Soils, fertilizers, feeding stuffs, insecticides, milk and the various agricultural products are complex materials and require special treatment for chemical analysis. This special treatment is the province of Agricultural Chemical Analysis, which may be considered as the application of methods of qualitative and quantitative analysis to materials of agricultural importance. Before proceeding to the analysis of any specific sample the student should know the source of the material at hand. He should also be familiar with the general properties of its constituents and understand the chemical processes involved in its production. To that end the following notes are provided. They consist of brief descriptive text, preliminary qualitative tests, and directions for quantitative analysis of the materials discussed. So far as practicable, important reactions have been expressed by equations. These should be completed by the student where only partially given. The notes for quantitative analysis have been adapted for the most part from the Methods of Analysis of the Association of Official Agricultural Chemists. Bul. 107. Bur. of Chem. U. S. Dept. Agric.

REFERENCE BOOKS ON AGRICULTURAL ANALYSIS

Prescott and Johnson, or any other good book on qualitative analysis.
Sherman, Organic Analysis (revised edition).
Hawk, Physiological Chemistry (revised edition).
Treadwell and Hall, or any other good book on quantitative analysis.

I. THE SOIL

The soil is a product of the decay and disintegration of organic and inorganic matter, and therefore contains those chemical elements which occur in rocks and in plant and animal tissues. The chemical elements of the soil which are essential to plant life, and which therefore particularly concern the agricultural chemist, are comparatively few in number. They include nitrogen, phosphorus, sulphur, potas-
sium, calcium, iron, magnesium and chlorine. Carbon, hydrogen and oxygen are also of importance in the soil as constituents of organic matter but they do not serve higher plants as food elements when they exist in this form.

Minerals in great number contribute to soil formation. Of these, quartz, feldspar, mica, apatite and limestone may be taken as typical examples. The first consists of silica, or silicon-dioxide. It is extremely resistant to weathering agencies and chemical solvents and is the chief constituent of poor, sandy soils. Feldspar may be either potassium-aluminum silicate or sodium-aluminum silicate, the latter containing also, in some cases, calcium. Feldspar is rather easily decomposed and in the case of orthoclase, the potassium feldspar, yields potassium to the soil-water, leaving a residue known as clay. Mica contains iron and magnesium in addition to the constituents of the feldspars and is both more complex and less easily disintegrated than the latter. Apatite is an example of the simpler soil constituents which are comparatively rich in plant food and readily dissolved by weathering agencies and strong chemical solvents. This mineral is a double salt of calcium with phosphoric acid and either hydrochloric or hydrofluoric acid. It is an important source of phosphorus. Limestone is calcium carbonate, a compound readily decomposed by acids with liberation of CO₂. It thus possesses value in controlling soil acidity as well as in supplying calcium. It is apparent, from what has preceded, that an extraction of the soil with strong acid removes some minerals completely but others only in part or hardly at all.

The organic constituents of the soil, a complex mixture classified as humus material, contain most of the soil supply of nitrogen. This organic matter has been derived largely from carbohydrates proteins and other organic structures furnished by plant residues, bacterial cells and such added materials as manures and fertilizers. Its constituents are mostly insoluble in water, but by fermentation processes the organic nitrogen is gradually converted to ammonia, which is finally oxidized by special bacteria to nitrates and nitrates. All of these latter forms are soluble in water and thus available to plants. The nitrogen content and absorptive capacity of soils are greatly dependent upon the amount of organic matter in them.

Analytical Methods

Chemical study of the soil may be considered under,—

A. Methods for measuring temporary supply of plant food.

B. Methods for measuring permanent or potential supply of plant food.

Temporary supply of plant food is measured by the amount of plant food in soils supposedly of immediate availability to plants. It is the expression of results obtained in an attempt to duplicate the action of natural agencies, such as root acidity, bacterial flora, and
plant decay, on the soil. Various weak solvents including water, carbonated water, carbonated water and ammonium chloride, and dilute acetic acid have been used for the purpose. Solutions of ammonium citrate and ammonium oxalate, a one per cent solution of aspartic acid, and solutions of mineral acids, such as N/200 HCl, and N/5 HNO₃, have been used also for extracting the soil. In 1894 Dyer of England, after extensive study of the acidity of plant-root sap, recommended a 1 per cent solution of citric acid as an approximation to the natural solvent agents in plant feeding. Of all methods proposed this appears to be most substantiated by field tests. An analysis of the extracts obtained with these various solvents has been considered an index to the store of readily available plant food in the soil. It should be understood, however, that any such arbitrary test is indicative only, and that true availability can be determined only by the growth of plants upon the soil in question.

Potential supply of plant food is an expression intended to cover the amount of food in a given soil that may become available to plants over a long period of time. To measure this capacity of the soil an attempt is made to simulate action of the most vigorous weathering agencies. For this purpose strong reagents must be employed. Concentrated mineral acids heated under pressure may dissolve silica and its complexes. The same result may be reached by the use of hydrofluoric acid or by fusion of the soil with alkalies or alkaline earths and subsequent solution in acids. These reagents proceed further, however, than do the natural agencies within reasonable limits of time. Finding that a solution of HCl attained and maintained under distillation a density of 1.115 (nearly 23 per cent strength), Owen was led to use it as an easily controlled reagent in soil analysis; and his method has been adopted for soil analysis by the Official Agricultural Chemists. This reagent effects only partial decomposition of the soil minerals.

Complete analysis of the soil can be made by resorting to fusion methods with alkalies or alkaline earths, excluding a given alkali from the fusion in which it is to be determined. This procedure converts all soil constituents to compounds which can be readily dissolved with mineral acids and gives the total invoice of the soil's supply of plant food.

2. Preliminary Tests

These tests should be conducted by the use of table reagents unless other strengths are specified. The table reagent consists of one volume of the concentrated reagent diluted with four volumes of water. Express the reactions of these tests by equations, so far as possible, reserving the left-hand pages of the notebook for this purpose.

Action of alkalis upon insoluble silicates. Weigh two portions of Kaolinite of 100 mgm. each. Mix one portion with about 2 gm. of a mixture of K₂CO₃ with Na₂CO₃ in equal amounts by weight. Fuse thoroughly in a small iron crucible. Extract the fused mass and the
unfused Kaolinite with about 10 c. c. hot water each and filter. Add excess of concentrated HCl to the filtrates. Explain the results.

\[ Al_2O_3 + 2SiO_2 + 2H_2O + 5Na_2CO_3 = Na_2AlO_3 + Na_2SiO_3 \]

Separation of silica from solutions of silicates. To about 5 c. c. of HCl add a nearly equal amount of waterglass. Break up the precipitate with a rod, filter and wash. Compare small portions of it with quartz sand for solubility in hot conc. HCl and 10 per cent NaOH. For this purpose, filter, add excess of HCl, evaporate to dryness and digest the residue with dilute HCl. What is the difference in chemical composition between the precipitate and the quartz sand?

Dry a little of the precipitate thoroughly by heating gradually in a porcelain crucible over a low flame. Now test its solubilities in the reagents previously used:

How would you quantitatively remove silica from acid extracts of soil?

\[ Na_2SiO_3 + 2XH_2O + HCl = \]

\[ H_2SiO_3 + NaOH = \]

\[ H_2SiO_3 + \text{heat} = \]

Precipitation of phosphoric acid by metals of soil. To 1 c. c. of 10 per cent sodium hydrogen phosphate solution slightly acidified with HCl add 5 c. c. of a 10 per cent solution of aluminum chloride. Add NH_4OH drop by drop until the precipitate formed requires several seconds to dissolve. Heat nearly to the boiling point, add ammonia in excess and boil for a few seconds. Filter, wash with water and test the filtrate and washings for P_2O_5 by making slightly acid with HNO_3, adding 10 c. c. of clear molybdic reagent and heating until perceptibly hot to the touch. Dissolve a little of the precipitate in nitric acid and test for phosphoric acid with molybdate solution as before. AlCl_3 + H_3PO_4 + NH_4OH = AlPO_4 + H_2PO_4 + 12(NH_4)MoO_4 + 21HNO_3 = (NH_4)_3PO_4 + 12MoO_3 + 21NH_4NO_3 + 12H_2O.

MoO_3 + 21HNO_3 = (NH_4)_3PO_4 + 12MoO_3 + 21NH_4NO_3 + 12H_2O.

Iron and aluminum are in excess over phosphoric acid in practically all soils. What is the composition of the precipitate formed when NH_4OH is added in excess to an acid extract of the soil?

Acid-soluble soil minerals. Shake about 10 gm. of loam soil in a small flask with about 30 c. c. of dil. HCl warming a little. Filter and make alkaline with NH_4OH as in the previous test. Now filter again and add to the filtrate a few drops of saturated (NH_4)_3C_2O_4 solution. What precipitate, if any, forms? What compound readily soluble in acids and giving this test is likely to be commonly found in soils?

After standing warm a few minutes, filter off the precipitate, add a few drops of sodium phosphate solution and make slightly alkaline with NH_4OH. What precipitate appears on standing?

\[ CaCO_3 + HCl = \]

\[ CaCl_2 + (NH_4)_2C_2O_4 = \]

\[ MgCl_2 + NH_4OH + NaH_2PO_4 = \]
Nitrate in soil. Shake up about 10 gm. of a rich garden soil with 25 or 30 c. c. of distilled water. Filter and concentrate to about 5 c. c. Cool and add a bright crystal of FeSO₄·7H₂O in a test tube. Now carefully deliver about 2 c. c. of strongest H₂SO₄ from a pipette so as to form a layer below the solution. Watch for the appearance of a brown ring between the acid and the solution, due to (FeSO₄)₂·NO. This is a test for nitrates. Explain the formation of calcium nitrate from farm manure and limestone tilled into the soil.

Why do not nitrates accumulate in soils of humid regions?
Ca(NO₃)₂ + H₂SO₄ →
6FeSO₄ + 2HNO₃ + H₂SO₄ → 2NO +

Organic matter in soil. Heat a thin layer of fertile soil in a covered crucible over a low flame. Charring indicates the presence of organic matter or humus. Which of the chemical elements of the humus produces the char? What are the sources of the organic matter of the soil? By what chemical processes is the organic matter of cultivated soils exhausted? How does tillage affect the humus content of soil?

2C₆H₄O₃NP (lecithin) + O → 2NH₃ +

Nitrogen in humus. Thoroughly mix in a mortar 5 gm. of soil rich in organic matter with about an equal weight of soda-lime (approximately 1 part NaOH + 2 parts CaO). Transfer to a test-tube, insert a loose wad of asbestos near the mouth of the t. t., and incline in a clamp. Close the t. t. with a one-holed stopper bearing a glass tube bent so that its distal end may be readily immersed in about 5 c. c. of distilled water in another test tube. Test the water with red litmus paper. Now heat the soil mixture gradually from top to bottom. Air will be expelled rapidly at first and water will collect in the asbestos, which will prevent it from running back and breaking the hot tube. What reaction is the source of this water? Heat for some time and then remove the receiving t. t. before allowing the residue to cool. What is the reaction to litmus of the distillate?

What compound has been produced? How was it formed?
CH₂CONH₂ (acetamide) + NaOH →
CH₃NH₂COOH (glycocoll) + O →

Methods for the Analysis of Soils

1. Directions for Taking Samples

Remove surface accumulations of decaying leaves, and debris, and take samples with a soil tube or spade to the desired depth. If the tract to be studied is not of uniform character divide into smaller tracts, that each may be uniform, and from such tracts take five or six representative samples to the depth of 6 ins., or to the change between the surface soil and the subsoil, in case such change occurs between the depth of 6 and 12 ins. Mix the samples of each depth thoroughly and take subsamples of 2 to 4 lbs., drying the latter in a well-aired, cool place.
The depth to which the sample of subsoil should be taken will depend on circumstances, but in ordinary cases 10 or 12 ins. of subsoil will be sufficient for the purposes of examination in the laboratory. The sample should be obtained in other respects precisely like that of the surface soil. The sampling should be done preferably when the soil is reasonably dry.

It is recommended that the weight of a given volume of soil as it lies in the field be taken for calculating the percentage results obtained by analysis to pounds per given area of the soil.

2. Quantitative Analysis of the Soil

Great care should be observed in preparing substances for this and all succeeding analytical work, as it is very important to have homogenous and representative samples. Soils should be air dried and pulverized by rubbing lightly with a rubber covered pestle. After sifting through perforations of 1 mm. diameter and thoroughly mixing, samples should be drawn and placed in tightly stoppered jars and carefully labelled.

Moisture.

Weigh out 5 gm. of the air-dried soil into a suitable weighed dish, dry at 100° C. for 5 hrs., cool in a desiccator and weigh. This determination should be made in dishes having covers fitted by ground glass edges. A pair of watch glasses with ground edges and provided with a clamp forms a suitable apparatus. During cooling and weighing the glasses should be clamped face to face to lessen absorption of moisture by the sample.

Record data in duplicate as follows:

- Weight of dish and soil
- Weight of dish and dried soil
- Loss of weight
- Per cent of moisture

Record all succeeding analytical data in this form.

Acid Insoluble Residue.

Weigh out duplicate 10 gm. portions of air dry soil on a watch glass and by means of glazed or smooth paper transfer to 200 c. c. Erlenmeyer flasks. To each flask add 100 c. c. of HCl of specific gravity 1.115. This is made approximately by mixing 275 c. c. of concentrated acid (sp. gr. 1.20) with 200 c. c. of distilled water. Add more water or acid as required until the hydrometer shows a specific gravity* of 1.115. Into each flask place a rubber stopper carrying a glass tube about 5 mm. in diameter and 50 cm. long, to serve as a reflux condensor. Set on the steam bath and digest for 10 hrs., shaking two or three times during this digestion. Remove, let settle and decant the solution into a hard glass beaker. Small quantities of insoluble material passing over will do no harm. Wash the remaining insoluble residue onto a 15 cm. filter with hot water.
setting the filtrate run into the beaker containing the decanted solution. Continue washing the residue until free from chlorides, saving the filter and its contents. To the solution add 5 c. c. conc. HNO₃ and evaporate to dryness on the steam bath. If the residue appears black repeat the evaporation with HCl and HNO₃, until all the organic matter has been oxidized and the residue looks yellow or orange in color. When the final evaporation is complete, add just sufficient conc. HCl to saturate the residue, add 10 to 20 c. c. water, warm on the bath to dissolve all soluble material, filter out the insoluble silica, wash free from chlorides and save the filter and its contents. Evaporate this filtrate to render insoluble any dissolved silica, take up with acid, filter and wash free from chlorides, preserving the filter as before.

The filtrate constitutes the acid extract of the soil, and may be used to determine the so called "potential supply of plant food." For methods of analysis see Official Methods, Bulletin 107, revised, p. 15. Dry the filter papers with contents. Transfer the latter to smooth paper and burn the filter papers in separate porcelain dishes, previously ignited and weighed. Add the silica and the main residue and ignite to constant weight. Do not allow a partial vacuum to form by cooling this large mass in a too tightly closed desiccator. Weigh as the insoluble residue and report as per cent of the soil.

Why is the organic matter removed from solution? Why is this done by means of nitric acid rather than by ignition? What is the source of the SiO₂ separated from the soil extract? What is the nature of the insoluble residue from the acid digestion?

\[
\begin{align*}
K_2O \cdot Al_2O_3 \cdot 6SiO_2 + 2HCl + 5H_2O &= Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + \\
Ca_5(PO_4)_2 + HCl &= \\
Protein + H_2O + HCl &= \\
Polysaccharide + H_2O + HCl &= \\
Waxes and resins + H_2O + HCl &= \text{no action} \\
C_{16}H_{33}O_3 + 8HNO_3 &= 8NO + 
\end{align*}
\]

**Total Nitrogen.**

Place 10 gm. of the soil (3 gm. in case of a peaty soil) in a 300 c. c. Kjeldahl digesting flask with 30 c. c. of strongest sulfuric acid, 10 gm. of sodium sulphate and 0.7 gm. of copper sulphate and boil gently for 2 hours after the liquid becomes transparent. Oxidize the residue by adding potassium permanganate in small amounts until the liquid retains a greenish color. After cooling, add 50 c. c. of water, shake vigorously, allow the heavy matter to settle and pour the supernatant liquid into an 800 c. c. Kjeldahl flask, repeat this process with four 50 c. c. portions of water. Conduct the distillation and remaining determination according to the Kjeldahl method for nitrogen in fertilizers and report the **per cent of nitrogen on the dry soil.**
Total Phosphorus Determination.

SODIUM PEROXID FUSION METHOD

Weigh 5 gm. of soil into a large iron crucible and mix to a thin paste with water. Using an iron rod, stir in 10 gm. of Na₂O₂, adding the latter in several portions and keeping just enough water present to prevent violent oxidation. Place the lid on the crucible so as to leave a narrow opening. Heat the mixture carefully by applying the flame of a Bunsen burner directly to the side of the crucible until the action starts. Keep the crucible covered until reaction is over and keep at a low red heat for 15 minutes. When cool, add hot water until the crucible is about half full, cover and leave on the steam bath for some time. By means of a spatula and hot water remove the fused mass from the crucible and transfer it to a 600 c. c. beaker. Make slightly acid with conc. hydrochloric acid, heat to boiling and test again with litmus. When slightly acid after boiling add 15 c. c. of concentrated hydrochloric acid and boil for 10 min. If the action has taken place properly no particles of undecomposed soil will remain in the bottom of the beaker, the suspended silicic acid will be white and the solution will appear yellowish-green in color. Transfer to a 500 c. c. volumetric flask and make up to the mark when cold.

Allow the silicic acid to settle and draw off 200 c. c. of the clear solution for analysis. In cases of soils abnormally rich in phosphorus, aluminum or ferric chloride should be added at this point, as directed by the instructor. To this solution add ammonium hydroxide drop by drop until nearly neutral. Then heat almost to boiling and add ammonium hydroxide in slight excess. Boil for about one minute and if no ammonia is then given off, as tested by litmus paper, add more until it can be detected. Filter, wash several times with hot water, pierce the point of the filter and return the precipitate to the original beaker by means of a stream of hot water. Digest any precipitate remaining upon the filter with hot, dilute hydrochloric acid, letting the solution run into the beaker containing the precipitate. Add more acid, and evaporate to complete dryness on the steam bath. Digest with dilute hydrochloric acid, filter out the silica and wash. If much silica is present, the evaporation and removal of silica should be repeated. Evaporate the filtrate to about 25 c. c., neutralize with ammonium hydroxide, clear up with a few drops of nitric acid, and then add 10 gm. of ammonium nitrate. To the hot solution add molybdate solution as directed (50 c. c. for every decigram of phosphoric acid (P₂O₅) and digest at 65°C. for 1 hr. Filter and wash with cold dil. HNO₃ (5 c. c. conc. HNO₃ per 100 c. c.) Test the filtrate for phosphoric acid by renewed digestion and addition of 5 to 10 c. c. molybdate solution. Deposit all molybdate waste of filtrates in jars provided for the same.

Dissolve the precipitate on the filter with three or four applications of conc. ammonium hydroxid followed by hot water and wash into a beaker to a bulk of not more than 100 c. c. Nearly neutralize with
hydrochloric acid, cool, and stir with 15 c. c. magnesia mixture added slowly from a burette. After fifteen minutes add 12 c. c. of conc. \( \text{NH}_2\text{OH} \) (and cover with watch glass and specific gravity 0.90), let stand for at least two hours. Filter on ashless paper, wash with dll. \( \text{NH}_2\text{OH} \) (9 c. c. conc. \( \text{NH}_2\text{OH} \) per 100 c. c.) until practically free from chlorides. Dry and ignite until white to gray and weigh as \( \text{Mg}_3\text{P}_2\text{O}_7 \). Calculate and report the per cent of \( \text{P}_2\text{O}_5 \).

Note. The yellow precipitate of this determination should be washed finally well into the point of the filter. Small amounts of precipitate clinging to the beaker need not be transferred to the filter if thoroughly rinsed. Solution of the precipitate is readily accomplished by two or three applications of a few c. c. of conc. \( \text{NH}_2\text{OH} \) followed immediately by additions of hot water. The solution is received in the same beaker used for the original precipitation. If the magnesium precipitate stands for a long time in ammoniacal solution, more conc. \( \text{NH}_2\text{OH} \) should be added at least one hour before filtering, to throw out phosphoric acid which may have redissolved in the weakened alkaline liquor.

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O} + 5\text{Na}_2\text{O}_2 & = \\
\text{C}_6\text{H}_3\text{P}_3\text{O}_9 \text{ (phytic acid)} + \text{Na}_2\text{O}_2 & = \text{Na}_4\text{P}_2\text{O}_7 + \\
\text{Na}_2\text{AlO}_3 + \text{HCl} & = \\
\text{Na}_4\text{P}_2\text{O}_7 + 4\text{HCl} + \text{H}_2\text{O} & = \text{H}_3\text{PO}_4 + \\
\text{(NH}_3\text{)}_2\text{PO}_4 + 2\text{MgO} + 24\text{HN}_2\text{OH} & = \\
\text{(NH}_3\text{)}_2\text{PO}_4 + \text{MgCl}_2 + \text{NH}_2\text{OH} & = \\
2\text{MgNH}_2\text{PO}_4 + \text{heat} & =
\end{align*}
\]

**Total Sulfur.**

Ten grams of soil are placed in a 100 c. c. nickel crucible, moistened with water, about ten gm. of a weighed 20 gm. portion of sodium peroxide added, and the mixture thoroughly stirred with a platinum rod. The crucible is placed over an alcohol flame and heated moderately until the mass is dry. The remainder of the sodium peroxide is then added, the cover placed on the crucible, strong heat applied until the mass melts, and kept in this condition for ten minutes. It is then allowed to stand over a lower flame for one hour. Why is a gas flame objectionable here?

The crucible is removed, cooled, placed in a 600 c. c. casserole, hot water added and the fused mass removed. It is neutralized with hydrochloric acid and then further acidified with 10 c. c. of hydrochloric acid. The volume is made up to about 450 c. c. and boiled for 15 min., or until no undecomposed soil particles remain on the bottom. The covered casserole is allowed to stand in the steam bath over night, filtered through a Nutsche and the residue thoroughly washed with successive small portions of hot water. The filtrate and washings if over 500 c. c. are evaporated below that volume, re-filtered and the volume made up to 500 c. c. Aliquots of 250 c. c. each are heated to boiling, barium chloride added, boiled for 5 min. and set aside on a steam bath for 24 hrs. The volume should not be al-
lowed to decrease as silicic acid may precipitate out if much evapora-
tion takes place. After standing for this length of time the barium
sulphate is filtered off, washed, ignited and weighed. Report as per-
cent total $\text{SO}_3$.

\[
(C_2H_4)_2S + 20 \text{Na}_2\text{O}_2 = \text{Na}_2\text{SO}_4 +
\]

**Total Potassium.**

**Reagents and Apparatus**

Decomposition of the soil is effected by heating it with its own
weight of ammonium chloride and eight times as much precipitated
calcium carbonate. The former salt must be pure. Correction for
alkalies in the carbonate must be made on the basis of control analyses
of this reagent.

The ignition may be made in a covered platinum crucible of ordinary
shape and of about 20 to 30 c. c. capacity heated to full redness for
not more than two-fifths of its height. The elongated form of crucible
with cap originally advocated by Smith is very much to be pre-
ferred, however, since it permits, when set at an angle through an
opening in the side of a fire clay cylinder, the application of the full
heat of the two burners; and perfect decomposition invariably results.

Weigh out $\frac{1}{2}$ gm. of fine soil. In a large agate mortar mix with
an equal weight of sublimed ammonium chloride, and grind the two
thoroughly together. Then add nearly the whole of a 4-gm. portion of
calcium carbonate and continue grinding till thorough mixing has
resulted.

The contents of the mortar are transferred to the long crucible,
the rest of the carbonate being used for rinsing off mortar and pestle.
The crucible is then capped and placed in an inclined position in a
clay cylinder or through a hole in a piece of stout asbestos board
clamped in a vertical position, and heated for about 10 min. by a low
flame placed at considerable distance beneath. As soon as the odor
of ammonia is no longer perceptible the nearly full flame of two
Bunsen burners is substituted, and continued for 40 to 50 minutes.
The sintered cake detaches readily from the crucible as a rule; if not,
it is softened up in a few minutes by hot water and digested in a
dish until thoroughly disintegrated. It is first washed by decanta-
tion, breaking any lumps by means of a pestle, and then thrown on
the filter and well washed with hot water. The residue should dis-
solve completely in hydrochloric acid without showing the least
trace of unattacked mineral, not even quartz, though sometimes a
few black particles of iron ores will dissolve but slowly.

**Separation of Calcium and Sulphuric Acid**

All but a trifling amount of the calcium is separated at boiling heat
in a large platinum dish by double precipitation by ammonia and
ammonium carbonate. The combined filtrates are evaporated to dry-
ness and the ammonium salts are carefully driven off by heating over the Bunsen burner.

Take up the residue with a little water and test for SO₄. If an appreciable amount is present add sufficient BaCl₂ to precipitate it. Filter and remove the excess of barium by precipitation with (NH₄)₂ CO₃. If the sulphur is not thus removed there is danger, if not certainty, of the potassium chloro-platinate carrying sodium sulphate. From the aqueous solution of the residue, but a few c. c. in volume, the rest of the calcium is thrown out by ammonia and ammonium oxalate. The filtrate, caught in an untaured platinum crucible or small dish, is evaporated to dryness and gently ignited; the residue is moistened with hydrochloric acid to decompose any alkali carbonate that may have been formed, again evaporated, ignited, and weighed. On solution in water a few tenths of a milligram of residue is invariably left, which should be collected, ignited, and weighed in the same crucible or dish in order to arrive at the weight of the chlorides.

Precipitation of Potassium

To the solution of the chlorides in a small porcelain dish an excess of chlorplatinic acid solution is added. The dilution should be such that when heated on the water bath any precipitate that may form wholly redissolves. Evaporation is then carried on till the residue solidifies on cooling. It is then drenched with alcohol of 80 per cent strength, filtered by decantation through a very small filter and washed by decantation with alcohol of the same strength. Avoid transferring the precipitate to the filter so far as possible. Dish and filter are now dried for a few minutes to remove adhering alcohol, the contents of the former are transferred to a weighed platinum crucible or very small dish and what still adheres to the porcelain is washed through the filter with hot water into the weighed receptacle. This is now placed on the steam bath and afterwards heated for one-half hour to 135° in an air oven. It is very important to cover the dish at first in the air bath, for decrepitation with resultant loss sometimes takes place if this is not! From the weight of K₂PtCl₆ compute the per cent of K₂O.

Humus Determination.

Place 10 gm. of the air dry soil (5 gm. in case of peat soil) in a gooch crucible, extract with 1 per cent hydrochloric acid until the filtrate gives no precipitate with ammonium hydroxid and ammonium oxalate, and remove the acid by washing with water. In the case of clay the washing should be done chiefly by decantation from a cylinder or tall beaker. This avoids clogging of the filter. With the aid of a wide-stemmed funnel, wash the contents of the crucible (including the asbestos filter), into a narrow glass-stoppered bottle, with 500 c. c. of 4 per cent NH₄OH. Mix 300 c. c. of water with 200 c. c. cone NH₄OH and add more water or ammonia until the hydrometer reads .9604 which indicates a 20 per cent solution of
NH₄OH. Dilute this to 4 per cent with water.) Allow to remain, with occasional shaking, for 24 hrs. During this time the bottle is inclined as much as possible without bringing the contents in contact with the stopper, thus allowing the soil to settle on the side of the cylinder and exposing a very large surface to the action of the ammonium hydroxid. Place the cylinder in a vertical position and leave for 12 hrs. to allow the sediment to settle.

For the convenience of students this time period may be altered, e.g. changed from 12 to 16 hours which can be included from 4 p.m. to 8 a.m. In any case, however, the arbitrary time periods specified must be followed closely.

Draw off 300 c. c. of the supernatant liquid with a pipette, without stirring up the sediment, place in a stoppered 500 c. c. flask and let stand for 48 hrs. Carefully pipette off 200 c. c. of the liquid, now rid of a large part of the clay, into a 250 c. c. beaker, evaporate on the steam bath and let the residue heat on the bath for 2 hrs. Dissolve the humus out with 200 c. c. of 4 per cent NH₄OH and filter through paper to separate flocculated clay. Evaporate 50 c. c. aliquots, dry at 100°C, and weigh. Then ignite the residue mildly, to oxidize organic matter, and again weigh. Calculate the humus from the difference in weights between the dried and ignited residues. Report as per cent of the dry soil.

\[ \text{Ca}_2\text{H}_2\text{O}(\text{OH})_2\text{COO}_2 \text{H}_2\text{O} + \text{HCl} = \text{Ca}_2\text{H}_2\text{O}(\text{OH})_2\text{COOH} + \text{NH}_4\text{OH} \]
\[ \text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O} + \text{heat} = \text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O} + \text{H}_2\text{O} \]

**Total Carbon.**

Six grams of sodium peroxide are placed in an iron crucible of 40 to 50 c. c. capacity and the soil added. The amount of sample to be taken will depend upon the amount of carbon present. For ordinary soils 1 to 2 gm. should be used, but for peat soils or other organic materials with a carbon content greater than 40 per cent the amount of sample should be reduced to .10 to .20 gm. Addition of .10 gm. of magnesium should be made for the purpose of accelerating the reaction. The charge is now well mixed with a stirring rod, covered with a tight cover, set in another iron or nickle crucible of about 120 c. c. capacity and this outer crucible also covered. This is done for the purpose of preventing absorption of gases from the flame of the burner during the fusion. The further precaution of projecting the bottom of the crucible through a hole in an asbestos board should be followed. The mixture is next ignited by applying the flame and regulating the heat so as to avoid too violent a reaction. This can generally be done by withdrawing the burner at the first sign of the beginning of the reaction. If the reaction proceeds with too great violence losses may occur and less sample should be taken. After the reaction has subsided the crucible should be heated 3 to 5 min. longer. The inner crucible and charge are
then placed in a desiccator and allowed to cool. When cool the crucible is put in a 4-in. funnel and the contents transferred to a 250 c. c. flask with carbon-dioxide-free water, keeping the volume down to 150 c. c. (carbon-dioxide-free water should be prepared by boiling one liter of distilled water for 10 to 20 min.) After the first addition of water to the crucible the funnel should be quickly covered with a watch glass and later washed off. If the fusion has proceeded properly there will be no residue of unburned carbon. The flask is next attached to the condenser head, the solution made acid with 25 per cent sulphuric acid and the carbon dioxide distilled into a tower of beads to which has been added 10 c. c. of 30 to 35 per cent NaOH with a bulb connector between condenser and bead tower.

After distilling over about 60 c. c. the apparatus is detached and the contents of the receiver transferred to a 250 c. c. flask by successive washings with small portions of carbon-dioxide-free water. This is easily accomplished by inclining the end of the pipette-like connector into the flask and pouring the wash water over the beads. The washing should be complete as indicated by phenolphthalein. It is always possible to completely wash the tower and keep within the 250 c. c. of volume. Phenolphthalein is next added to the solution and 25 per cent sulphuric acid run in until the color begins to change. Care should be taken not to overshoot the end point or low results may follow. The solution is now made up to 250 c. c. and aliquots of 50 c. c. taken for titration. A few drops of phenolphthalein are added and the titration continued with N/10 sulphuric acid to a neutral reaction. At this point when the carbon exists as acid carbonate, methyl orange is added and the titration continued until a change of color occurs. Use only 1 to 2 drops of a dilute solution of methyl orange. The number of c. c. of N/10 acid used during the titration with methyl orange as an indicator, minus the blank, multiplied by the carbon factor .0012 gives the weight of carbon in 50 c. c. of the solution. A correction blank is run in the same manner as above described to determine the carbon in the peroxide and the reagents used. Report the carbon as per cent of the soil.

Carbon Dioxide.

Place 10 gm. of the air-dry soil (5 gm. in case of soils rich in limestone) in the distilling flask of the apparatus. This flask should be fitted with a dropping-funnel and a delivery arm leading into an inverted condenser. The absorption train should consist of a sulfuric-acid absorption bulb, a bulb of 40 per cent KOH solution, a calcium chloride tube, a soda-lime tube, and an aspirator bottle arranged in successive order from the condenser. The potash bulb and calcium chloride tube are weighed at the beginning of the experiment.

Having the apparatus carefully joined together, test it for leaks by letting the water flow from the aspirator bottle. If it is tight the
bubbling of gas through the various bulbs will cease. Now add drop by drop 20 c. c. of 20 per cent hydrochloric acid to the soil from the funnel, regulating the addition of acid by the rate at which the carbon dioxide comes off—the bubbles should not pass through the absorption bulbs faster than about 2 per second. After all the acid has been added close the glass stop-cock, and heat the flask gently to the boiling point of the solution. Boil for two or three minutes, and then before removing the flame cautiously open the stop-cock and admit air into the apparatus. Care must be observed lest a sudden rush of air enters the apparatus. Remove the flame and draw air through the apparatus for 5—10 minutes. A soda-lime tube should be fitted into the funnel containing the hydrochloric acid so as to remove the carbon dioxide contained in the air. Remove the bulbs previously weighed and weigh again. Report the increase in weight, as per cent of carbon dioxide.

What compound in the soil is the chief source of the evolved carbon dioxide? What function does it serve in the soil? Why is not NaOH used to absorb the CO₂?

\[
\text{CaCO}_3 + \text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{KOH} + \text{CO}_2 = \text{K}_2\text{CO}_3
\]

**Nitrification Experiment.**

Wash 500 to 600 gm. of medium fine sand with distilled water and spread it on paper to dry. Mix with the dry sand about 0.3 gm. K₂HPO₄, 0.5 gram CaCO₃, and 2.0 gm. fresh garden soil. Place in a large petri dish or percolator, cover with a mulch of cotton, and determine the weight of the system. Now add 50 c. c. of N/20 NH₄Cl, and enough distilled water to increase the moisture content to 50 per cent of the water-holding capacity of the sand, by weight, as directed. Maintain the above moisture content. After about 3 weeks leach out the sand with distilled water to a volume of 500 c. c., filtering through paper.

Evaporate 10 c. c. of standard nitrate solution to dryness in a porcelain dish on a water or steam bath and treat the same as the percolate below, finally diluting the solution to 100 c. c. This standard colorimetric solution has the strength of 1 part of NO₃ per million, or 0.001 mgm. NO₃ per c. c.

Evaporate 10 c. c. of the extract to dryness in a porcelain dish on a water bath, removing the dish as soon as it is completely dry. Add 1 c. c. of phenoldisulphonic acid reagent and stir thoroughly with the rounded end of a glass rod so as to loosen the residue and bring the acid well in contact with every portion of it. The time of action on the nitrate should be about 10 min. At the end of this time the acid is diluted with about 15 c. c. of water and made alkaline with ammonium hydroxide, a yellow color being developed when the solution becomes alkaline. This is then diluted to 100 c. c. and compared with the standard colorimetric solution by means of a colorimeter. With diameter of plungers and divisions of scales
equal, the depths of liquid giving equal intensity of color in this
instrument vary inversely as the concentrations of NO₃. If the
color of the unknown is too intense for direct comparison with the
standard, an aliquot portion may be diluted to definite volume and
the strength of this determined. Calculate the milligrams of nitro-
gen as nitrate recovered from the sand and express as per cent of
nitrification, as follows:

Milligrams N as NH₄ in Nutrient Solution=
Milligrams N as NO₃ in 10 c. c. percolate=
Milligrams N in total percolate=
Per cent nitrification=

State the purpose of the following substances used in the above ex-
periment: Potassium phosphate, garden soil and calcium carbonate.

Explain what has happened in the course of this experiment.

\((NH₄)₂SO₄ + O = HNO₃ +\)
\(CaCO₃ + HNO₃ =\)
\(CaCO₃ + H₂SO₄ =\)
\(H₂SO₄ + Ca(NO₃)₂ = 2HNO₃ + CaSO₄=\)
\(C₆H₅(OH)·(SO₂H)₂ (Phenol disulphonic acid) + HNO₃=\)
\(C₆H₅(OH)·(SO₂H)₂ (NO₂) (Nitro phenol disulphonic acid + H₂O\)
\(C₆H₅(OH) (SO₂H)₂ + 3NH₃·OH = C₆H₅(ONH₂) (SO₂NH₂)₂NO\)
(Yellow ammonium nitro-phenol disulphonate) + 3H₂O

II. FERTILIZERS AND MANURES

Fertilizers and manures are substances which, when added to the
soil, either increase the supply of such elements as may be lacking
for the growth of crops, or otherwise bring about changes favorable
to their growth. When furnishing food in themselves these subst-
ances are termed direct fertilizers: when acting in other ways,
they are classed as indirect fertilizers. In analytical work we shall
deal mostly with direct fertilizers.

The soil elements most drawn upon by the plant and so most fre-
cently exhausted are Nitrogen and Phosphorus. Sulphur is also
very low in amount and freely used by plants, but has not been
given commercial value in fertilizers. On the other hand, potassium
is very abundant in most soils, but a very large part of it is in un-
available forms. It is in common use as an ingredient of fertilizers
and is given commercial value. Consequently, our commercial fer-
tilizers contain compounds of N, P and K either singly or in mix-
tures, a mixture of all three being termed a “complete fertilizer.”

Farm yard manure is a natural complete fertilizer.

A great variety of materials is used in the production of commer-
cial fertilizers, many industries turning their by-products to account
in this direction. To a basal or “filling” material, nitrogen may be
added in the form of “Chili saltpetre” (sodium-nitrate) from deposits
in arid regions, potassium as sulphate or chlorid from brines and
salt deposits; and phosphorus in the form of apatite from Canada

2—G. A. C.