65</td>
<td>Rutile</td>
<td>4.2 &quot; 4.3</td>
</tr>
<tr>
<td>Calcareous spar</td>
<td>2.65 &quot; 2.80</td>
<td>Heavy spar</td>
<td>4.3 &quot; 4.7</td>
</tr>
<tr>
<td>Anorthite</td>
<td>2.67 &quot; 2.76</td>
<td>Pyrites</td>
<td>4.9 &quot; 5.2</td>
</tr>
<tr>
<td>Black mica</td>
<td>2.74 &quot; 3.13</td>
<td>Magnetic iron ore</td>
<td>4.9 &quot; 5.2</td>
</tr>
<tr>
<td>Muscovite</td>
<td>2.76 &quot; 3.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

E. Determination of the content of quartz.—Since it is frequently of interest to determine the content of quartz in the sand, as well as the dust and the finest particles, J. Hazard has for this purpose proposed an indirect method, since no process is known for the direct separation of quartz in a mixture with orthoclase, albite, and oligoclase, it being always attacked in the disintegration of these silicates.

The finely pulverized material is, according to Hazard, fused with 2 parts concentrated sulphuric and 1 part distilled water, in a hard Bohemian glass tube, and for six hours exposed to a temperature of 482° F. in a tubular furnace, whereby any muscovite, biotite, garnet, tourmaline, talc, amphibole, hypersthene, diallage, and pyroxene present is completely disintegrated, while
orthoclase, albite, and oligoclase remain undecomposed. The contents of the glass tube are brought into a dish and the particles adhering to the sides of the tube removed by means of a glass rod provided with a piece of rubber tubing. Before filtering off, the fluid is strongly diluted. The superficially washed-out residue is then brought together with the filter into moderately dilute potash lye, in order to dissolve the silica separated from the silicates, and then digested for one hour upon the water bath. The solution is diluted with water, filtered off and the substance upon the filter first washed with hot dilute potash lye, and later on, with hot dilute hydrochloric acid. The thoroughly dried filter, together with its contents, is incinerated in a platinum crucible and weighed.

The procedure is now exactly the same as in the silicate analysis. The powder in the platinum crucible is mixed with five times its quantity of anhydrous sodium carbonate and first heated over an ordinary burner, and, later on, over a blast lamp, until the mass flows quietly and no more bubbles of carbonic acid are evolved. The hot crucible is placed upon a cold iron plate, whereby, in consequence of the rapid cooling off, the mass readily becomes detached from the sides of the crucible. The melt, as well as the crucible itself, is brought into a beaker, and, after pouring distilled water upon it and covering the beaker with a watch-crystal, the contents are heated to boiling. Now, by means of a pipette, introduced through the lip of the beaker, add in small proportions concentrated hydrochloric acid in excess, and heat the fluid until no more effervescence takes place. Then add a few drops of nitric acid and evaporate the fluid,
together with the silicate separated, in a porcelain dish upon a water bath to pulverulent dryness. As soon as the fluid commences to become thickly-fluid, it has to be constantly stirred with a glass pestle, so that no larger cubes of common salt can form. In order to separate the silica as a powder entirely insoluble in acids, it is necessary to expel the hydrochloric acid as completely as possible. This is best effected by adding, as soon as the powder in the dish becomes dry, some hot water and again evaporating, with constant stirring, to pulverulent dryness. After cooling, moisten the powder with hydrochloric acid, pour hot water over it, and, after several times washing out the silica in the dish with hot water, bring it upon the filter and rinse it with hot water until a drop running off shows no turbidity when mixed with nitrate of silver. Before incinerating the filter with the silica in the platinum crucible, it must be completely dried at 212° F. It is advisable to finally ignite the silica over the blast-lamp, whereby it slags somewhat together and is no longer hygroscopic when weighed after cooling in the desiccator. The filter ash is deducted after weighing.

In the filtrate from the silica, alumina and calcareous earth are determined by successive precipitation with ammonia and ammonium oxalate according to the methods previously described (p. 68 and p. 86).

For the orthoclase and albite, whose silica is contained in the total quantity of silica obtained from the soda melt, Hazard has calculated the equivalent quantity of silica from the alumina found and deducted it from the total quantity of silica. The remainder represents the quartz present in the soil. For orthoclase and albite the proportion of alumina to silicate is $1 : 3.50878$. 
In the presence of lime the alumina equivalent to the lime is calculated according to Tschermak's formula for anorthite in the proportion of 1 calcareous earth: 1.83214 alumina. The alumina thus obtained is deducted from the weighed total alumina, and the quantity of silica required for the albite and orthoclase calculated to the rest of alumina. For the alumina of the anorthite, the quantity of silica belonging to it and to be deducted from the total silica is calculated from the proportion 1 alumina: 1.16959 silica.

E. Determination of the elementary composition of the soil.—If the soil to be examined is of homogeneous nature, as, for instance, may be the case with pure clays, marly sands, or sands of the subsoil, it may frequently be of interest to learn the elementary composition of the entire soil. For this purpose it is advisable to simultaneously effect a disintegration with sodium carbonate, as well as with fluoric acid, the analytical results obtained being best controlled in this manner.

a. Disintegration with sodium carbonate.—For disintegration with sodium carbonate pulverize dust fine 1 to 2 grammes of the total soil in an agate mortar and dry the powder at 212° F. Then pour it from a weighing tube into a platinum crucible and mix it by means of a platinum spatula with 5 or 6 times its weight of anhydrous sodium carbonate. The mass in the covered crucible is heated, first over an ordinary burner, and finally fused over the blast lamp until it flows quietly and no more carbonic acid escapes. The glowing crucible is placed upon a cold iron plate whereby the melt quickly congeals and later on can be readily detached from the crucible. The dissolution of the melt in hydrochloric acid
and separation of silica are effected in the manner given on p. 97. In the filtrate from the silica the alumina, ferric oxide, oxide of manganese, calcareous earth and magnesia are determined according to the methods previously given. Such substances as titanic acid, sulphuric acid, chlorine and phosphoric acid which occur only in small quantities in the soil cannot be determined with sufficient accuracy in the quantity used, and, therefore, need not to be noticed.

If the substance used is free from organic or carbonaceous matter, the content of ferrous oxide may be determined by disintegrating a special sample of the total soil with sulphuric acid in a closed glass tube (p. 84), separating the residue from the fluid by filtering in a current of carbonic acid and determining the ferrous oxide in the fluid by titration with potassium permanganate solution (p. 89).

b. Disintegration with fluoric acid. — Disintegration with fluoric acid is best effected by simultaneously combining with it a determination of loss by ignition. For this purpose 1 to 2 grammes of the finely pulverized substance dried at 212° F. are first gently heated in a platinum crucible and then vigorously ignited over the blast lamp. After cooling in the desiccator the loss by ignition is determined by weighing. The mass which is slagged together, and, in the presence of lime, often fused, is moistened with distilled water and then strong fluoric acid is poured over it. The crucible is now covered, and after placing in it a small platinum spatula of stout platinum wire to the handle of which a cork is secured, allow the acid to act upon the substance 2 or 3 days, stirring frequently, until a pasty mass is formed.
Then, with frequent stirring, evaporate the contents of the crucible to dryness upon the water bath, in order to expel the silica as silicon-fluoride. The crucible being held obliquely, the dry residue in it is moistened, with concentrated sulphuric acid in order to convert the fluorides into sulphates. The excess of sulphuric acid is expelled by heating the crucible placed obliquely so that a very small flame acts upon it from the edge; this is done to prevent the substance from scattering. When the mass is dry, it is dissolved from the crucible by means of hydrochloric acid and water, and with the aid of a wash bottle brought into a beaker. When covered with a watch-crystal and boiled continuously, the mass should dissolve entirely clear. Now, for the oxidation of the ferrous oxide, add some bromine water, boil the fluid until the excess of bromine is completely expelled and determine the aluminia, oxides of iron and manganese, calcareous earth, magnesia, potash, and soda.

VII.

DETERMINATION OF THE PLANT-NOURISHING SUBSTANCES.

In the determination of the plant-nourishing substances we may proceed either by separately determining the nourishing substances at the time present and available in the soil, and those which only gradually become available, or by determining from the start the sum-total of those already present and of those which in a conceivable space of time may become active by processes of
weathering and decay. In the first case the processes taking place in nature will have to be imitated as closely as possible, this being approximately effected by successively treating the soil with agents constantly increasing in strength.

A. Determination of the plant-nourishing substances in soil extractions.—The above-indicated requirements are best fulfilled by the following fluids, which in very comprehensive soil investigations are successively allowed to act upon the soil:—


If only the sum-total of the plant-nourishing substances present and of those which will shortly become active is to be determined, the soil is directly treated with boiling concentrated hydrochloric acid, the other extractions being omitted.

I. Extraction of the soil with cold distilled water.—By treating the soil with cold distilled water, only the constituents soluble in water can, of course, be extracted. Such constituents, independent of humus substances, are chiefly chlorides, sulphates, and nitrates of calcium, magnesium, potassium, and sodium. Hence, only these substances will have to be determined.

The aqueous extract of the soil is prepared as follows: Bring into a glass flask of 2 liters capacity, and which can be closed with a rubber cork, 500 grammes of air-dry fine soil (less than 2 millimeters in diameter), and pour over it 1000 cubic centimeters of distilled water, less the volume which would escape in drying
500 grammes of fine soil at 212° F. For this purpose determine at the same time the water escaping from about 20 grammes of the same fine soil when continuously heated. First weigh the air-dry sample in a weighing-flask, then spread it out in as thin a layer as possible upon a watch-crystal, and heat it for 2 hours at 212° F. in a drying-chamber. Now, with the aid of a brush bring the dried substance, while hot, into the heated weighing-flask, close the latter hermetically, and let it cool in the weighing room. The determination of the water escaped at 212° F. can only be relied on when, after repeated drying and again weighing, no noticeable difference in weight is obtained. The quantity of soil weighed out for extraction is allowed to remain in contact with the water for two days, being in the meanwhile frequently shaken, and, after settling, the supernatant fluid is drawn off by means of a siphon provided with a suction pipe. The fluid is then filtered through a dry filter into two measuring flasks, one of 500 and the other of 300 cubic centimeters capacity.

1. Determination of the bases in the aqueous extract.—Evaporate the 300 cubic centimeters of the aqueous extract; which correspond to 150 grammes of fine soil dried at 212° F., in a small weighed platinum dish upon the sand bath, dry the residue at 212° F., and weigh it after cooling in the desiccator. Now, gently ignite the platinum dish, and after cooling in the desiccator, weigh it again. By this means the sum-total of the substances dissolved in water, as well as the incombustible matter contained therein, is learned. If the latter is less than 0.5 gramme, the separation of the alkalies and alkaline earths cannot be accurately carried out, on account of
the small quantity which would have to be weighed. It is, therefore, best to repeat the aqueous extraction with such a quantity of fine soil that the amount of extract intended for the determination of the bases contains at least 1 to 0.5 gramme of dissolved substances. The residue obtained by igniting is dissolved with the addition of some hydrochloric acid in distilled water and filtered in case traces of silica are found. The fluid is then heated to boiling, and traces of iron and alumina, which, as a rule, reach the fluid only by turbid filtering, are precipitated with ammonia. In the filtrate the calcareous earth is precipitated in the manner given on pp. 67 and 68. The filtrate of calcium oxalate is evaporated in a capacious platinum crucible, and, after drying, moderately ignited to expel the excess of sal ammoniac. The process of drying can be essentially accelerated by constant stirring with a platinum spatula. The residue is taken up with a few drops of water, brought into a small beaker, and the solution, if not clear, is again filtered through a small filter.

The magnesia is now precipitated by ammonium carbonate, the solution of which is prepared as follows: Dissolve 230 grammes of sublimed sesquicarbonate of ammonia in 180 cubic centimetres of ammonia of 0.92 specific gravity, and add sufficient water to make the volume of the fluid exactly 1 liter. This solution must be added in considerable excess. If much magnesia is present, a voluminous precipitate is at first formed which, on stirring is, however, completely redissolved. The fluid is now allowed to stand quietly for twenty-four hours, during which time a fine crystal-
line precipitate consisting of ammonium magnesium carbonate is formed. This salt is filtered off, washed with ammonium carbonate solution, and when a drop running off leaves no residue when evaporated upon a platinum sheet, dried at 212° F. in the drying chamber. The precipitate, together with the filter, is heated in the platinum crucible, and when the filter is carbonized, strongly ignited, the crucible being placed in an oblique position. The precipitate, which consists of magnesia, must be perfectly white after ignition.

The filtrate from the ammonium magnesium carbonate contains the *alkalies*. It is brought into a capacious platinum dish, which is covered with a watch-crystal and heated upon the water-bath. As soon as the decomposition of the ammonium carbonate begins, the flame is made somewhat smaller to prevent the fluid from foaming over, and the latter is then heated until no more bubbles of carbonic acid escape. The watch-crystal is then removed and rinsed off with distilled water, and the fluid evaporated in a smaller weighed platinum dish upon the water-bath. The residue is moistened with a few drops of hydrochloric acid, again evaporated, and the covered platinum dish dried in the drying chamber at a temperature gradually raised to 392° F. By this means loss by the decrepitation of the water inclosed in the common salt while igniting the salt in the platinum dish is avoided. The platinum crucible is only slightly ignited, the alkaline chlorides being volatile at a strong red heat. After cooling in the desiccator the platinum crucible is weighed. In this manner the sum total of the chlorides of potassium and sodium are learned.
To separate the potassium from the sodium, take up the chlorides with a few drops of water and add solution of platinum chloride in excess. Now, in an atmosphere free from ammonia, evaporate the fluid on a covered water-bath (Fig. 15) until it possesses a syrupy consistency and the platinum chloride commences to separate in it in a crystal-line form. After cooling, add one part of a mixture of 55 cubic centimeters of absolute alcohol and 15 cubic centimeters of ether, and allow the fluid to stand under a glass-bell for 12 hours, stirring it several times in the meanwhile. Then filter it through a weighed filter and wash the precipitate remaining upon the filter with some alcohol containing ether until the fluid running off is no longer colored.

A greater number of weighed filters may be best prepared as follows: Treat several filters first with hydrochloric acid, and, after thoroughly sweetening them with distilled water, dry them continuously at 212° F. in the drying closet. Then bring them hot into a weighing flask, also heated to 212° F., and weigh the flask after cooling. By successively taking out the filters, and each time reweighing the flask, the weights of the filters are obtained, which are best noted upon them with a pencil.
The precipitate of potassium platinum chloride is thoroughly washed upon the filter, then dried at 212° F. brought hot, together with the filter, into a weighing tube and weighed after cooling. By deducting the weight of the weighing tube, and of the filter, from the weight last obtained, the quantity of potassium platinum chloride present is obtained. To obtain the equivalent quantity of potassium multiply by the factor 0.193.

Instead of weighing the potassium platinum chloride upon a weighed filter, the salt may be decomposed and the potassium determined from the platinum obtained. In this case add to the precipitate in the filter some pure oxalic acid and ignite the mass in a weighed porcelain crucible provided with a cover; finally, in order to reduce all the platinum, conduct a current of water upon the crucible and allow the substance to cool in it. To remove the potassium chloride, the platinum is washed with water by repeated decantation, and, after drying and again igniting, weighed. To obtain the equivalent quantity of potassium, multiply the platinum by the factor 0.477.

To obtain the sodium, calculate the potassium to potassium chloride by multiplying by the factor 1.584, deduct the potassium chloride from the sum of the chlorides, and multiply the sodium chloride thus obtained by the factor 0.530.

If many sulphates are present among the soil-salts soluble in water, which may be the case with soils very rich in gypsum, it is better, after precipitating the magnesia with ammonium carbonate and evaporating the solution, to add a few drops of sulphuric acid and then ignite strongly in a weighed platinum dish. In doing
this, a small piece of ammonium carbonate has to be held by means of a pair of tweezers in the dish in order to convert the acid alkaline sulphates into neutral. The alkaline sulphates being very refractory, ignition may finally be carried to an initial red heat. After weighing, dissolve the sulphates in water, compound them with platinum chloride, and evaporate the solution to a syrupy consistency upon the water-bath. Now dissolve the mass, according to Finkener's directions, in a mixture which, for 30 cubic centimeters of hydrochloric acid, contains 150 cubic centimeters of absolute alcohol and 35 cubic centimeters of anhydrous ether. When the whole has stood for one hour, bring the precipitate upon a weighed filter and wash it with a mixture of hydrochloric acid, alcohol, and ether, in the above-mentioned proportions until the fluid runs off clear. Then, to remove the hydrochloric acid, wash with alcohol containing ether, dry the filter at 212° F. and weigh it, together with the potassium platinum chloride upon it, in the manner given on p. 107.

To determine the sodium in this case, multiply the potassium by the factor 1.851, deduct the potassium sulphate thus obtained from the total of the sulphates, and multiply the remaining sodium sulphate by the factor 0.437.

2. Determination of the acids in the aqueous extract.

a. Determination of chlorine.—If the aqueous extract of the soil contains no sulphuric acid or only a trace of it, which is recognized by filtering off a small sample of the supernatant water and compounding the clear filtrate with some nitric acid and barium chloride solution, the
chlorine may first be determined. Otherwise the sulphuric acid is first precipitated.

Compound the 500 cubic centimeters of aqueous extract mentioned on p. 102 with a small quantity of pure sodium carbonate and evaporate to about 100 cubic centimeters. In case anything has been separated, the fluid is filtered, compounded with nitric acid and heated. From the boiling hot solution, the chlorine is precipitated with silver nitrate solution, stirring constantly with a glass rod, until the precipitate balls together and the fluid becomes entirely clear. The silver chloride thus obtained is filtered off, washed with hot water, dried at 212° F., and, after detaching it as much as possible from the filter, brought into a previously weighed porcelain crucible. The filter is incinerated by itself upon the lid of the crucible and then added to the silver chloride in the crucible. Since by incineration the particles of silver chloride adhering to the filter have been partially reduced to silver, saturate the filter ash with a drop of nitric acid which is allowed to drop into the crucible from a glass rod. Then heat somewhat in order to dissolve the silver and add one drop of hydrochloric acid. The crucible is then heated, first very moderately, and then gradually more strongly, and, when no more vapors of nitrous acid escape, so strongly that the silver chloride fuses together to a regulus. Now allow the crucible to cool in the desiccator, then weigh it and deduct the filter ash. The quantity of the silver chloride found multiplied by the factor 0.247 gives the quantity of chlorine in the aqueous extraction (500 cubic centimeters equal to 250 grammes of soil dried at 212° F.).

b. Determination of sulphuric acid.—If the aqueous
extract of the soil contains sulphate, the sulphuric acid, as previously mentioned, is precipitated before the chlorine. Evaporate the 500 cubic centimeters mentioned on p. 107, to 100 cubic centimeters, filter, and into the boiling hot solution precipitate the sulphuric acid with barium nitrate solution.

Since the heavy precipitate consisting of barium sulphate generally carries down with it other salts, it must be again digested for some time with dilute hydrochloric acid, after being washed with hot water, dried and weighed. Then pour the supernatant hydrochloric acid through a very small filter and wash the precipitate, without taking it from the crucible, by decanting with hot water. Evaporate the filtrate and wash-water nearly to dryness in a platinum dish and bring the precipitate thereby separated also upon the filter. After washing, drying and incinerating the latter, add it to the other precipitate in the platinum crucible and ignite at a moderate red heat. Weigh the crucible after cooling in the desiccator.

The barium sulphate multiplied by the factor 0.343 will give the weight of sulphuric acid \((\text{SO}_3)\) present.

d. Determination of nitric acid.—Pour over 1000 grammes of the air-dry fine soil 2000 cubic centimeters of distilled water less the quantity of water calculated from the determination of the hygroscopic water which would escape from 1000 grammes of soil in drying at 212° F. Allow the soil to remain in contact with the water for forty-eight hours, shaking frequently. Then remove the supernatant clear fluid by means of a siphon provided with a suction-tube, and filter it through a dry filter into a liter-flask. One liter of this soil extract is
equal to 500 grammes of soil dried at 212° F. Compound this quantity of aqueous extract with a small quantity of pure sodium carbonate and evaporate it to about 100 cubic centimeters upon the water-bath. Any precipitate formed is filtered off, washed, and the filtrate again evaporated to 100 cubic centimeters.

For the determination of the nitric acid in these 100 cubic centimeters, it is best to use the method originated by Schoening and variously modified by T. Schulze as well as by Fruehling and Grouven, Reichardt, and Tiemann. It is based upon the reduction of the nitric acid by a solution of ferrous chloride in hydrochloric acid to nitric oxide, expelling the latter by boiling and collecting it. The chemical process takes place according to the following equation:

$$6\text{FeCl}_2 + 2\text{KNO}_3 + 8\text{HCl} = 4\text{H}_2\text{O} + 2\text{KCl} + 3\text{Fe}_2\text{Cl}_6 + 2\text{NO}; \text{ or } 6\text{FeCl}_2 + 2\text{HNO}_3 + 6\text{HCl} = 4\text{H}_2\text{O} + 3\text{Fe}_2\text{Cl}_6 + 2\text{NO}.$$

This method can be especially recommended, since the accuracy of the result is not in the least impaired even by the presence of dissolved humus constituents.

a. Tiemann's modification of Schoenig-Schulze's method for the determination of nitric acid.—Tiemann's modification has the advantage of yielding very accurate and reliable results with the use of an apparatus distinguished for simplicity.

The aqueous extract evaporated to 100 cubic centimeters is brought into a glass flask, A (Fig. 16), of one-half-liter capacity. It is closed by a doubly perforated rubber cork. Two glass tubes bent in the shape of a knee fit accurately into the perforations of the rubber cork. The tube, $c b a$, is at $a$, drawn out into not too
fine a point and projects about 2 centimeters below the rubber cork, while $c f g$ is exactly even with the lower surface of the cork. Both these tubes are connected by means of thin black rubber tubing with the tubes, $c d$ and $g h$. The rubber tubing can be hermetically closed by two strong clips, $c$ and $g$. The end of the tube $g h$ enters the so-called crystallizing glass dish, $B$, and projects with the point, which is bent upwards and covered with rubber tubing 2 to 3 centimeters into the measuring tube, $C$. The latter is graduated into tenths of cubic centimeters, and, like the glass dish, $B$, is filled with thoroughly boiled 10 per cent. soda lye prepared by dissolving 12.9 parts of caustic soda in 100 parts of water.

The fluid to be examined for a content of nitric acid is first boiled for one hour, the tubes being at first left
open and without $gh$ dipping into the dish $B$, in order to expel the air from the flask $A$ by aqueous vapor. The end of the tube $efgh$ is then brought into the caustic soda dish, without, however, dipping in the measuring tube, and the aqueous vapors are allowed to escape partially through the soda lye and partially through the tube $abcd$. After a few minutes, the tube is pressed together, at $g$, with the fingers; and when all the air has been expelled, the soda lye will reascend in the vacuum of the tube $gh$, which is recognized by a gentle blow on the fingers. If this is the case, the tube behind the place pressed together is closed with the clip $g$, and the vapors are allowed to escape through $abcd$. The fluid is kept boiling until evaporated to 10 cubic centimeters. The gas flame is now removed, the rubber tubing immediately closed at $c$, with the clip, and the tube $cd$ filled with thoroughly boiled water. Should an air bubble remain at $c$, it is removed by pressing with the finger.

The measuring tube is now filled with thoroughly boiled soda lye, and, after closing the opening with the thumb so that no air bubbles can enter, the tube is inverted and immersed over the lower end of the tube $gh$ into the soda lye.

When the tubes $e$ and $g$ are pressed together by the external pressure of air, the nearly saturated solution of ferrous chloride or ferrous sulphate compounded with some hydrochloric acid is brought into a beaker on the upper portion of which 20 cubic centimeters are divided off by two strips of paper pasted on the outside. Another beaker is filled with concentrated hydrochloric acid. Now dip the tube $cd$ into ferrous chloride solution,
and, after opening the clip $c$, allow 15 to 20 cubic centimeters to run into the flask. Then dip the tube $e\ d$ into the concentrated hydrochloric acid and let a small quantity of it rise twice until all the ferrous chloride is rinsed out of the tube $a\ b\ e\ d$. At $b$ a small bubble of hydrochloric acid is frequently formed, which completely disappears on heating the flask. Now heat the flask very moderately until the rubber tubings begin to swell up somewhat; then substitute the finger for the clip at $g$, and, as soon as the gas-pressure becomes somewhat stronger, allow the nitric oxide, expelled from the solution by heating, to pass over into the measuring tube. The boiling of the fluid is continued until an increase of the volume of gas in the measuring tube is no longer perceptible. By the vigorous absorption of hydrochloric acid gas by the soda lye, a crackling noise is made, but the end of the tube $g\ h$ being protected, as previously mentioned, by rubber tubing, its fracture need not be feared.

When the operation is finished, the tube $g\ h$ is removed from the dish, the measuring tube closed beneath the soda lye with the thumb, and, after shaking it, together with the soda lye still in it, in order to remove any traces of hydrochloric acid, immerse it in a large glass cylinder filled with water of $59^\circ$ to $64^\circ$ F.

The volume of nitric oxide can be read off after twenty minutes. For this purpose immerse the measuring tube so far into the water of the cylinder that the fluid in the measuring tube is at the same level with the fluid outside of it. In this case the nitric oxide is under the prevailing atmospheric pressure as indicated by the barometer.
Before reading off the volume of gas the measuring tube should be placed as vertically as possible. In reading off the volume of gas, the centre of the dark zone formed by the water drawing up on the glass is taken as the actual surface of the water, and the quantity of nitrogen evolved noted in whole and tenths of cubic centimeters.

The volume of every gas measured over water, hence in a moist state, is dependent on the temperature of the surroundings, the pressure of the atmosphere and the tension of the aqueous vapor. Hence, in reading off the volume of gas, the temperature of the water in the cylinder is noted as well as the height of the barometer, and the volume is calculated with regard to the tension of aqueous vapor at 0° C. and a pressure of 760 millimeters of mercury. The condition in which a dry volume of gas is, at 0° C., and a pressure of 760 millimeters is designated as the normal condition.

According to Mariotte's law, the volume of gas is inversely as the pressure, and since the expansion of a gas by heat amounts for each degree C. to \( \frac{1}{273} \) of the volume it occupies at 0° C., it follows, that in calculating the volume of gas to the normal state, the pressure exercised by the moist state must be deducted from the height of the barometer.

\[ V_0 = \frac{V \cdot 273 \cdot (B - f)}{(273 + t) \cdot 760} \]

In this formula \( V_0 \) means the volume of gas at the normal temperature (0° C.), \( V \) the volume of gas read off at the height of the barometer \( B \), and the temperature \( t \), while \( f \) indicates the tension of the aqueous vapor in the millimeters of pressure of mercury at \( t^o \) C.
The tension of the aqueous vapor is found from the following table:

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To calculate the nitric oxide found to nitric acid in grammes, multiply the number of cubic centimeters of nitric oxide calculated to the normal state by the factor 0.002413.

b. W. Wolf's method of determining the nitric acid by means of zinc in alkaline solution.—This method, which is distinguished by simplicity and accuracy, is based upon the reduction of nitrates to ammonia gas by zinc in alkaline solution through the hydrogen formed thereby.

Since the presence of humus substances impairs the experiment, the 1000 cubic centimeters of aqueous extract (p. 110) to be used for this purpose must, in case they show a brown coloration, be boiled with the addition of some pure milk of lime, whereby the humus substances are separated. After filtering the latter off, the excess of lime in the filtrate is precipitated by the introduction of pure carbonic acid and, after again filtering, the filtrate is evaporated to 100 cubic centimeters.
Now bring the fluid into a glass flask of about ½ liter capacity and compound it with soda lye, so that it contains about 14 grammes of soda. Close the flask quickly with a perforated rubber cork and insert a cylindrical funnel tube in the perforation. Close the top of the funnel tube with a rubber cork through which passes an open glass tube. Bring into the funnel tube glass beads moistened with hydrochloric acid, so that the hydrogen evolved can escape free from ammonia. The evolution of hydrogen is induced by placing a spiral of sheet zinc and sheet iron soldered together in the fluid. This gas is allowed to act upon the nitrates 4 to 5 hours at an ordinary temperature. The rubber cork is then carefully withdrawn, its lower surface rinsed off and, after rinsing the hydrochloric acid adhering to the glass beads into the flask by means of a wash-bottle, the spiral, which must also be rinsed off, is taken from the fluid with the aid of tweezers. Now quickly add some soda lye to the fluid, and connect the flask by means of the rubber cork with a glass receiver, in the other end of which a knee-shaped tube is inserted through a rubber cork. This glass tube reaches into an Erlenmeyer boiling flask containing about 10 cubic centimeters of pure dilute hydrochloric acid. The end of the tube in the receiver should not dip into the fluid, but be just above its surface. Now boil the fluid which contains the nitrogen in the form of ammonia until one-half of it has been distilled into the receiver.

The determination of the ammonium chloride contained in the distillate can be effected in various ways:

1. Determination of the ammonium chloride as ammonio-platinum after the conversion of the nitric acid into
ammonium chloride.—The above-mentioned distillate, which contains the sal ammoniac is evaporated to a small volume upon the water-bath and compounded in excess with pure platinum chloride solution free from nitric acid. The whole is then evaporated nearly to dryness upon the water-bath and a mixture of 2 volumes of absolute alcohol and 1 of ether added. The residue remaining undissolved, constituting a heavy pale-yellow powder, is brought upon a filter previously weighed and dried at 257° F., and washed with alcohol containing ether, of the above-mentioned composition. It is then dried at 257° F. and weighed in a tarred weighing flask. The result is not effected by a darker color of the precipitate.

If the metallic platinum is to be weighed, it is only necessary to heat the ammonio-platinum in a crucible covered with a lid. Heating must, however, be effected very gradually as otherwise the escaping vapors of chlorine and ammonium chloride might readily carry away particles of platinum. After detaching the precipitate as much as possible, the filter is incinerated by itself and then added to the mass. To obtain the equivalent of nitric acid, multiply the ammonio-platinum by 0.241, or the platinum by 0.547.

2. Volumetric determination by the Knop-Wagner azotometer of the nitrogen in the ammonium chloride after converting the nitric acid into ammonium chloride.—This method is based upon the process that a sal ammoniac solution is decomposed by sodium bromide solution, nitrogen being liberated: 3(BrONa) + 2(NH₄Cl) = 3(BrNa) + 3(OH₂) + 2HCl + 2N.

The solution of sodium bromide is prepared as fol-
lows: Dissolve 100 grammes of caustic soda in 1250 cubic centimeters of distilled water, cool the solution and add, with constant shaking, 25 cubic centimeters of bromine. This lye is gradually decomposed by light and must, therefore, be kept in a dark bottle. Fifty cubic centimeters of it are capable of evolving 130 to 150 cubic centimeters of nitrogen from sal ammoniac solution.

The Knop-Wagner azotometer (Fig. 17) is arranged as follows: The bottom of the developing vessel is cemented in a metallic ring and loaded with lead. It is partitioned off into divisions by a glass wall not reaching quite to the top; one of these divisions is filled with sal ammoniac solution and the other with bromine lye. It is necessary to constantly retain a determined proportion of volume of the two fluids. Hence, the distillate mentioned on p. 117 is evaporated nearly to dryness in a porcelain dish and, after filling a pipette, holding 10 cubic centimeters, with distilled water, a few drops are added to dissolve the sal ammoniac. This solution is poured through a long funnel-tube into one of the divisions of the developing vessel, the porcelain dish and funnel-tube being rinsed out with the water remaining in the pipette. Into the other division 50 cubic centimeters of bromine lye, prepared according to the directions given above, are introduced by means of a pipette. The developing vessel being closed with a rubber cork, it is immersed in the cooling vessel so that the rubber cork is just covered with water. This cooling vessel, as well as the tall glass cylinder, is filled with cool water of the same temperature. Through the rubber cork of the developing vessel passes a glass tube provided with
a glass stop-cock which is connected by means of rubber tubing with the graduated glass tube in the cylinder.

The glass stop-cock is loosened or taken out, and the communicating tubes inclosed in the glass cylinder are filled with water by compressing the rubber ball provided with a hole, the clip being opened at the same time. By discharging the water through the clip, the lower meniscus of the surface of the water is exactly brought to the 0 point of the graduated tube. After 5 minutes the glass stop-cock is firmly replaced, but so that the developing vessel remains in communication with the graduated tube. Now wait 5 minutes, and
then observe whether the surface of the water in the graduated tube has risen in consequence of the contraction of the air due to cooling off. This being the case the glass stop-cock is once more loosened, then firmly replaced and, after 5 minutes, the height of water in the graduated tube again observed. This is repeated until the water level remains constant at the 0 point. The developing vessel is now taken from the cooling cylinder and, after discharging 20 to 30 cubic centimeters of water through the clip, the bromine lye is gradually allowed to flow into the sal ammoniac solution by inclining the developing vessel. The evolution of nitrogen is promoted by swinging the glass. The glass stop-cock is now closed, and, after vigorously shaking the developing flask, the stop-cock is again opened and the developed nitrogen allowed to pass into the graduated tube, this operation being repeated three times. The developing vessel is now replaced in the cooling cylinder and brought into communication with the graduated tube by means of the glass stop-cock. After 15 minutes it has acquired the same temperature as before, and sufficient water is either discharged or added through the clip to bring the level in the two communicating tubes to the same height. Now read off the number of cubic centimeters of nitrogen evolved, the temperature indicated by the thermometer in the cylinder, and the height of the barometer.

Since the fluid in the developing vessel has absorbed a not inconsiderable quantity of nitrogen, it has to be taken into calculation. In order to utilize, for this purpose, the following table by Dietrich, it is necessary always to use exactly 10 cubic centimeters of the fluid
to be examined and 50 cubic centimeters of bromine lye of the above-mentioned concentration, since the quantity of gas absorbed also changes with the concentration and quantity of the fluid.

*Dietrich's table for the absorption of nitrogen in 60 cubic centimeters developing fluid (50 cubic centimeters of bromine lye and 10 cubic centimeters of water), with a specific gravity of the lye of 1.1, and such a strength that 50 cubic centimeters correspond to 200 cubic centimeters of nitrogen, with an evolution of 1 to 100 cubic centimeters of nitrogen.*

<table>
<thead>
<tr>
<th>Evolved : ccm.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbed : ccm.</td>
<td>0.06</td>
<td>0.08</td>
<td>0.11</td>
<td>0.13</td>
<td>0.16</td>
<td>0.18</td>
<td>0.21</td>
<td>0.23</td>
<td>0.26</td>
<td>0.28</td>
</tr>
</tbody>
</table>

| Evolved : ccm. | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  | 19  | 20  |
| Absorbed : ccm. | 0.31 | 0.33 | 0.36 | 0.38 | 0.41 | 0.43 | 0.46 | 0.48 | 0.51 | 0.53 |

| Evolved : ccm. | 21  | 22  | 23  | 24  | 25  | 26  | 27  | 28  | 29  | 30  |
| Absorbed : ccm. | 0.56 | 0.58 | 0.61 | 0.63 | 0.66 | 0.68 | 0.71 | 0.73 | 0.76 | 0.78 |

| Evolved : ccm. | 31  | 32  | 33  | 34  | 35  | 36  | 37  | 38  | 39  | 40  |
| Absorbed : ccm. | 0.81 | 0.83 | 0.86 | 0.88 | 0.91 | 0.93 | 0.96 | 0.98 | 1.01 | 1.03 |

| Evolved : ccm. | 41  | 42  | 43  | 44  | 45  | 46  | 47  | 48  | 49  | 50  |
| Absorbed : ccm. | 1.06 | 1.08 | 1.11 | 1.13 | 1.16 | 1.18 | 1.21 | 1.23 | 1.26 | 1.28 |

| Evolved : ccm. | 51  | 52  | 53  | 54  | 55  | 56  | 57  | 58  | 59  | 60  |
| Absorbed : ccm. | 1.31 | 1.33 | 1.36 | 1.38 | 1.41 | 1.43 | 1.46 | 1.48 | 1.51 | 1.53 |

| Evolved : ccm. | 61  | 62  | 63  | 64  | 65  | 66  | 67  | 68  | 69  | 70  |
| Absorbed : ccm. | 1.56 | 1.58 | 1.61 | 1.63 | 1.66 | 1.68 | 1.71 | 1.73 | 1.76 | 1.78 |

| Evolved : ccm. | 71  | 72  | 73  | 74  | 75  | 76  | 77  | 78  | 79  | 80  |
| Absorbed : ccm. | 1.81 | 1.83 | 1.86 | 1.88 | 1.91 | 1.93 | 1.96 | 1.98 | 2.01 | 2.03 |

| Evolved : ccm. | 81  | 82  | 83  | 84  | 85  | 86  | 87  | 88  | 89  | 90  |
| Absorbed : ccm. | 2.06 | 2.08 | 2.11 | 2.13 | 2.16 | 2.18 | 2.21 | 2.23 | 2.26 | 2.28 |

| Evolved : ccm. | 91  | 92  | 93  | 94  | 95  | 96  | 97  | 98  | 99  | 100 |
| Absorbed : ccm. | 2.31 | 2.33 | 2.36 | 2.38 | 2.41 | 2.43 | 2.46 | 2.48 | 2.51 | 2.53 |

Calculate first to the normal condition, according to the formula given on p. 115, the quantity of nitrogen read off in the graduated tube, taking into consideration the tension of the aqueous vapor. Then take from Dietrich's table the quantity of gas absorbed at the volume evolved. Add this to the quantity of nitrogen calculated to the
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normal state and the equivalent quantity of nitric acid is obtained by multiplying by the factor 0.0048452.

3. Special method in the examination of peat.—Peat moors, which are to be cultivated, require special examination. A determination of ash by carefully igniting the substance dried at 212° F. will always have first to be executed. The content of carbonic acid in the ash is to be determined and deducted from the per cent. of ash.

About 10 grammes of the ash are used for an aqueous extract, and the calcareous earth, magnesia, potassium, sodium, sulphuric acid, and chlorine contained therein are determined. The residue remaining from the aqueous extract is boiled with concentrated hydrochloric acid, and, after separating the silica, alumina, ferric oxide, calcareous earth, magnesia, potassium, sodium, and phosphoric acid are determined. The residue remaining thereby is, after boiling with sodium carbonate solution, designated as sand.

II. Extraction of the soil with carbonated water.—Pour over 1500 grammes of air-dry soil in a flask 6000 cubic centimeters of water $\frac{1}{4}$ saturated with carbonic acid, less the quantity of water escaping from the air-dry soil at 212° F. Then close the flask and shake. The water $\frac{1}{4}$ saturated with carbonic acid is prepared by completely saturating, at an ordinary temperature and with a medium pressure of air, 1500 cubic centimeters of distilled water with carbonic acid and diluting with 4500 cubic centimeters of distilled water. The soil remains in contact with the water for three days, the flask being frequently rolled upon a soft support. The soil is then allowed to settle and 5000 cubic centimeters
of the supernatant clear fluid are siphoned off in two separate portions, one of 1000 and the other of 4000 cubic centimeters. The two fluids are then allowed to stand quietly in hermetically closed flasks for twenty-four hours, when they are filtered off clear without stirring up the sediment. During this operation the filtering funnel should be kept covered.

The 1000 cubic centimeters, which correspond to 250 grammes of soil dried at 212° F., are now gradually evaporated to dryness in a small weighed platinum dish upon the water-bath. The residue is dried in the air-bath at 257° F., and quickly weighed after cooling in the desiccator. By this means the sum total of the substances dissolved in the carbonated water is found. The mass is then moderately ignited, several times moistened with ammonium carbonate, again ignited, cooled in the desiccator, and once more weighed. In this manner the sum total of the refractory inorganic salts is obtained, and their content of carbonic acid can best be determined by the method given on p. 64. The determination of the carbonic acid being finished, the fluid in the flask may further be used for the qualitative determination of the presence of the various constituents.

The greater portion of the carbonated aqueous extract (4000 cubic centimeters corresponding to 1000 grammes of the soil dried at 212° F.) is also filtered. In case the filtrate is not entirely clear, E. Wolff proposes to evaporate the fluid to 400 cubic centimeters, slightly over-saturate it, while still hot, with hydrochloric acid, and to filter off the small quantity of insoluble clay. To destroy the humus substances, as well as to oxidize the iron, the fluid is compounded with a
few drops of nitric acid and evaporated to pulverulent dryness by heating it in a porcelain crucible, several times moistening the substance with water when it becomes dry, and rubbing it to a powder with a glass pestle. The mass is then moistened with hydrochloric acid, and, after adding boiling water, the fluid is filtered to separate silica. In the filtrate, *alumina, ferric oxide, phosphoric acid, calcareous earth, magnesia, sulphuric acid, potassium, and sodium* are determined.

The fluid is now heated to boiling and compounded with ammonia slightly in excess. A weighable precipitate of *ferric oxide* will only be formed with acid humus soils. If, however, the precipitate is too small to be weighed, redissolve it by adding a few drops of hydrochloric acid, compound the boiling-hot solution with a few drops of very dilute ferric chloride solution and again precipitate with ammonia slightly in excess. The precipitate contains the entire quantity of phosphoric acid dissolved in the carbonated water as ferric phosphate (FePO₄). Filter the precipitate off, wash it with hot water until a drop running off from the funnel is no longer made turbid by silver nitrate, and then detach it as much as possible from the filter with a feather. The particles of the precipitate still adhering to the filter are dissolved with hot dilute nitric acid by allowing the latter to fall drop by drop upon the filter and placing the beaker containing the detached precipitate underneath the filter. Wash the filter with hot water. Then heat the fluid in the beaker and add nitric acid until the precipitate is dissolved. The solution is evaporated to a small quantity in a porcelain dish and rinsed with as little water as possible into the beaker.
Precipitation of the phosphoric acid with ammonium molybdate and weighing as magnesium pyrophosphate.—

The ammonium molybdate solution required for the precipitation of the phosphoric acid is prepared as follows: Dissolve 40 grammes of ammonium molybdate in 80 cubic centimeters of concentrated ammonia and 320 cubic centimeters of distilled water and slowly pour the fluid, with constant stirring, into a mixture of 480 cubic centimeters of nitric acid (1.18 specific gravity), and 120 cubic centimeters of water.

Of the solution thus prepared, add an abundant quantity to the fluid to be examined, and let the mixture stand for twelve hours at 104° F. During this time the phosphoric acid separates as ammonium phosphomolybdate in the form of a yellow granular crystalline precipitate. Now siphon off a small portion of the supernatant clear fluid, and test it as to whether a precipitate is again formed after once more adding ammonium molybdate solution and standing for some time. If such is the case, the test sample is again added to the whole, and, after adding fresh ammonium molybdate solution, it is again allowed to stand for twelve hours at 104° F.

The supernatant fluid is then poured off through a small filter, and the precipitate in the beaker repeatedly washed, by decanting, with a mixture of 100 parts of ammonium molybdate solution, 20 parts of nitric acid of 1.2 specific gravity, and 80 parts of water. To be sure that all the iron is in the filtrate, the wash-water running off from the filter towards the end of the operation should not yield a precipitate on being compounded with ammonia. Now place the beaker containing the
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washed precipitate under the funnel, dissolve any particles of the precipitate adhering to the filter in a few drops of concentrated ammonia, and wash the filter with a mixture of one volume ammonia and three volumes water. If the precipitate in the beaker does not dissolve entirely clear, the fluid must be again poured through the filter before washing the latter. To the clear filtrate add, drop by drop, hydrochloric acid until the yellow precipitate formed thereby only disappears after repeated shaking. Then precipitate the phosphoric acid as ammonium magnesium phosphate with magnesia mixture. The magnesia mixture is prepared as follows: Dissolve 1 part of crystallized magnesium sulphate and 2 parts of ammonium chloride in 8 parts of water, and 4 parts of ammonia. The precipitate is washed, as given on p. 71, with ammoniacal water, dried, ignited, and weighed as magnesium pyrophosphate. To calculate from this the phosphoric acid, multiply the weighed quantity by the factor 0.64.

* Determination of the phosphoric acid as ammonium phospho-molybdate, according to R. Finkener.*—By this method the precipitation of the phosphoric acid with magnesia mixture is avoided, and it has the further advantage that even in the presence of very small quantities of phosphoric acid, a comparatively large weight is brought upon the balance.

When the phosphoric acid has been precipitated, after adding 25 per cent. ammonium nitrate, with ammonium molybdate in the manner described on p. 126, the precipitate is brought upon a small filter and washed with a solution of ammonium nitrate, which contains 20 per cent. of the salt and is previously mixed with \( \frac{1}{30} \) its volume of nitric acid. Washing is finished when the
solution running off is no longer immediately colored by yellow prussiate of potash.

When the greater portion of the ammonium nitrate has been removed by washing with some water, the precipitate is injected by means of a wash-bottle from the filter into a weighed porcelain crucible. What adheres to the paper is detached with heated liquid ammonia, and after concentrating this solution by evaporating and oversaturating it with nitric acid, it is also brought into the crucible. After the fluid is first evaporated upon

Fig. 18.

the water-bath, the crucible is placed by means of a triangle upon Finkener’s drying stand (Fig. 18), in which the flame is cooled off by three different wire screens placed one above the other. Only a moderate
heat is required for the expulsion of the ammonium nitrate. The operation is finished when a watch-crystal placed over the crucible is not tarnished. The ammonium phospho-molybdate remaining in the crucible contains for 1 part of phosphoric acid \((P_2O_5)\) 24 parts of molybdate \((M_6O_3)\). It is placed, while hot, in the desiccator filled with sulphuric acid and, when cold, quickly weighed since it is hygroscopic. To calculate the salt to the equivalent quantity of phosphoric acid \((P_2O_5)\), multiply the weighed quantity by the factor 0.03794.

Further treatment of the soil extract prepared with carbonated water.—The filtrate from the precipitate with ammonia (p. 125) is heated to boiling and the calcareous earth precipitated with ammonium oxalate in the manner given on p. 68 et seq.

After the calcium oxalate has been filtered off, evaporate the fluid to about 10 cubic centimeters, compound it with a few drops of hydrochloric acid until it shows an acid reaction, and precipitate the sulphuric acid with barium chloride solution without, however, adding too large an excess of it. The precipitate, consisting of barium sulphate, is treated in the same manner as described on p. 109 for the determination of sulphuric acid in the aqueous extract.

In the filtrate the excess of barium sulphate is precipitated by a few drops of sulphuric acid, the precipitate filtered off and the fluid after being neutralized with ammonia is evaporated, with constant stirring, to dryness in a platinum dish. The ammoniacal salts are then expelled by igniting, the residue is taken up with some hydrochloric acid and water, and filtered in case some more barium sulphate has separated. From the
very concentrated solution, the magnesia is precipitated by ammonium carbonate (compare p. 104 et seq.). Weigh
the alkalies as sulphates and separate the potassium by precipitating with platinum chloride and taking up the
precipitate with the mixture of hydrochloric acid, alcohol and ether, in the manner described on p. 108.

III. Extraction of the soil with cold concentrated hydrochloric acid.—Pour over 200 grammes of air-dry
soil in a cylinder, which can be closed with a glass stopper, 400 grammes of pure concentrated hydrochloric
acid and allow the latter to act upon the substance at the ordinary temperature of a room, for forty-eight hours,
shaking the cylinder frequently. The hydrochloric acid is then much diluted, poured off through a filter, and
the soil washed by repeatedly decanting it with hot water until a drop running off from the funnel shows
no reaction with silver nitrate.

The separation of the dissolved substances is effected in the same manner as with soil treated with boiling
concentrated hydrochloric acid.

IV. Extraction of the soil with boiling concentrated hydrochloric acid.—Only in a few cases will it be possible
to simultaneously prepare the four extracts mentioned on p. 102, they requiring much labor and time.
Hence, as a rule, the experimenter will have to be satisfied with one extract, and, in such a case, it is best to
choose that with boiling concentrated hydrochloric acid, which, as previously mentioned, contains the sum-total
of all the plant-nourishing substances available at the present and becoming active in the future.

Of sand soils weigh out 100 grammes, and of clay soils 50 grammes of the air-dry fine soil. Bring the
weighed out quantity into an Erlenmeyer boiling flask and pour over it, in the first case, 200, and in the latter, 100 cubic centimeters of pure concentrated hydrochloric acid of 1.15 specific gravity. Put the boiling flask upon a sand-bath (Fig. 19), and place upon it a small funnel, c, with a short tube, using, however, the precaution of inserting between the neck of the flask and the funnel a small piece of a glass rod, b, bent at an angle of 45°, so that in boiling the vapors can escape unrestrained, and the scattering of the fluid through the funnel tube is prevented.

The soil is boiled with the acid exactly one hour. Then add a large excess of distilled water, stir with a glass rod, and allow the soil to settle. When the supernatant fluid is clear, pour it off through a filter and wash the soil in the boiling flask by decanting with hot water until a drop running off from the filter shows no turbidity with silver nitrate.

The clear filtrate is compounded with some nitric acid, and, to separate the dissolved silica, is then brought to dusty dryness in a porcelain dish upon the water-bath. The separation of the silica must be very carefully done, as otherwise it will erroneously affect the determination of phosphoric acid.

The filtrate from the silica is compounded hot with ammonia, the ferric oxide and alumina being thereby precipitated. Then add a few drops of acetic acid
until the fluid shows a slight acid reaction and boil again. The precipitate which, as a rule, is considerable, is brought upon two large rapidly filtering filters, thoroughly washed with hot water, and then detached as much as possible from the filters with the aid of a feather. The particles adhering to the filters, as well as the detached precipitate, are dissolved in hot dilute nitric acid. Bring the solution into a flask of 500 cubic centimeters capacity, and take 100 cubic centimeters of it by means of a pipette for the determination of iron and alumina. The remaining 400 cubic centimeters are evaporated to a small quantity and used for the determination of phosphoric acid according to the method described on p. 127. In the 100 cubic centimeters, precipitate the ferric oxide and alumina with ammonia, weigh the ignited precipitate, dissolve it in hydrochloric acid or potassium sulphate, and determine the iron by titration with potassium permanganate solution in the manner described on p. 87 et seq.

The total filtrate of the principal precipitate is compounded with ammonium sulphide, whereby the manganese is precipitated as manganous sulphide. The precipitate is filtered, washed with water containing ammonium sulphide, and, after drying, incinerated, together with the filter, in a weighed crucible. Now add some flowers of sulphur, heat the crucible in a current of hydrogen and let it also cool in it. The green residue in the crucible consists of manganous sulphide (M₄S₉), which, after cooling in the desiccator, is weighed. The equivalent quantity of manganous oxide is obtained by multiplying the manganous sulphide by the factor 0.877.
The filtrate from the precipitate with ammonium sulphide is over-saturated with hydrochloric acid and boiled until the, at first, milky sulphur separated, balls together on the bottom, and the supernatant fluid is clear. The sulphur is filtered off, the filter washed, and the calcareous earth, magnesia, and alkalies are determined in the filtrate in the manner given on p. 104 et seq.

If the quantity of silica separated in soluble form in the extract with hydrochloric acid is to be determined, the silica which has been dissolved in the hydrochloric acid and separated in an insoluble form in evaporating the latter, must be weighed as well as that remaining in soluble modification in the soil. For this purpose repeatedly boil the soil-residue from the extract with hydrochloric acid with concentrated sodium carbonate solution to which some soda lye has been added. Then filter off the soil and over-saturate the filtrate with hydrochloric acid by covering it with a watch crystal and slowly adding the acid drop by drop. The fluid is then evaporated to dusty dryness, the residue taken up with hydrochloric acid, diluted with distilled water and the silica, separated in an insoluble form, ignited and weighed in the manner described on p. 97 et seq.

B. Determination of some important substances for the nourishment of plants, which can either not, or only partially, be determined in the soil-extracts. 1. Determination of the total nitrogen in the soil. a. Kjeldahl's method.—This process was devised by J. Kjeldahl, of Copenhagen. It is based upon the theory that the substance, which is to be used dry, is so altered by boiling for some time with an abundant quantity of concentrated sulphuric acid, that by the succeeding oxidation
with dry pulverulent potassium permanganate, all the nitrogen is converted into ammonia. A modified process adapted for the investigation of soils is as follows:—

The substance dried at 212° F. is poured from a long thin weighing tube into a boiling flask of 100 cubic centimeters capacity, care being had that no substance remains adhering in the neck. With humus and peat soil 0.5 to 1 gramme of the finely pulverized soil is used, and with humus sand soils and fat and clammy soils 2 to 5 grammes. Then add 20 cubic centimeters of a mixture of 16 volumes of pure concentrated sulphuric acid, 4 of pure fuming sulphuric acid, and 2 grammes of anhydrous phosphoric acid, place the boiling flask in an oblique position upon the sand-bath and boil the fluid until it has acquired a wine-yellow color. Then remove the flame, and, after cooling somewhat, add to the solution, while still hot, an excess of dry pulverulent potassium permanganate in small portions until the solution has acquired a blue-green color. After cooling, the solution is brought into a boiling flask holding one liter (Fig. 20), and diluted with distilled water to 200 cubic centimeters. The boiling flask is connected by means of a rubber cork with an obliquely ascending glass tube expanding to a bulb, which enters a glass receiver. From the other end of the receiver a tube leads into an Erlenmeyer boiling flask which contains some pure dilute hydrochloric acid in which, however, the tube need not to dip. Now open the rubber cork, add to the fluid 80 cubic centimeters of soda lye which contains 50 grammes of caustic soda, and quickly replace the cork upon the boiling flask. Now distil the fluid
for half an hour, during which time the ammonia is completely expelled and absorbed by the hydrochloric acid in the receiver. The hydrochloric acid is evaporated to dryness, rinsed with 10 cubic centimeters of distilled water into the developing vessel of the Knop-Wagner azotometer and the nitrogen determined volumetrically by decomposing the sal ammoniac with bromine lye (compare p. 118).

b. Determination of the nitrogen by combustion with soda lime.—For this determination use a tube of hard glass of the form shown in Fig. 21. Before drawing the tube out it is thoroughly cleansed, and, after heating,
dried by sucking out the air. Now first slip into the tube a loosely fitting plug of asbestos, previously ignited, and then a layer of 3 to 4 cubic centimeters of soda lime free from nitric acid previously moderately heated in a porcelain dish, and which, for use, should have a temperature of 104° to 122° F. Now weigh out 1 to 10 grammes of fine soil finely pulverized and dried at 212° F., and mix it in a porcelain mortar with some warm, finely pulverized soda lime and about \( \frac{1}{2} \) gramme of pure cane sugar. Introduce the mixture, while warm, into the combustion tube, forcible pressure being carefully avoided. The mixture is followed by a layer of soda lime used to rinse the mortar. Then add enough granulated soda lime to fill the tube to about 4 centimeters of the open end and place another plug of ignited asbestos at the end. In the tube is inserted, by means of a rubber cork, the end of a Will-Varrentrapp apparatus, which is previously filled, by means of a pipette, to one-quarter of its volume with pure distilled water, and 1 cubic centimeter of pure concentrated hydrochloric acid, as shown in Fig. 21. The hydrochloric acid used must first be tested as to its purity; and should leave no residue after evaporating with platinum chloride and taking up the mass with alcohol.

Before placing the tube in the combustion furnace, a free passage is formed for the evolved gases by a few gentle taps. The tube is then gradually heated commencing at the fore part nearest the cork and progressing slowly towards the tail. Care must be taken to keep the fore part of the tube at a moderate red heat throughout the process. The addition of sugar is claimed to promote the conversion of the nitrogen into ammonia.
Combustion is finished when no more black carbonaceous particles are perceptible in the substance. Now break off the point of the ascending tube and at the same time put out the gas. Then by means of an aspirator connected by rubber tubing with the end of the Will-Varrentrapp apparatus draw a slow current of air through the apparatus. Now pour the fluid from the Will-Varrentrapp apparatus into a porcelain dish, rinse out with water, and evaporate nearly to dryness. By now taking the residue up with some water, the greater portion of tarry substances formed by combustion remains in the dish. The fluid containing the sal ammoniac is evaporated nearly to dryness in a small dish upon the water-bath, and the nitrogen determined either volumetrically in the Knop-Wagner azotometer (see p. 118 et seq) or weighed as ammonio-platinum (see p. 117).

2. Determination of the ammonia contained in the soil.—As a rule soils contain but small quantities of ammoniacal gas and ammoniacal salts, they being generally rapidly oxidized to nitric acid. To determine them, it is best to fill the soil taken from the field in its natural moist condition into a wide-necked glass flask, close the latter hermetically and use the soil for analysis as soon as possible after being taken from the field. The methods based upon distilling the soil compounded with water with soda lye or manganic oxide and catching the escaping ammonia in a receiver do not yield accurate results, since after the expulsion of the ammonia already formed, the nitrogenous organic substances are also attacked and constantly yield small quantities of ammonia. The following method can, however, be recommended:
Schlossing's modified method for the accurate determination of the ammonia in the soil.—Introduce 100 grammes of the soil into a liter flask, and at the same time determine, from the loss, the water which escapes at 212° F. from about 20 grammes of the sample used, so that later on the content of ammonia can be calculated to substance dried at 212° F.

Pour over the soil in the flask, 100 cubic centimeters of distilled water, and add from a burette concentrated hydrochloric acid, until any carbonic acid present is completely expelled, and the fluid contains an excess of hydrochloric acid. To the measured quantity of hydrochloric acid, previously tested as to its purity by evaporating with platinum chloride, add sufficient distilled water to make exactly 400 cubic centimeters of fluid. Then close the liter flask with a rubber cork, shake vigorously and allow the soil to settle, for which 6 to 12 hours are required. The supernatant clear fluid is then quickly poured through a dry, folded filter, and 200 cubic centimeters of the filtrate, corresponding to 5 grammes of the soil used, are taken out with a pipette. Evaporate these 200 cubic centimeters to 10 cubic centimeters in a room free from ammonia and rinse them into a half liter flask, so that the fluid amounts to about 100 cubic centimeters. Now add concentrated soda lye until it is present in excess, introduce some granulated zinc into the flask and distil off one-half of the fluid through a receiver into an Erlenmeyer boiling flask, which contains some dilute hydrochloric acid for the reception of the ammoniacal gas. When distillation is finished, the distillate is evaporated nearly to dryness and the nitro-
gen volumetrically determined in the Knop-Wagner azotometer.

If, now, the cubic centimeters of nitrogen calculated to the normal condition are multiplied by the factor 0.001525, the content in grammes of ammoniacal gas (\( \text{NH}_3 \)) in 50 grammes of the soil used is obtained.

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VIII.

DETERMINATION OF THE SUBSTANCES IN THE SOIL INJURIous TO THE GROWTH OF PLANTS.

The presence of certain substances in the soil may essentially influence the growth of plants, and in many cases render it even entirely impossible. Among these so-called poisons to cultivated plants may be included: Humic acids showing an acid reaction, too large quantities of common salt, free sulphuric acid, ferrous sulphate, and iron bisulphide. In many cases the establishment of the presence of these substances suffices without the necessity of their quantitative determination. Their presence can be partially shown in preparing the aqueous extract for the determination of the plant-nourishing substances.

1. *Proof of the presence of free humic acids in the soil.*—If the aqueous extract of a humus soil shows a distinct acid reaction towards litmus-paper; and when the presence of sulphuric acid cannot be established by barium chloride, the acid will have to be traced back to humus substances. Soils showing this phenomenon generally also suffer from too much moisture, and the
field will have to be sufficiently drained by ditches or raised by carting sand upon it. Liming and marling will also be of advantage for fixing the humic acids.

2. *Determination of the content of common salt in the soil.*—Voelker's and Grandeaup's investigations have shown that a soil becomes unproductive when its content of common salt exceeds 0.1 per cent. In discussing the aqueous extract for the estimation of the plant-nourishing substances, the determinations of the content of chlorine and sodium have been considered. In most cases the quantity of chlorine found can be directly calculated to sodium.

3. *Determination of the ferrous sulphate, free sulphuric acid, and iron disulphide.* The occurrence of ferrous sulphate (green vitriol) or free sulphuric acid is dependent on the presence of iron disulphide in the soil. Iron pyrites which, according to Fleischer's investigations, are occasionally found in the soil, yield by their oxidation through oxygen free sulphuric acid and ferrous sulphate \( \text{FeS}_2 + 7 \text{O} = \text{SO}_3 + \text{FeSO}_4 \). These combinations will always be formed when not sufficient bases, especially lime, are present for their saturation. The presence of iron disulphide in the sands under peat moors has several times caused complete failures in the establishment of the Rimpau moor-dam cultivation, in which such sand was brought upon the moor. Hence, it is of importance to examine the moor soil to be cultivated, as well as the sand to be used, in regard to these injurious substances.

In the Prussian moor experimental station at Bremen, the following methods are used:—

Of the moor or sand to be examined, an aqueous
extract is prepared and tested for the presence of ferrous oxide by adding solution of red prussiate of potash. The presence of ferrous oxide is immediately recognized by the blue coloration of the fluid. Any acid reaction is determined by litmus paper.

In the aqueous extract of 100 grammes of soil, potassium, sodium, calcareous earth, magnesia, ferrous or ferric oxide, chlorine, and sulphuric acid are determined, and the bases calculated to the acids present. The excess of sulphuric acid can be designated as free.

a. *Determination of the content of sulphur in the soil by ignition.*—Ignite 20 grammes of the fine soil extracted with water and dried in a Bohemian glass tube in a current of air, whereby any iron pyrites present are decomposed and the sulphur is transformed into sulphuric and sulphurous acids.

First slip a plug of glass-wool into the tube (Fig. 22), then pour the substance loosely upon it and insert another plug of glass-wool. The tail end of the tube communicates with a vessel filled with water which serves for controlling the current of air to be used in the combustion. The fore part of the tube is drawn out, bent at a right angle downward and connected with an absorbing vessel filled with potash lye free from sulphuric acid. By means of the aspirator attached to the absorbing vessel a current of air can be constantly conducted through the combustion tube. Between the absorbing vessel and the aspirator is first a funnel tube with glass beads moistened with potash lye, and next a bulb tube containing some neutral litmus solution, which during the operation should not change its color. The tube is placed in a combustion furnace and gradually heated to
a red heat, commencing at the tail and progressing slowly towards the fore part. When the tube is ignited throughout its whole length, the products of distillation condensed in the drawn out portion of the tube are

finally, by means of a flame, forced down as far as possible, so that when the operation is finished they can be readily rinsed out with the wash-bottle. The potash lye is oversaturated with hydrochloric acid, compounded with bromine, to convert the sulphurous acid into sulphuric acid, and the bromine removed by boiling. Now precipitate the sulphuric acid with barium chloride, observing the precautionary measures given on p. 110, since the heavy precipitate in the concentrated common salt solution generally carries alkali down with it. With peats it is advisable to ignite the substance in a current of oxygen.

By igniting the soil in a tube the entire quantity of sulphuric acid contained in it is not obtained, but in the
investigations of the moor experimental station at Bremen this method has proved itself as sufficiently accurate.

From the above-mentioned methods, Fleischer calculates the sulphuric acid present in a form injurious to plants as follows:

1. Present as free acid (the residue of sulphuric acid which remains after calculating the acid to the bases of the aqueous extract).

2. Sulphuric acid contained in ferrous sulphate (calculated from the content of ferrous oxide in the aqueous extract).

3. Sulphuric acid which may be formed from iron disulphide (obtained by igniting the soil extracted with water).

b. Determination of the content of sulphur in the soil by disintegration with bromine.—Fuse 5 to 10 grammes of the finely powdered soil extracted with water with 20 cubic centimeters of distilled water and 5 cubic centimeters of pure bromine free from sulphuric acid in a Bohemian glass tube, and gradually heat, with frequent shaking, to 158° F. upon the water bath. By the bromine the sulphur present is oxidized to sulphuric acid. When entirely cold the tube is opened in the manner described on p. 84, the contents are rinsed into a beaker, diluted with water, and heated until an odor of bromine is no longer perceptible. Now filter the soil off, and precipitate the sulphuric acid in the filtrate in the above-mentioned manner. The sulphuric acid obtained from the aqueous extract is then deducted from the total sulphuric acid, and the rest calculated to sulphur by multiplying it by the factor 0.4.
In the presence of large quantities of gypsum this method is not available, as, in this case, all the sulphates are not extracted by the aqueous extract.

IX.

DETERMINATION OF VARIOUS PROPERTIES OF THE SOIL WHICH ARE DEPENDENT PARTIALLY ON PHYSICAL AND PARTIALLY ON CHEMICAL CAUSES.

A. Weight of the soil.—We distinguish the specific gravity, and the absolute volume or liter weight of the soil. For determining them the following methods are suitable:—

1. Determination of the specific gravity.—A thin glass flask of about 100 cubic centimeters capacity, and provided with a ground-glass stopper, drawn out to an open capillary tube, is filled up to the end of the capillary tube with distilled water of 60.8° F. The flask being carefully cleansed with a piece of leather, is then accurately weighed upon a chemical balance. The flask is then emptied, and a weighed quantity (about 20 grammes) of the soil dried at 212° F., and boiled with distilled water is, when cold, introduced, and sufficient water of 60.8° F. added to entirely refill the flask. It is then weighed. By adding the weight of the soil used to the weight of the flask filled with water and deducting therefrom the weight of the flask filled with water and the soil, the difference expresses the weight of a volume of water which is equal to that of the quantity of soil used. Since, by this means the proportion of the
weights of equal volumes of soil and water are found, the specific gravity of the soil can, therefrom, be deduced by dividing the weight of the soil with the weight of the water it has displaced.

2. *Determination of the volume weight.*—The volume or liter weight can be determined in two ways, by bringing the soil into a measuring vessel, either in an air-dry state, or saturated with water.

Only the first-mentioned method is, according to R. Heinrich’s experiments, required for soils containing but little humus, it yielding nearly the same results as saturation with water.

For this purpose fill a measuring cylinder of 100 cubic centimeters capacity, with air-dry soil pulverized as uniformly as possible, by introducing the soil in small portions and compacting it by gently tapping the vessel upon a cork support until a diminution in volume no longer takes place. According to the kind of soil, one-half to one hour will be required for this process, care being taken that during the operation the measuring vessel is always filled with soil up to the mark. Determine at the same time with a special sample the hygroscopic water which escapes at 212° F., the volume weight ascertained by weighing being always referred to substance dried at 212° F.

By dividing the volume weight of the soil with the weight of the same volume of water the *apparent specific gravity* of the soil is obtained.

By now dividing this apparent specific gravity with the specific gravity of the soil, the quotient expresses the *porosity* of the soil, *i.e.*, the space which in soils in a dry state (its volume being put = 1) is occupied by
particles of air. This porosity is frequently calculated to 100 parts by volume of the soil.

To determine the volume of a soil completely saturated with water, vigorously shake, according to E. Wolff, 25 to 30 grammes of finely pulverized, air-dry soil, whose volume weight is known, in a graduated tube with water containing 1 per cent. of sal ammoniac, and allow to settle. The volume is read off after twenty-four hours. In the calculation the proportion existing between the volume of soil in a saturated state and the same volume of soil in a dry state is fixed by taking the latter as the unit.

B. Behavior of the soil towards nourishing substances. —The power of the soil to retain separate substances presented to it in solution is termed absorption, and is dependent partially on chemical, and partially on physical causes, though opinions differ in this respect. It has been ascertained that the soil takes up more from concentrated than from more dilute solutions, and that the absorbed substances can be again partially withdrawn from the soil by washing with much water. The content of humus and clay has great influence upon the absorbent power of the soil, the latter, it is claimed, being also essentially increased by zeolitic minerals.

The greater or smaller absorbent power of a soil being generally in direct proportion to its fertility, a determination of this important property is of great value, since it has a bearing on practical agriculture, especially as to the rational treatment and application of farm-yard manure and the economical use of artificial manures.

In order to imitate nature as closely as possible, very dilute nourishing solutions must be used for such experiments.
1. Testing the absorbent power of the soil with $\frac{1}{10}$ or $\frac{1}{100}$ normal solutions.—For making these experiments the following salts are very suitable: Ammonium chloride, potassium nitrate, calcium nitrate, magnesium sulphate, and monocalcium phosphate.

Ammonium chloride, calcium nitrate, and magnesium sulphate can be readily prepared as chemically pure anhydrous salts, and in this state weighed in a closed weighing tube. The $\frac{1}{10}$ normal solution of these salts is prepared as follows: Weigh out exactly $\frac{1}{10}$ of their molecular weight in grammes, which is equivalent to $\frac{1}{10}$ of the atomic weight of hydrogen $=1$, and dissolve it in 1000 cubic centimeters of distilled water of 60.8° F. The quantities of salt required for 1 liter are as follows: Ammonium chloride = 5.35 grammes, potassium nitrate = 10.11 grammes, magnesium sulphate = 6.00 grammes.

Since calcium nitrate forms a very deliquescent salt, and, therefore, cannot be directly weighed, a solution somewhat more concentrated than $\frac{1}{10}$ normal solution is prepared. In every 20 cubic centimeters the content of calcium monoxide is determined by gravimetric analysis, and the mean of two determinations taken if their first decimals agree. Now calculate the quantity of nitric acid equivalent to the calcium monoxide, and compute with how many cubic centimeters of water the solution prepared will have to be diluted in order to contain 8.2 grammes of calcium nitrate in 1 liter.

To determine the absorption of phosphoric acid, monocalcium phosphate ($\text{CaH}_4[\text{PO}_4]_2 + \text{H}_2\text{O}$) is very suitably used, this soluble phosphorus salt being introduced into the soil by the superphosphates of commerce. For its preparation Fesca proposes the following method: Com-
pound a solution of commercial sodium phosphate with glacial acetic acid, precipitate it with calcium chloride solution, and wash the precipitate by decanting until the wash water shows no reaction with silver nitrate. Then bring the precipitate in a moist state into cold concentrated phosphoric acid until saturated. From the filtered solution, in a heated room, the monocalcium phosphate separates in crystals in 2 to 3 weeks. The crystals are rinsed off with anhydrous ether, pressed between blotting paper, and dried over sulphuric acid.

This salt being soluble without decomposition only in a very dilute solution, Fesca made his absorbent experiments with a \(\frac{1}{10}\) atomic solution which contained in 1 liter of water 2.5 grammes of monocalcium phosphate corresponding to 1.4 grammes of phosphoric acid (\(P_2O_5\)).

The coarser admixtures of the soil possessing no absorbent power, soil passed through a 0.5 millimeter sieve is always used.

For the determination of the absorption, 50 grammes of the soil are left in contact with 200 cubic centimeters of the normal solution for 48 hours, with frequent shaking, at a uniform temperature of 62.6° F. The soil is then allowed to settle, and after pouring the supernatant clear solution through a dry filter, the substance, the absorbed quantity of which is to be learned, is determined in 100 cubic centimeters of the filtrate. Experiments have shown that in most cases it suffices to determine the absorbent power of the soil for potassium, phosphoric acid, and nitrogen. In order to proceed as uniformly as possible it is best to follow Fesca's proposal to use exactly 400 cubic centimeters of normal solution for 100 grammes of substance. The absorption-
coefficient, i.e., the quantity of the absorbed substance in milligrammes is always referred to 100 grammes of air-dry fine earth (less than 0.5 millimeter in diameter).

2. Determination of the absorption-coefficient according to Knop.—The following method for the rapid determination of the absorption-coefficient has been proposed by Knop. He always uses for the experiments air-dry fine earth, by which he understands the portion of the soil which has passed through a wire sieve with 400 meshes to the square centimeter. When using a sieve with round holes, the soil passed through holes 0.5 millimeter in diameter, though somewhat coarser than the material used by Knop, will, according to Fesca, be found suitable for the experiment.

In case the soil is very binding it is boiled with water and passed through a sieve with holes 0.5 millimeter in diameter with the aid of a stiff brush. For the experiment use 50 or 100 grammes of the perfectly air-dry fine earth and add 5 or 10 grammes of elutriated powdered chalk. Pour over this mixture in a cylindrical vessel, which can be effectually closed, a solution of ammonium chloride so prepared that one cubic centimeter of it on being decomposed with sodium bromide evolves exactly 1 cubic centimeter of nitrogen (in the normal state). Such a solution is obtained by dissolving exactly 5 grammes of freshly sublimed sal ammoniac in 1040 cubic centimeters of water of 63.5° F. Now add to 50 grammes of fine earth 100, or to 100 grammes of fine earth, 200 cubic centimeters of this sal ammoniac solution and let the soil remain in contact with it, with frequent shaking, for 48 hours. Then allow the soil to settle and pour the supernatant clear fluid through a dry
filter. From the filtrate take quickly, by means of a pipette, 20 or 40 cubic centimeters, and, after adding one drop of pure hydrochloric acid, evaporate nearly to dryness in a small porcelain dish upon the water-bath. Rinse the sal ammoniac remaining in the porcelain dish with 10 cubic centimeters of water into one of the divisions of the developing flask of the Knop-Wagner azotometer, decompose it with 50 cubic centimeters of bromeine lye, and determine the nitrogen volumetrically. The volume of nitrogen read off is, with due consideration of the tension of the aqueous vapor, the height of the barometer, and the temperature, calculated to the normal condition, and the nitrogen which remains absorbed in the 60 cubic centimeters of fluid (see p. 118 et seq.) added. In case the soil possesses no absorption, 20 or 40 cubic centimeters of nitrogen must be obtained. Knop understands by absorption the loss of nitrogen which 200 cubic centimeters of sal ammoniac solution suffer when in contact with 100 grammes of soil. Hence, the cubic centimeters of nitrogen determined in the azotometer must be deducted from the number of cubic centimeters of sal ammoniac solution used, and the difference calculated to 100 grammes of air-dry soil less than 0.5 millimeter in diameter.

For judging the fertility of a soil the determination of Knop's absorption-coefficient is of great value, since, though in exceptional cases an entirely unproductive soil may happen to possess great absorption, a soil with slight absorption can never be classed with very fertile soils. Knop considers absorptions of from 0 to 5 degrees as insufficient, of from 5 to 10 as sufficient, while those of
from 10 to 10 higher degrees progressively increase the value of the soil.

In the valuation of the soil by absorption, it must always be borne in mind that it would be entirely wrong to judge the soil by this property alone, since a single property favorable for the soil may, as regards its value, be entirely nullified by others exerting an unfavorable influence.

C. Behavior of the soil towards water. 1. The power of retaining moisture in the soil.—The amount of moisture retained by a soil is generally in direct ratio to its contents of organic matter and its state of division. A proper degree of fineness in the particles of the soil is very important to obtain, especially if it is subjected to drought. During dry weather plants require a soil that is both retentive and absorptive of atmospheric moisture, and that soil which has this faculty will evidently raise a more vigorous crop than one without it. Regarding this condition of retaining moisture, the materials which are most influential in soils may be arranged in the following order: Organic matter, marls, clays, loams, and sands. For the determination of the power of the soil to retain moisture the following methods may be mentioned:—

a. By experiments in the laboratory.—Pour over 100 grammes of the air-dry fine soil 100 cubic centimeters of distilled water and effect the thorough saturation of the soil by stirring with a glass rod. Now rinse the soil with 100 cubic centimeters of water, admitted from a pipette, upon a filter saturated with water. The water running off is caught in a graduated cylinder of 200 cubic centimeters capacity, and when nothing more drips
off, the quantity is read off in cubic centimeters. The difference between the quantity of water used (200 cubic centimeters) and that caught corresponds to the quantity of water retained by the soil. This behavior of the soil, which corresponds to its comparatively highest degree of looseness, has been designated the greatest or full capacity for water. It is calculated for 100 parts by weight, as well as for one liter of the soil dried at 212° F.

This full capacity may also be determined as follows: Stir up 100 grammes of the air-dry soil (less than 2 millimeters in diameter) in the above-mentioned manner with any desired quantity of water in excess, and bring the whole with the aid of a wash-bottle into a previously weighed funnel in the point of which a small filter is inserted. Cover the funnel with a watch crystal, and when, after standing for some time, no more water drips off, weigh it. Both these methods are quite suitable for very pervious soils, but with very clayey or humus soils have the disadvantage that the dripping off of water already ceases when the mass in the filter is still in a thinly-pasty condition.

Since, in order to obtain accurate comparable results, it is necessary for the samples of soil to be always in the same state of looseness, a method for laboratory experiments has been proposed by which this is sought to be attained as nearly as possible. For this purpose cylindrical tubes of zinc sheet (Fig. 23), exactly 16 centimeters long and 4 centimeters in diameter, are used. Their volume would, therefore, be 201.06 cubic centimeters. The bottom of the tube consists of fine nickel wire gauze. Below the gauze a piece of zinc tube perforated
on the sides is soldered over it. Before use a piece of moistened fine linen is placed upon the wire gauze bottom, and after tying a piece of rubber over the lower end, the lower portion of the cylinder is filled with water up to the gauze bottom. Now pour 200 cubic centimeters of water of 60.8° F. into the cylinder and make a mark exactly over the level of the water. The edge of zinc sheet above this mark is filed off, so that the cylinder with the linen rag has a capacity of exactly 200 cubic centimeters, and may, at the same time, be used for the determination of the volume weight of the soil. After placing the moist linen rag in the cylinder the latter is first weighed and then filled, constantly tapping it against a soft support, with the uniformly divided air-dry soil. The soil is finally accurately leveled with a knife. The cylinder is again weighed and then placed in a glass dish containing water, so that the gauze bottom dips about 4 to 5 millimeters in the water. Over several tubes thus prepared a heavy glass bell shutting out the air is placed. In this manner the soil is then allowed to absorb water from below until saturated. According to the condition of the soil, its saturation with moisture will be observed on the surface in a longer or shorter time. The cylinders are allowed to remain under the glass bell until after
repeated weighing, for which purpose they are placed in a shallow porcelain dish, they show an approximately constant weight. In weighing the temperature and height of the barometer are to be observed. The increase in weight corresponds to the total quantity of water absorbed which can be directly calculated for the volume of soil.

Another method corresponding still more to the natural conditions has been used by A. Mayer. He uses two glass tubes 0.75 and 0.25 meter long, and 2 centimeters in diameter. The upper shorter end is connected with the longer by a short rubber tube. The lower end of the long tube is closed by tying a piece of linen over it. The tubes are then filled with air-dry fine soil, they being gently tapped against a soft support during the operation. Then pour enough water upon the soil transitorily to establish its full capacity for water. By now waiting for some time the column of water sinks down. When no more water drips off below, the rubber tube is disconnected, and on this place a sufficient quantity of soil is taken out, quickly weighed, and the water retained by it determined by drying at 212° F. With the assistance of the apparent specific gravity (p. 145), the capacity for water of the weight of soil can be calculated to the volume of soil. To the smallest quantity of water retained by the soil thus obtained, Mayer has applied the term *absolute capacity for water*. On account of their very slight permeability this method cannot be used with very clayey soils.

*b. Determination of the water capacity of the soil in its natural bed in the open field.*—The following process was
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devised by R. Heinrich, and deserves to be preferred to the experiments in the laboratory. To saturate the soil in its natural bed in the field, a round sheet-metal cylinder, 20 cubic centimeters in diameter and 40 centimeters long, is used. The lower end of the cylinder consisting of strong sheet iron is sharpened and forced into the soil by means of the feet. For this purpose the cylinder is on both sides provided with a ledge, while to diminish the fall of the water to be poured in and not to mechanically reduce the soil to mud, a fine sieve is placed in the upper portion of the cylinder. When the cylinder has been firmly forced into the soil so that no water can run out on the side, it is entirely filled with water. The water is then allowed to soak into the soil, the latter being covered with a board or sheet of parchment paper to protect it against evaporation and other influences. Sample taking is effected after 18 to 24 hours, since only then, according to Heinrich's experiments, the quantity of water retained remains constant for some time. After removing the cylinder, dig out with a spade the soil up to the centre of the spot terminated by the cylinder, using, however, the precaution of gently forcing the surface of the spade away from the sample to be taken. The uppermost layer of soil, from 2 to 4 centimeters thick, is removed, a piece cut out of the centre with a knife, brought into a powder flask of known weight and hermetically closed. The quantity of water which the soil retains is determined by continuous drying at 212° F. of the weighed sample in the flask and calculated to 100 grammes as well as to 1 liter of soil. Small stones over 0.5 centimeter in diameter contained in the sample are later on sorted out and their weight deducted. The
small quantity of water adhering to these stones need not be noticed.

The method just described has later on been modified by Heinrich so that the soil is lifted out to the sub-soil and the cylinder placed upon the sub-soil. The top soil is then replaced in its former position outside the sheet-metal cylinder, while the rest of the soil is rubbed through the sieve with as little water as possible, so that all the coarser stones remain behind. For the determination of water the soil is, after about 24 hours, lifted out with a gouge-bit, the lower opening of which corresponds to a surface of 1 square centimeter.

2. The evaporating power of the soil.—In determining the evaporating power of the soil, it must also be sought to imitate as closely as possible the natural conditions by exposing a sufficiently thick layer of soil to the alternating influence of the direct rays of the sun and to the shade. It is best to use for this purpose the cylindrical zinc tubes with sieve bottoms described on p. 152. According to E. Wolff, they are surrounded with a narrow shell of thick paste-board, and, after being filled with soil in a state of full water capacity, are placed alongside each other in a small wooden box whose shiftable lid is provided with apertures corresponding to the diameter of the cylinders, so that the lateral radiation of the sun is entirely shut out. This box is placed in the open air, the zinc tubes being taken from the paste-board shells every 24 hours and their decrease determined by weighing, whereby the temperature of the surrounding air, its moisture, the height of the barometer at the time being, and the cloudy or cloudless state of the sky have to be noted. Since the weight of the air-dry soil used, as well
as the largest quantity of water retained by it, is known, the evaporating capacity can be given either in per cent. of the substance dried at 212° F., or in per cent. of the total quantity of water absorbed.

3. The filtrating power of the soil.—By the filtrating power of the soil is understood its property of allowing the water to percolate in a longer or shorter time. To determine this, a square zine box 25 centimeters high and 3 centimeters wide, provided below with a funnel-shaped piece with discharge-pipe, is, according to E. Wolff, employed. The discharge-pipe of the funnel-shaped piece is closed with cotton, projecting somewhat from the pipe. The funnel-shaped piece is filled with coarse quartz sand. The cotton and sand are saturated with water, when the apparatus is weighed. Now bring into the box, tapping it constantly against a soft support, a layer of air-dry soil 16 centimeters thick, and weigh. Then pour water over the soil and again weigh the box when no more dripping off takes place. Thus the full water capacity is obtained.

Now pour upon the soil, without stirring it up, a layer of water 8 centimeters deep and determine how much time it takes until no more dripping off from the discharge-pipe takes place. The filtering capacity of this layer of soil 16 centimeters thick, and in a state of full water capacity for a column of water 8 centimeters high, is given in feet. Since, however, in repeating the experiment more time is almost always consumed in filtering than in the first trial, the experiment has to be repeated five or six times, and the mean of the results taken. For very clayey soils this method is not available, since
the water poured upon the soil remains standing without running off.

The experiment may also be made by each time allowing exactly 50 centimeters to drop into a graduated cylinder and noting the time thereby consumed.

4. Capillary attraction of the soil.—To determine the capillary attraction by experiment, the lower ends of glass tubes each 100 centimeters long and 2 centimeters in diameter, are closed with fine muslin by drawing a rubber ring over them, $D$ (Fig. 24). Fill the tubes, tapping them gently, with air-dry fine soil (less than 2 millimeters in diameter), and insert them 1 to 2 centi-
metres deep in a glass dish, B (Fig. 24), containing water. It is recommended to use for the experiment the stand A (Fig. 24), which is arranged for ten tubes, C, which, in order to keep them suspended in the water, are above secured by rubber rings, E.

With the aid of a meter rule it is now ascertained how much time the fluid consumes in ascending 20, 30, 40, 50, 60, 70 centimeters, and in what time the maximum ascent is reached. The water absorbed by the soil from the glass dish B must constantly be replaced.

The experiment may also be made by measuring the heights to which the fluid has risen in 24, 48, 72, 96, 120 hours.

When the experiment is finished, it is also of interest to cut up the tubes into pieces 1 decimeter long, and to separately determine the content of water in them. It may here be remarked that the tubes of 100 centimeters length may also be used for the purpose of determining how deeply and rapidly a column of water of determined height (for instance, 10 centimeters) penetrates from above into the air-dry soil.

D. Behavior of the soil towards gases. 1. The absorbent capacity of the soil for aqueous vapor.—To determine the saturation-degree of the soil in a space filled with aqueous vapors, bring 10 grammes of the air-dry soil into a shallow zinc box with a bottom-surface of 25 square centimeters, spreading it out as uniformly as possible. After weighing the box with the soil, place another weighed box of the same size, but empty, together with the first, upon a tripod under a glass bell dipping in water. In the glass bell hang a thermometer, and at each weighing read off the temperature.
After 24 hours weigh the zinc box filled with soil, as well as the empty one, and deduct the increase in weight of the latter from the increase in weight of the former. Repeat the weighings at intervals of 24 hours, until, with the same conditions of temperature, an approximately constant weight is obtained. The moisture retained is calculated for 100 grammes of the soil dried at 212° F., and designated as the absorbent capacity for aqueous vapor.

2. The absorbent power of the soil for the oxygen of the atmospheric air.—The absorbent power of the soil for oxygen is traceable to chemical and physical causes. Its fixation chemically is effected by the oxidation of ferrous oxide combinations, metallic sulphides, and humus substances which may be present in the soil. The physical absorption is dependent on the condensation of the gas upon the surface of the particles of soil. The chemical fixation of the oxygen preponderates by far, and from it a judgment can frequently be formed regarding the condition of the humus substances, they being found in the soil in a more or less readily decomposable state corresponding to the greater or smaller absorption of oxygen. According to W. Wolf, 50 or 100 grammes of soil are compounded with so much distilled water that the soil to be examined contains 20 per cent. of it. The soil is enclosed, together with an accurately measured quantity of air, in bottles of 500 centimeters capacity, and the change in the volume of air in from 8 to 14 days observed, the quantity of carbonic acid formed in place of the oxygen, which has disappeared, being at the same time determined.

If simply the absorption-coefficient of the soil for
oxygen is to be determined, thoroughly moisten, according to F. Schulze, 25 grammes of soil in a small flask with quite concentrated potash lye, connect the flask with an azotometer in which a determined volume of air is shut off by mercury and repeatedly shake the flask during the experiment. The decrease (after one to four days) in the volume of air contained in the entire apparatus gives the quantity of oxygen absorbed.

G. Ammon, in his article "Untersuchungen über das Condensationsvermögen der Bodenkonstituenten für Gas,"* sums up the most interesting results of his experiments as follows:—

1. The condensation of the gases by the soil is dependent on physical and chemical processes.

2. The absorption of gas in the soil brought about by chemical processes is of greater moment than that caused by surface attraction. The former is principally effected by the ferric oxide and next by the humus substances.

3. The gases in being condensed by the soil are either absorbed as such, or they suffer thereby chemical changes.

4. The gases are generally condensed in a higher degree the more readily, they otherwise change their aggregate state and the more readily they are decomposed.

5. The condensation of the gases in the soil is the greater, the finer, under otherwise equal conditions, the particles of soil are.

6. The largest quantities of gases are condensed by the soil at a temperature between zero and 10° C., while

from that point on, the quantity of gases absorbed decreases with the rise and fall of temperature.

3. The ventilating power of the soil.—The ventilating power of a soil, i.e., the greater or smaller resistance opposed by different soils in a wet state to the passage of the air, has been justly considered, by R. Heinrich, as a very important property for judging of it. Whether drainage can be carried out in a field or not is solely dependent, it is claimed, on this property.

The experiment is made, according to Heinrich, as follows: After the soil has been saturated by means of the sheet cylinder described on p. 155, under determination of the water capacity in the open field, and a constant water capacity has been obtained, a square box of strong zinc sheet C (Fig. 25), 100 square centimeters in cross-section and 20 centimeters high, is 10 centimeters deep sunk into the soil. On the outside of the box, 10 centimeters from the bottom, a strip of zinc sheet, 5 centimeters wide, is soldered on at a right angle, so that by this means the box can be forced by the foot into the soil to the above-mentioned depth, and, therefore, incloses a cube of earth of 1000 cubic centimeters. The portion of the box above the soil serves as an air-chamber and is connected with the flask B, of ten liters capacity, by a tube soldered on, on the side. By the admission of water by means of a siphon from the flask A, standing at a higher level, into the flask B, the air in the latter is compressed and forced through the soil. The flask B is provided with a manometer, D, by which the air-pressure can be measured. By raising or lowering the water reservoir A, the air-pressure can be increased or decreased at will.
In making the experiment, water is allowed to flow in until the manometer shows the desired pressure. Then shut off the water by closing the clip and wait one or two minutes. If the pressure decreases during this

Fig. 25.

"tim" admit more water until the first pressure has been again attained. By continuing the experiment in this manner, the time required to force 10 liters of air, at a determined height of the manometer, through 1 liter of soil is ascertained.

E. Behavior of the soil towards heat. 1. Determination of the heat-absorbent power of the soil.—A cylindrical glass vat 4 centimeters high and 16 centimeters in diameter, covered outside with thick asbestos pasteboard, is entirely filled with air-dry fine soil, then placed in a wooden box the lid of which is provided with an aperture corresponding to the cross-section of the glass vat
and exposed for 6 hours to the direct rays of the sun. By a maximum thermometer, imbedded 1 centimeter deep in the soil, the temperature to which the soil during this time has been heated is then ascertained. The experiment is repeated under as equal conditions as possible by imbedding the thermometer 2, 3 and 4 centimeters deep and determining the maximum temperature to which the soil has been heated.

The heating capacity of a soil is dependent on various conditions. The specific heat of the soils, i.e., their different behavior regarding the absorption of varying quantities of heat units to increase their temperature 1° C., will have to be taken into consideration, further their color and their more or less inclined position.

With soils saturated with moisture as found in the field, their greater or smaller content of water is, however, of the greatest importance as regards the absorption of heat. While 1 kilogramme of water requires 100 units of heat to be raised 1° C., an equal weight of clay requires only 17.8, and an equal weight of sand only 12.8 units of heat for the same increase in temperature. To this, it must further be added, that a moist soil is considerably cooled off by the evaporation taking place on its surface. Hence, a field suffering from moisture may always be designated as cold.

Investigations regarding the maximum and minimum temperatures of the soil in a day, week or month are of great value when the results are compared with the temperatures of the air at the time being and referred to the plant-production of the soil. It is best to use for this purpose maximum and minimum thermometers accord-
ing to the Six-Kapeller system, which are imbedded 1, 2, 5, 10 centimeters deep in the soil.

2. The heat-conducting power of the soil.—The heat-conducting power of the soil is determined by filling, with constant tapping against a soft support, a thin spherical glass flask of 1 liter capacity with air-dry fine soil and at the same time fixing the bulb of a mercury thermometer in the centre of the flask. The latter is then brought into a drying chamber provided with a gas-pressure regulator and heated to 212° F. Now accurately observe the time required to heat the soil to its centre from its original temperature to 212° F.

The experiment may also be made by heating the soil in the same vessel to 212° F. and, determining, by the thermometer sticking in the soil, the time required for the soil to cool off to its initial temperature.

From his experiments Wollny has deduced the following general results:—

1. During the warmer season of the year and with warm weather, a compact soil is on an average warmer than a loose soil.

2. During the colder seasons of the year (spring and fall), and also in the warmer season, whenever there is a sudden and considerable fall in the temperature, a compact soil is, on an average, colder than a loose soil.

3. During the warmer season of the year, and with warm weather, a compact soil is considerably warmer during the day, but commonly colder during the night than a loose soil.

4. At the time of the daily maximum of the temperature of the soil the difference mentioned under 1 is greatest, but at the time of the daily minimum, either
very small or an equalization or even an inverse ratio takes place.

5. In a compact soil the variations in temperature are considerably greater than in a loose soil.

6. The causes of the above-mentioned phenomena are due to the better heat-conducting power of a compact soil as compared with a loose soil.

F. Cohesion and adhesion of the soil.—To determine the degree of firmness with which the particles of soil in a dry state cohere together, knead, according to the method proposed by Schübler, the soil together with water and shape the mixture in a mould to rods 5 centimeters long and 1 centimeter wide. After completely drying the rods in the air, the pressure required to cut them through is determined by placing weights upon a suitable apparatus provided below with a dull edge.

Another method to determine the coherence of the soil in a wet state was devised by R. Heinrich. The soil is uniformly saturated with water so that the content of water amounts to exactly 50 per cent. of the highest water-capacity of the experiment in the laboratory. The soil is then pressed between two sheet-iron plates, one side of which is in the centre provided with a hook. The layer of soil between the sheet-iron plates should be from 5 to 10 centimeters. The upper plate is then suspended from a thread, while to the lower a small basket is secured, into which sand in small portions is introduced until the column of soil tears apart. The plate torn away, together with the basket and the adhering soil, is then weighed. Their weight corresponds to the force required to break up the coherence of a layer of earth one decimeter in cross-section. This method
is, of course, only available for soils in which the adhesion to the iron plate is greater than the coherence of the soil.

Regarding the *adhesion* of moist soils to iron and wood, the sample to be examined is, according to Heinrich's directions, also moistened with 50 per cent. of water of its highest water capacity, and after bringing it into a larger vessel, the surface of the soil is leveled as much as possible. A plate of sheet-iron or beech wood one square decimeter in cross-section is then pressed firmly upon the soil, so that a complete contact of the soil with the metal or wood takes place. To the hook of the plate is fastened a cord which runs over a pulley and carries a small basket. The latter is loaded with sand until the plate tears loose from the soil. The force required to overcome the adhesion corresponds to the weight of the basket and of the portion of cord reaching to the summit of the pulley, less the weight of the plate torn off and the other end of the cord.

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X.

GENERAL RULES FOR SOIL-ANALYSIS.

It is, of course, self-evident that in the examination of determined varieties of soil not all the methods discussed in the preceding sections will need to be employed. The course of soil-analysis cannot be regulated according to a pattern with fixed limits, but must, in each case, be adapted to the questions to be decided. However, in order to obtain comparable results, it is necessary
to agree on certain fixed rules. Proceeding from the point of view that the chief purpose of soil-analysis is to be of service to agriculture and forestry, the general rules to be applied to the examination of soils and the question which deserves special consideration shall here be briefly summed up:

1. The profile of the entire soil, as far as of importance for the nourishment of plants, must be included in the examination. This, in most cases, will embrace the top-soil and the more shallow and deeper subsoils.

2. Whenever possible, accurate analyses by graining with the round-hole sieve and elutriating with Schoene's apparatus should be executed with the three above-mentioned layers of soil, and always with the top-soil if not derived from moor-soil. From such analyses important conclusions regarding the physical properties of the top-soil and subsoil can be drawn, and a thorough knowledge of the mechanical mixture of the soil is of great value for judging it. For the mechanical analysis the air-dry total soil is to be used.

3. For judging the subsoil, it is further of importance to determine its content of carbonate of lime, as well as of clay, the latter by disintegration of the clayey particles, less than 0.5 millimeter in diameter, with sulphuric acid in the closed tube (p. 83).

4. If the layers of the subsoil are to be utilized for meliorating purposes, they must be examined as to the substances useful and injurious to the growth of plants contained in them. Of the useful substances, it will be primarily necessary to determine the content of carbonate of lime and phosphoric acid, and of the injurious
ones, the presence of ferrous sulphate, free sulphuric acid, and iron disulphide.

5. In all chemical and physical examinations of the top-soil, fine soil less than 2 millimeters in diameter, dried at 212° F., is to be used, and the results must be referred to it.

6. In regard to the separation of the soil-constituents, the content of lime, clay, humus, and sand in the fine soil of the top-soil, dried at 212° F., is to be determined.

7. Exclusive of moor-soils, the determination of nitrogen is only to be executed with top-soils.

8. For the determination of the plant-nourishing substances the extraction with boiling concentrated sulphuric acid is preferably to be used, and, as a rule, only the top-soil (fine soil less than 2 millimeters in diameter) need to be considered. In making the experiment, calcareous earth, magnesia, potash, phosphoric acid, and sulphuric acid must first of all be determined. However, the substances not belonging to the actual plant-nourishing substances, such as silica, alumina, ferric oxide, oxide of manganese, and sodium must also be taken into consideration.

9. For the determination of Knop's absorption-coefficient, air-dry fine earth less than 0.5 millimeter in diameter is to be used. The experiments can only be executed with top-soils, for the judging of which they are of great importance.

10. Of the physical examinations the water capacity (if possible in the open field) and the capillary attraction are chiefly to be considered.
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