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PART I: BASE EXCHANGE EQUATIONS APPLIED TO IOWA SOILS

PART II: ACID OXIDATION METHOD FOR DETERMINING SOIL CARBON

by

Clyde L. Ogg

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Soil Chemistry

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TABLE OF CONTENTS

PART I: BASE EXCHANGE EQUATIONS APPLIED TO IOWA SOILS

Page

I. INTRODUCTION 5

II. HISTORICAL 7

III. EXPERIMENTAL 18

  A. Materials 18

    1. Soil samples 18

    2. Preparation of solutions 19

      a. Ammonium acetate 19

      b. Hydrochloric acid 19

      c. Sodium hydroxide 19

      d. Potassium permanganate 20

      e. Sodium thiosulfate 20

      f. Potassium bromide - potassium bromate . 20

    3. Standardization of solutions 20

      a. Hydrochloric acid 20

      b. Sodium hydroxide 21

      c. Potassium permanganate 21

      d. Sodium thiosulfate 21

      e. Potassium bromide - potassium bromate . 21

  B. Procedure 22

    1. Exchangeable bases liberated in equilibrium with a displacing ion 22

T7364

Page

a. Calcium 23

b. Magnesium 24

c. Sodium and potassium 25

d. Total bases liberated from the soil . . 26

2. Total exchangeable bases by leaching . . . 27

C. Results 27

1. Base exchange equations applied to Clarion loam 27

2. The effect of soil-water ratio on S as obtained by Vageler's equation 43

3. Base exchange equations applied to Shelby loam 48

4. Base exchange equations applied to Tama silt loam 51

5. Base exchange equations applied to Conover silt loam, Fayette silt loam, Lindley fine sandy loam, Millsdale loam and a second Clarion loam 52

6. Application of Vageler's and Gapon's equations to exchangeable H^+ in hydrogen saturated Clarion loam, No. 1062 58

7. Effect of the pH of leaching solutions on the exchange capacity of Soil No. 1062 . . 66

8. pH and buffering capacity of ammonium acetate solutions 67

IV. DISCUSSION 71

V. SUMMARY 77

VI. LITERATURE CITED 79

PART II: ACID OXIDATION METHOD FOR DETERMINING SOIL CARBON

Page

I. INTRODUCTION 82

II. HISTORICAL 84

III. EXPERIMENTAL 99

- A. Apparatus 99
- B. Procedure 102
- C. Results 106
  - 1. Determination of total carbon 106
  - 2. The effect and removal of chlorides 111
  - 3. Preliminary removal of carbonates 112
  - 4. Wet oxidation with the addition of H_2O_2 . . 115

IV. DISCUSSION 117

V. SUMMARY 125

VI. LITERATURE CITED 127

VII. ACKNOWLEDGMENT 129

I. INTRODUCTION

Numerous studies have been made on the different phases of base exchange in soils. The methods for determining exchangeable bases, exchangeable H^+ and exchange capacity have been many and varied.

Theories concerning the nature of base exchange have undergone several changes since Way's discovery of the phenomenon in 1852. The main point in contention has been whether the exchangeable bases are adsorbed by the soil particles or held by chemical bonds or whether both attractive forces play a part in base exchange. The more recent studies have been in favor of the theory that the reaction is chemical in nature, particularly for the inorganic fraction of the soil.

A number of equations have been derived which were intended to express the mathematical relations between the exchange capacity, the amount of bases displaced and the amount of displacing salt. An equation proposed by Vageler and Woltersdorf (29) and a similar equation derived by Gapon (11) have been found to be satisfactory expressions of base exchange phenomena in some soils. Greene (14) pointed out that the supposed constants in Vageler's equation varied with a change in relative amounts of soil and water but that a ratio of one part soil to five of water was suitable for most soils.

The purpose of this study was to test both Vageler's and Gapon's equations on some Iowa soils and to determine the effect of varying the soil-water ratio on the validity of Vageler's equation.

No attempt was made to arrive at a new method for determining exchangeable bases or base exchange capacity nor to test various known methods. The common method of leaching with ammonium acetate was used since this salt produced a solution whose pH approached neutrality. It was not intended to study the nature of the base exchange material nor the nature of the reaction except as indicated by the success or failure of the equations used.

II. HISTORICAL

In keeping with the physical and chemical concepts of base exchange, two types of equations have been developed. Equations for adsorption on the surfaces of solids, such as Langmuir's (18) and Freundlich's (8), represent the physical point of view. The chemical concept of base exchange has led to the development of equations based on the law of mass action.

Langmuir's equation for the adsorption of gases on solids, as given by Getman and Daniels (13), is $y = \frac{a \cdot b \cdot p}{1 + ap}$ in which y is the weight of material adsorbed per unit surface of adsorbing material, a and b are constants, and p is the pressure of the gas. Concentration, c, may be used in place of p, and y may be expressed as the weight of adsorbed material per unit weight of adsorbent. Getman and Daniels call attention to the fact that Langmuir's equation holds well for low pressures but decreases in accuracy as the pressure is increased.

By plotting the amount of base adsorbed by a soil against the amount of base added in solution, Vageler (29) obtained a hyperbolic curve which was expressed by the formula, $y = \frac{S \cdot C \cdot x}{1 + Cx}$. By inverting this equation he obtained $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}\left(\frac{1}{x}\right)$, a straight line equation in which y is the number of milliequivalents of base adsorbed per unit weight of soil, S and C are constants, and x is the number of milliequivalents of displacing ion added per unit weight of soil. The constant, S, represents the total base exchange capacity of the soil. Vageler stated that he arrived at this equation independently of Langmuir's equation, but he pointed out the similarity between the two equations.

Langmuir's (18) equation was developed for the adsorption of gases on solids; it was applied only to cases in which a monomolecular film was formed and the gas was being adsorbed on a surface free from foreign material. The equation has been found to be very satisfactory when these conditions exist. Adsorption in soils takes place under markedly different conditions since it is an exchange adsorption and many bases capable of being adsorbed by the soil are present in the solution at equilibrium. Bases liberated by the displacing cation counteract the adsorption of the displacing ion. Therefore, from a theoretical viewpoint, the term $\frac{C}{S}(\frac{1}{x})$ should take into account the base liberated in the equilibrium solution, unless the amount of displacing ion is so large that the amount of base liberated is negligible by comparison. Jenny's data (16) confirm this since he found that Vageler's equation was satisfactory only when high concentrations of displacing ion were used. In Vageler's equation (29) the terms x and y were expressed in milliequivalents per hundred grams of soil rather than in terms of concentration in solution. Therefore, the amount of water present in the soil or the concentration of ions in the equilibrium solution did not receive any consideration in the equation. Gapon (12) called attention to the fact that dilution of a solution containing mono- and divalent cations in equilibrium with a soil caused the monovalent ion to be displaced from the soil by the divalent ion. Eaton and Sokoloff (7) found that the amounts of Na, and usually K and Mg, were higher in aqueous extracts than in displaced soil solutions but that the amounts of Ca were lower. From this it would seem that some expression of the amount of water in the soil or the concentration of the ions should be included in Vageler's (29) equation when the displacing and displaced ions have different valencies.

Regardless of these criticisms Vageler's (29) equation was found to give satisfactory results on some Danish soils. Steenberg (27) used the equation to calculate the amount of displacing ion that should be added to a soil in order to displace sufficient Mn to prevent Grey Spot disease in plants. Greene (14) made a study of Vageler's equation as applied to some Sudan soils and came to the conclusion that a 1:5 soil-water ratio should be used. He found that by increasing the soil-water ratio, the value for S in Vageler's equation decreased. He also recommended that the amount of salt added to the soil, in the two experiments necessary to evaluate S and C, should vary by a ratio of 1 to 8. Jenny (16) observed that the equation was more satisfactory for determining S as the amount of x increased. This was expected since the term $\frac{C}{S}(\frac{1}{x})$ would approach zero as x is increased and therefore the value of y would approach S as a limit. In addition, the amount of base liberated from the soil would be negligible as compared to the amount added.

The law of mass action was used by Gapon (11) to develop the equation, $\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty} (\frac{C_1}{C_2})$. This equation was applied only in cases where the displacing and displaced ions had the same valence. When the valencies were not equal, that is C_1 divalent and C_2 monovalent, the last term in the equation was written $\frac{1}{K\Gamma_\infty}(\frac{\sqrt{C_1}}{C_2})$. This form of the equation corresponded to the chemical equation, $XCa_{\frac{1}{2}} + NH_4^+ \rightleftharpoons \frac{1}{2}Ca^{++} + XNH_4$. The terms in Gapon's equation were Γ, the amount of cation absorbed, expressed in moles per 10 g. soil; Γ_∞, total absorption capacity per 10 g. soil; K, equilibrium constant for the reaction; C_1, the concentration of the displaced ion in moles per liter; and C_2, concentration of displacing ion in moles per liter at equilibrium. Gapon obtained a straight line when $\frac{1}{\Gamma}$

was plotted against $\frac{C_1}{C_2}$, regardless of the concentration and volume of solution used.

The terms Γ, Γ_∞, and K correspond to the terms y, S, and C in Vageler's (29) equation. However, the last term in Gapon's equation $\frac{1}{K\Gamma_\infty}(\frac{C_1}{C_2})$ takes into account the effect of the cations displaced from the soil on the equilibrium established, whereas Vageler's term $\frac{1}{x}$ fails to do this. By expressing C_1 and C_2 in moles per liter, Gapon's equation automatically takes into account the effect of soil-water ratio on the equilibrium and on the amount of bases displaced.

Since Gapon's equation (11) was a straight line equation, only two determinations were required to evaluate K and Γ_∞. The amount of base absorbed when two different amounts of displacing ion were added was measured, and the two sets of values for $\frac{1}{\Gamma}$ and $\frac{C_1}{C_2}$ were plotted. A straight line was drawn between the two points and extrapolated to the y axis. The intercept of the line, $\frac{1}{\Gamma_\infty}$, represented the reciprocal of the exchange capacity of the soil, and the equilibrium constant was determined from the slope of the line, $\frac{1}{K\Gamma_\infty}$.

Marshall and Gupta (19) determined potentiometrically the activities of the different ions involved in the exchange equilibrium in clays. These activities were substituted into the mass law equation, and the dissociation constant was found to vary with changes in concentration of the displacing ion. They came to the conclusion that no one of the base exchange equations which have been proposed was satisfactory over a sufficiently wide range of concentration.

The change in the equilibrium constant with a change in the amount of displacing ion added was also noted by Aten (2). He stated that when the log. $\frac{X_AC_B}{X_BC_A}$ was plotted against X_A in the equation log. $\frac{X_AC_B}{X_BC_A} = aX_A$ log. K, a straight line resulted. He proposed the equation $\frac{X_A}{X_B} = k_1(\frac{C_A}{C_B})e^{aX_A}$. The terms X_A and X_B were the number of ions of A and B absorbed, k and a were constants, and C_A and C_B were the respective concentrations in solution.

When Gapon (11) derived his equation, he assumed areas of active adsorbing surface rather than compound formation between the soil and exchangeable ions. When compounds are considered to be formed, the assumption of formation of mixed crystals was found by Vanselow (30) and Fudge (9) to give the best results. The mass law equation gave values for K which were too high when soils with low base exchange capacity were studied by Fudge. He found that the equation $\frac{dy}{dx} = K(A - y)$ gave more satisfactory results than the mass law equation. In this equation K and A were constants and x and y were the amounts of cation added and absorbed, respectively.

Jenny (16) tested three different formulas (Ganssen's, Vageler's and Wiegner's) for ionic adsorption in soils but discarded them as being unsatisfactory and introduced a new term, "symmetry value". This value expressed the per cent replaceable ion exchanged when a soil was treated with an amount of base equivalent to the exchange capacity of the soil. For example, if a soil having 60 m.e. of exchangeable NH_4^+ was treated with 60 m.e. of Na^+ and 20 m.e. of NH_4 was liberated, the "symmetry value" would be $\frac{20}{60} \times 100 = 33.3\%$. Jenny stated that since exchange reactions were not dilute solution reactions, the chemical laws for dilute solutions, such as the Wiegner-Freundlich equation, could not be expected to hold. Jenny tested the equation derived by Ganssen (10) from the mass action law and found that the equilibrium constant was affected by dilution, by the method used to determine it, and by a time factor. The equation was $K = \frac{x^2}{(m \cdot n - x)(g - x)}$ in which m was the exchange complex in grams; n, total exchangeable bases per gram; g, the amount of salt added; and x, the amount of salt absorbed.

Wiegner (31) applied Freundlich's adsorption equation to base exchange in soils. The equation was $\frac{x}{m} = Kc^{\frac{1}{n}}$ in which $\frac{x}{m}$ was the amount adsorbed per gram adsorbent; c, the concentration at equilibrium of the displacing ion; and K and n, constants. This equation was compared with

Vageler's by Jenny (16) and found to be less satisfactory when high concentrations of salt solutions were used.

Fudge (9) was able to obtain better results by using the equation $y = KC^{\frac{1}{p}}$ than by the mass law equation. Antipov-Karataev and Antipova-Karataeva (1) claimed that Freundlich's adsorption isotherm was satisfactory for KCl solutions up to 0.8N, but not above. They found that the law of mass action, even when using activities instead of concentrations, could not be applied when solutions more concentrated than 0.1N were used.

The fact that organic matter plays an important part in base exchange in most soils caused Williams (32) to make a somewhat different approach to the problem. He calculated the base exchange capacity by $B = 0.57K + 6.3C_O$; B was the base exchange capacity of the soil and K and C_O were the per cent clay and total oxidizable carbon, respectively. This equation gave fairly uniform results on the soils tested and was used to determine the degree of unsaturation by subtracting the exchangeable bases found by experiment from the exchange capacity calculated by the equation.

The use of ammonium acetate for the determination of exchangeable bases was proposed by Schollenberger (25) since he believed it superior to NH_4Cl. He pointed out the following three advantages in using ammonium acetate:

1.) It was a neutral salt, 2.) it was a good buffering agent, and 3.) it had less solvent effect on the soil than did NH_4Cl. To obtain the exchangeable bases in the soil he leached 100 g. of soil with 750 ml. of 2N ammonium acetate solution. Brown and Walker (4) compared Schollenberger's ammonium acetate method with Parker's barium acetate - ammonium chloride method on some Iowa soils and found that the two gave comparable results.

After an examination of several methods for the determination of base exchange capacity, Puri and Uppal (22) came to the conclusion that the titration method was the only correct one since exchange capacity varied with pH. Pyranishinikov and Lukovnikov (23) also came to the conclusion that adsorption capacity seemed to be a function of the hydrogen-ion concentration. They found little Fe and Al adsorption above pH 5 and that Al was more effective than Fe in displacing Ca from the soil.

Kawashima (17) noted that soils treated with HCl at room temperature suffered a decrease in exchange capacity. Hillkowitz (15) found the same thing to be true and was unable to restore the exchange capacity to the original value by neutralization with bases. However, HCl solutions less than 0.1N did not have deleterious effect on the zeolite complex in soils.

Cation and anion exchange were attributed to the amphoteric properties of the soil by Mattson (20).

Schofield (24) wrote equations to connect the change in exchange capacity with pH. He believed the reaction $\equiv SiOH \rightleftarrows \equiv Si{-}O^- + H^+$ took place at high pH's. This was used to explain the increase in negative charges on clay particles or the increase in exchange capacity at higher pH's. Positive charges at low pH's were attributed to the following reaction: $-Al{=}O + H^+ \rightleftarrows -\overset{+}{Al}{-}OH$. This reaction would shift to the right and develop positive charges in the soil as the concentration of the hydrogen ion was increased. Schofield (24) found three types of clays: 1.) The type whose cation exchange decreased with pH until a constant value was obtained and no positive charges developed, 2.) the type whose cation exchange decreased continuously with decreasing pH but never reached zero exchange, and 3.) the type whose cation exchange decreased with pH until it became zero and anion exchange was developed. Tyulin and Bystrova (28) attributed the increase in adsorption of Ca from $Ca(OH)_2$ over that obtained from $CaCl_2$ to the coagulation of negative clay and positive R_2O_3 gels which then acquired a negative charge.

The amphoteric properties of the clay colloids affect the exchange capacity of this material, but this effect in a soil is conditioned by the presence of organic matter which has been shown to have a marked base exchange capacity. Slater and Byers (26) found the exchange capacity of organic colloids to be very high as compared to the inorganic colloids in the soil. Mitchell (21) found as high as 65% of the base exchange capacity of some soils to be due to the organic fraction. Weight for weight organic matter was found by Craig (5) to have twenty times the exchange capacity of the clay colloids. Demolon and Barbier (6) concluded that colloidal clay was a factor in the fixation of humus colloids and that cations on the clay, especially Ca, conditioned the formation of the complex. This combination of humus and clay colloids was thought by Barbier (3) to have a greater exchange capacity than either fraction taken separately.

Since Vageler's equation had been applied to soils with a certain degree of success and since Gapon's equation appeared to express base exchange in terms of the law of mass action, it was decided to test these two equations on some Iowa soils.

III. EXPERIMENTAL

A. Materials

1. Soil samples.

Soil samples were from the top 6-2/3" of cultivated Iowa soils. All samples were ground to pass a 1-mm. sieve, mixed well, air dried and stored in stoppered jars. The grinding was done with a rubber pestle in order to avoid breaking individual soil particles and thereby changing the exchange complex of the soil.

Soil No.	Soil Series and Type	County
1062	Clarion loam	Story
4C	Clarion loam	Story
7C	Conover silt loam	Dallas
9C	Fayette silt loam	Hardin
11C	Lindley fine sandy loam	Dallas
12C	Millsdale loam	Hardin
17C	Shelby loam	Dallas
19C	Tama silt loam	Hardin

2. Preparation of solutions.

a. Ammonium acetate. Ammonium acetate solutions were made by weighing a calculated amount of the salt, dissolving it in a minimum amount of distilled water, transferring this solution to a volumetric flask and diluting to the mark.

b. Hydrochloric acid. Enough concentrated HCl to make approximately 7 liters of 0.2N acid was measured in a graduate and transferred to a 2-gal. carboy. Distilled water was added to make the total volume approximately 7 liters and the carboy placed on a rocker shaker for two hours or more. After removing from the shaker, the solution was allowed to stand for several hours, preferably overnight, before standardization. The solution was siphoned from the carboy as needed.

c. Sodium hydroxide. Approximately 56 g. of NaOH pellets were dissolved in distilled water and the solution poured into approximately 7 liters of distilled water in a 2-gal. carboy. This was shaken for two or more hours and allowed to stand several hours before standardizing. No attempt was made to eliminate carbonates from the solution since methyl orange indicator was used in the standardization and in all titrations. The solution was protected from the CO_2 of the air by a $CaCl_2$ tube containing either ascarite or sodalime. The solution was siphoned from the carboy as needed.

d. Potassium permanganate. An amount of $KMnO_4$ calculated to make 7 liters of 0.1N solution was dissolved in a minimum amount of distilled water, the solution filtered and added to 7 liters of distilled water in a 2-gal. carboy which had been painted black. After shaking for two hours on a rocker shaker, the solution was allowed to stand overnight before standardization.

e. Sodium thiosulfate. The thiosulfate solution was made by dissolving 60 g. of $Na_2S_2O_3 \cdot 5H_2O$ in about 7 liters of distilled water, shaking two hours and allowing the solution to stand for three days before standardization.

f. Potassium bromide - potassium bromate. This solution contained approximately 11 g. of $KBrO_3$ and 37 g. of KBr in 7 liters of water. The two salts were dissolved in distilled water, diluted to approximately 7 liters, shaken two hours, and allowed to stand overnight before being standardized.

3. Standardization of solutions.

a. Hydrochloric acid. The HCl solution was standardized against reagent grade Na_2CO_3 which had been oven dried at 110°C. and cooled in a desiccator over $CaCl_2$. A quantity of Na_2CO_3 equivalent to 20-25 ml. of HCl was accurately weighed and dissolved in approximately 100 ml. of distilled water. This solution was titrated with the

HCl solution to be standardized until the methyl orange end point was reached. The first appearance of brown throughout the solution was taken as the end point.

b. Sodium hydroxide. The sodium hydroxide solution was standardized against standard HCl solution using methyl orange as indicator.

c. Potassium permanganate. Standardization of the $KMnO_4$ solution was accomplished by weighing oven-dried, reagent grade $Na_2C_2O_4$, dissolving it in 100 ml. distilled water, adding 10 ml. of 10% H_2SO_4 and heating the solution to 80°C. This heated solution was titrated with $KMnO_4$ solution until a faint purple color due to excess $KMnO_4$ existed for fifteen seconds or longer.

d. Sodium thiosulfate. The $Na_2S_2O_3$ solution was standardized against standard $KMnO_4$ by adding a measured amount of permanganate to a solution containing excess HCl and KI, allowing the solution to stand for about five minutes and titrating the iodine liberated. Approximately 1 ml. of starch solution was added when the color of the iodine solution became pale yellow, and addition of thiosulfate was continued until the disappearance of the blue starch-iodine color was noted.

e. Potassium bromide - potassium bromate. Bromine solution (KBr-$KBrO_3$) was added to a solution containing 5 ml. of 10% KI and 10 ml. 2N HCl in approximately 100 ml.

solution. The resulting solution containing liberated iodine was allowed to stand for approximately three minutes and titrated with standard $Na_2S_2O_3$ solution to the starch-iodine end point.

B. Procedure

The procedure described below was used in determining the exchangeable bases liberated when a soil was allowed to come to equilibrium with a salt solution and in determining the total exchangeable bases in a soil.

1. Exchangeable bases liberated in equilibrium with a displacing ion.

Since Vageler's and Gapon's equations are equations for a straight line, only two points should be necessary to fix the line. In order to obtain the data for these two points, it was necessary to determine the amount of bases liberated by two solutions of different concentrations in equilibrium with a soil. According to Greene (14), the amount of displacing ion added in the two experiments should differ by a factor of 8, that is the concentration of one solution should be 8 times that of the other.

Fifty grams of air-dry soil that had passed a 1-mm. sieve was placed in a 500-ml. bottle. To this, 250 ml. of an ammonium acetate solution containing 50 m.e.

(3.85 g.) or 400 m.e. (30.8 g.) was added and the mixture shaken for two hours on a rocker shaker at room temperature. The solution was allowed to stand until the soil particles settled well, preferably overnight, and the supernatant liquid was siphoned off. The solution was then filtered through an asbestos mat held in a Buchner funnel. A few milliliters of the solution was drawn through the funnel and discarded; the rest of the solution was filtered and a 100-ml. aliquot pipetted out for analysis.

a. Calcium. The 100-ml. aliquot was heated just to boiling, 1-2 ml. of 6N acetic acid was added to lower the pH and make certain that no Mg was precipitated with the calcium, and 5 ml. of a 5% ammonium oxalate solution was added with vigorous stirring. The calcium oxalate formed was allowed to settle for one hour, filtered through Whatman's No. 30 filter paper and washed 5 times with small amounts of cold distilled water. Between 10 and 20 ml. of 10% sulfuric acid was poured over the CaC_2O_4 and allowed to drain into the receiving beaker. A small hole was then punched in the bottom of the paper and any undissolved CaC_2O_4 was washed into the beaker with 60-80 ml. of distilled water. The solution was heated to 80°C. and titrated with standard $KMnO_4$ to the end point or slightly past. The filter paper on which the CaC_2O_4 had been caught was then placed in the solution and swirled a few times with a stirring rod. If the purple color disappeared, more $KMnO_4$ was added until the solution remained colored for thirty seconds or longer. Care was taken to avoid macerating the filter paper, for if this happened the end point faded badly and caused high results.

b. Magnesium. The filtrate from the calcium determination was heated to 60°C., 2 ml. of 5% 8-hydroxyquinoline solution in 2N acetic acid was added and 6N NH_4OH added slowly with constant stirring until the magnesium quinolate just started to precipitate. The solution was allowed to stand for one to one and a half hours, filtered through Whatman's No. 30 paper, washed well with very slightly ammoniacal water and the precipitate dissolved by pouring 50 ml. of 2N HCl through the filter, followed by 25 ml. of distilled water. The acid solution was placed in a 125-ml. glass stoppered bottle and titrated with standard KBr-$KBrO_3$ solution using methyl orange as indicator. From 0.2 to 0.3 ml. excess bromine solution was added, allowed to stand one minute with the bottle stoppered and the excess titrated with standard $Na_2S_2O_3$. This was done by adding 2-3 ml. of 10% KI solution and titrating the iodine liberated to a pale yellow color, then adding about 1 ml. of starch solution and continuing the titration to the disappearance of the blue color. Methyl orange was slowly brominated in this solution, and it was necessary to add several drops of indicator to maintain a pink color during the titration. The titration was continued until a fresh drop of methyl orange failed permanently to color the solution. Since some of the bromine was used by the indicator it seemed advisable to determine the amount of bromine solution needed to destroy the methyl orange in one drop of indicator. By counting the number of drops of indicator used, a blank was calculated and subtracted from the amount of bromine used in the titration of a sample. If too large an excess of bromine solution was added, bromine was lost from the solution and high results were obtained.

c. Sodium and potassium. The filtrate from the magnesium determination was evaporated to dryness in a porcelain evaporating dish, the residue dissolved in 5 ml. of 5% oxalic acid and re-evaporated to dryness. This oxalate residue was ignited in a muffle furnace until the oxalates were converted into carbonates or oxides. After cooling, the ignited residue was dissolved in excess standard HCl by warming almost to boiling on a hot plate, cooling and titrating the excess acid with standard NaOH using methyl orange as indicator. The walls of the evaporating dish were rubbed down with a rubber policeman before back titrating with the NaOH.

The salts were converted to the oxalates by oxalic acid as it was found that more satisfactory results could be obtained by igniting oxalates instead of acetates. The ignition was carefully controlled since both insufficient and too much heating cause low results. A series of controls were run in order to determine the correct time and temperature for the ignition. It was found that there was only a narrow temperature range which would give quantitative conversion of the oxalates to carbonates or oxides without loss of sample, thus making it necessary to control the conditions of the ignition rather carefully. The ignition procedure adopted was to place the evaporating dishes containing the dry residues in a cold muffle furnace with the rheostat set at a point that would bring the oven to a cherry red heat in seventy to seventy-five minutes. The samples were removed as soon as this temperature was obtained.

d. Total bases liberated from the soil. When the total amount of bases liberated from the soil was desired rather than the amount of individual bases, the 100-ml. aliquot was acidified with 5 ml. of 5% oxalic acid and evaporated to dryness in a porcelain dish. The residue was treated with 5 ml. of 5% oxalic acid, re-evaporated, ignited and titrated as described under the determination of sodium and potassium.

2. Total exchangeable bases by leaching.

Twenty-five grams of air-dry soil was placed in a Büchner funnel which contained a filtering medium prepared by placing a well-fitting filter paper on the bottom, covering this with a layer of asbestos and then inserting a second filter paper. The soil was leached with 5 successive 100-ml. portions of 1N ammonium acetate. Each portion of solution was allowed to filter by gravity for approximately fifteen minutes and the remaining solution drawn through by suction. The resulting leachate was diluted to 500 ml. in a volumetric flask and 100-ml. portions pipetted out for analysis. The solution was analyzed for bases by the procedures just described.

C. Results

1. Base exchange equations applied to Clarion loam.

In order to test Vageler's and Gapon's equations on a typical Iowa soil, a Clarion loam topsoil No. 1062 was used. Clarion loam is one of the most highly developed soils of Iowa, the topsoil has a medium to low acidity and the subsoil contains lime at a depth of 30-33 inches. Amounts of soil ranging from 6.25 g. to 100 g. were treated with 50 to 800 m.e. of ammonium acetate in solutions varying from 125 to 1000 ml. In each case the soil was allowed to come to equilibrium with the ammonium acetate solution and the bases determined as described. Table I presents the results obtained.

In the table "m.e. NH_4^+ added" represents the milliequivalents of NH_4^+ added as ammonium acetate and "m.e. base per 100 g. soil" is the milliequivalents of Ca, Mg, Na and K liberated from 100 g. of the soil. The term $(\frac{1}{x})$ represents the reciprocal of the milliequivalents of NH_4^+ ion added per gram soil and $(\frac{1}{y})$ the reciprocal of the milliequivalents of base liberated per gram soil. In this study, the terms y and Γ were used to express the amount of bases released by the soil rather than the amount of base absorbed, as defined by Vageler and Gapon. If the exchange was equivalent and a negligible amount of H^+ was displaced, then the amount of base absorbed and released would be the same. However, the amount of NH_4^+ ion used to displace H^+ in highly unsaturated soils would be appreciable when compared to that used to displace the bases. The amount of H^+ released by the ammonium ion was not measured because of the difficulty of titrating the free acid in the presence of ammonium acetate. Since the H^+ was not determined, the terms S and Γ_∞, in Vageler's and Gapon's equations respectively, were defined as the total exchangeable bases held by the soil. This definition of y and Γ was used to determine whether or not the equations could be used to calculate the amount of base that would be exchanged by a given amount of displacing base.

If the ammonium ion is absorbed in amounts equivalent to the bases liberated, then $(\frac{y}{x-y})$ expresses the ratio at equilibrium of the bases displaced and the displacing ion, in which y is the milliequivalents of bases liberated and x is the milliequivalents of displacing ion added. The values x and y in the term $(\frac{y^2}{x-y})$ are the same as in $(\frac{y}{x-y})$ but are expressed in milliequivalents per 100 g. soil rather than per gram soil for convenience in graphing. The terms $\sqrt{C_1}$ and C_2 express in moles per liter the square root of the concentration of the displaced ions (over 95% divalent) and the concentration of the displacing ion at equilibrium, respectively, and $\frac{1}{\Gamma}$ is the same as $\frac{1}{y}$.

The terms x-y, expressed in milliequivalents per 100 g. soil, and C_2, expressed in moles per liter, are the equilibrium concentrations of the displacing ion. The symbol x represents the milliequivalents of displacing ion added and y is the milliequivalents of base displaced. Two assumptions were made when x-y was called the equilibrium concentration of the displacing ion. First, it was assumed that the exchange was nearly equivalent and that any deviation from equivalent exchange was negligible when compared to x. Second, the amount of displacing ion, x, exchanged

TABLE I

Bases Exchanged from Clarion Loam No. 1062

No.	g. Soil	ml. Sol'n.	m.e. NH_4^+ Added	m.e. Base/ 100g. Soil	$\frac{1}{y}$	$\frac{1}{x}$	$\frac{\sqrt{C_1}}{C_2}$	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$	S obtained by plotting Vageler's	Gapon's	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$
1	6.25	250	50	16.0	6.25	.125	.072	2.04	.327	20.0	19.7	20.3	20.7
2	6.25	250	400	19.2	5.21	.016	.0097	.39	.075				
3	12.5	125	50	14.9	6.72	.25	.224	3.87	.580	19.4	19.6	20.0	20.1
4	12.5	125	400	18.9	5.31	.031	.0303	.59	.113				
5	12.5	250	50	13.8	7.25	.25	.304	3.60	.495	19.6	19.8	20.4	20.8
6	12.5	250	400	18.7	5.34	.031	.043	.59	.110				
7	25	125	50	12.9	7.75	.50	.304	6.90	.895	18.3	18.2	18.2	18.7
8	25	125	400	17.5	5.72	.063	.0417	1.10	.193				
9	25	250	50	12.3	8.14	.50	.418	6.55	.815				
10	25	250	200	15.9	6.30	.125	.114	2.03	.324	18.3*	18.4*	18.7*	19.4*
11	25	250	400	17.2	5.82	.063	.0585	1.09	.187	18.8 **	19.0**	19.0**	19.2**
12	25	250	800	18.0	5.55	.031	.0298	.57	.102				
13	25	500	50	11.1	9.00	.50	.556	5.9	.565	18.2	18.5	19.1	20.8
14	25	500	400	16.8	5.95	.063	.081	1.06	.179				
15	25	1000	50	(7.0)	(14.3)	.50	.615	3.6	.254	15.0	15.7	17.3	---

TABLE I (Cont'd.)

										S obtained by plotting			
No.	g. Soil	ml. Sol'n.	m.e. NH_4^+ Added	m.e. Base/ 100g. Soil	$\frac{1}{y}$	$\frac{1}{x}$	$\frac{\sqrt{C_1}}{C_2}$	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$	Vageler's	Gapon's	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$
16	25	1000	400	(13.0)	(7.70)	.063	.102	.82	.106				
17	37.5	125	50	12.5	8.00	.75	.369	10.4	1.30	17.7	17.9	18.0	18.5
18	37.5	125	400	16.8	5.95	.094	.0503	1.60	.270				
19	37.5	250	50	11.5	8.70	.75	.506	9.45	1.09	17.9	17.9	18.5	19.6
20	37.5	250	400	16.7	6.00	.094	.071	1.59	.268				
21	50	125	50	11.3	8.85	1.00	.424	12.75	1.44	17.3	17.5	17.8	18.7
22	50	125	400	16.2	6.17	.125	.058	2.07	.336				
23	50	250	50	10.6	9.43	1.00	.577	11.9	1.26				
24	50	250	100	12.5	8.0	.50	.298	6.67	.835	$17.3^{\#}$	$17.6^{\#}$	$18.0^{\#}$	$19.4^{\#}$
25	50	250	200	13.8	7.25	.25	.151	3.38	.495				
26	50	250	400	16.0	6.25	.125	.081	2.04	.326	$18.0^{\#\#}$	$18.2^{\#\#}$	$18.4^{\#\#}$	$19.0^{\#\#}$
27	50	250	800	17.0	5.88	.063	.041	1.07	.183				
28	50	500	50	9.7	10.3	1.00	.735	10.7	1.04	17.2	17.3	17.8	20.3
29	50	500	400	15.5	6.45	.125	.112	1.98	.308				
30	50	1000	50	7.4	13.5	1.00	.941	8.0	.592	16.2	17.2	19.7	---

TABLE I (Cont'd.)

No.	g. Soil	ml. Sol'n.	m.e. NH_4 Added	m.e. Base/ 100g. Soil	$\frac{1}{y}$	$\frac{1}{x}$	$\frac{\sqrt{C_1}}{C_2}$	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$	S obtained by plotting Vageler's	Gapon's	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$
31	50	1000	400	14.2	7.05	.125	.153	1.80	.258				
32	75	250	50	10.1	9.90	1.50	.721	17.8	1.81	15.2	15.0	15.2	15.8
33	75	250	400	14.1	7.09	.19	.093	2.72	.383				
34	100	250	50	7.85	12.75	2.00	.740	18.6	1.46	13.5	13.8	14.2	15.9
35	100	250	400	12.4	8.05	.25	.102	3.20	.396				

S by leaching = 19.1, 19.1, 19.2; ave. = 19.1

*** S values for experiments No. 9 & 11**
**** S values for experiments No. 10 & 12**
# S values for experiments No. 23 & 26
## S values for experiments No. 24 & 27

for H^+ was assumed to be negligible when compared to the equilibrium concentration x-y. The value of C_2 was obtained by converting x-y to moles per liter.

To determine whether or not a straight line could be obtained by plotting $\frac{1}{y}$ against $\frac{1}{x}$ for the Vageler equation, $\frac{1}{y} = \frac{1}{S} + \frac{1}{CS}(\frac{1}{x})$, or $\frac{1}{\Gamma}$ against $\frac{\sqrt{C_1}}{C_2}$ for the Gapon equation, $\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}(\frac{\sqrt{C_1}}{C_2})$, the values in Table I, for 25 and 50 g. soil in 250 ml. solution with varying amounts of ammonium acetate, were graphed in Fig. 1. It can be seen that the points for neither equation produced a straight line. When a curve was drawn through the points and extrapolated to the y axis, the intercept $\frac{1}{S}$ was approximately the same for both equations. The values for S, calculated from the equations, varied from 19.2 to 18.5 and were fairly close to the value for the total exchangeable bases obtained by leaching (19.1). Similarly, it can be seen from Fig. 2 that a smooth curve was obtained when $\frac{1}{y}$ was plotted against $\frac{1}{x}$ for 50 and 400 m.e. ammonium acetate in 250 ml. solution with varying amounts of soil and that S (19.2) calculated from the intercept agreed very well with S by leaching (19.1). When the same amounts of soil and salt were used and the volume of solution changed from 250 to 125 and 500 ml., three smooth curves resulted, each with the same intercept on the y axis. This is shown in Fig. 3. No points are shown for the center curve as it was traced from Fig. 2.

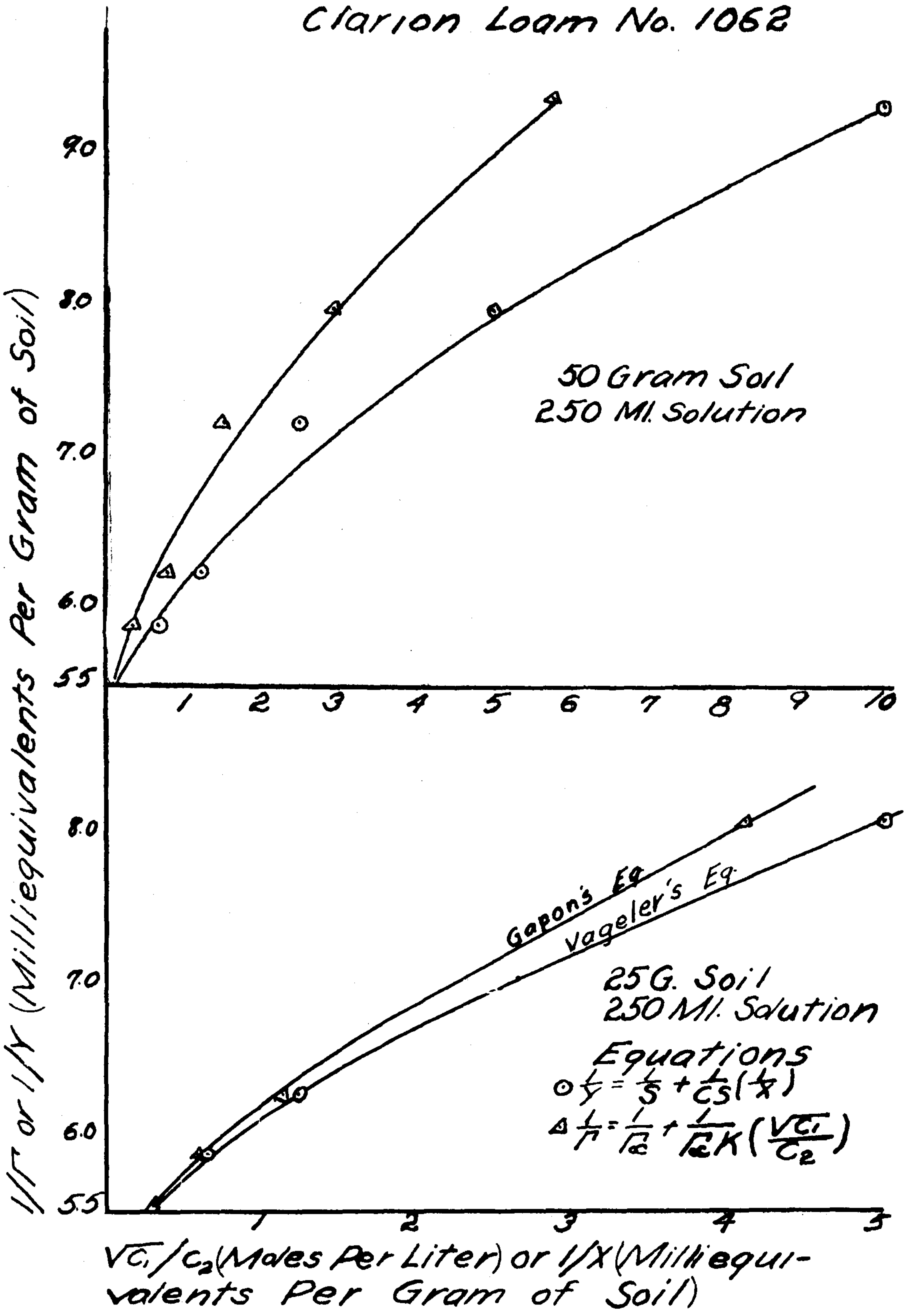

Fig. 1. Comparison of Gapon's + Vageler's Equations

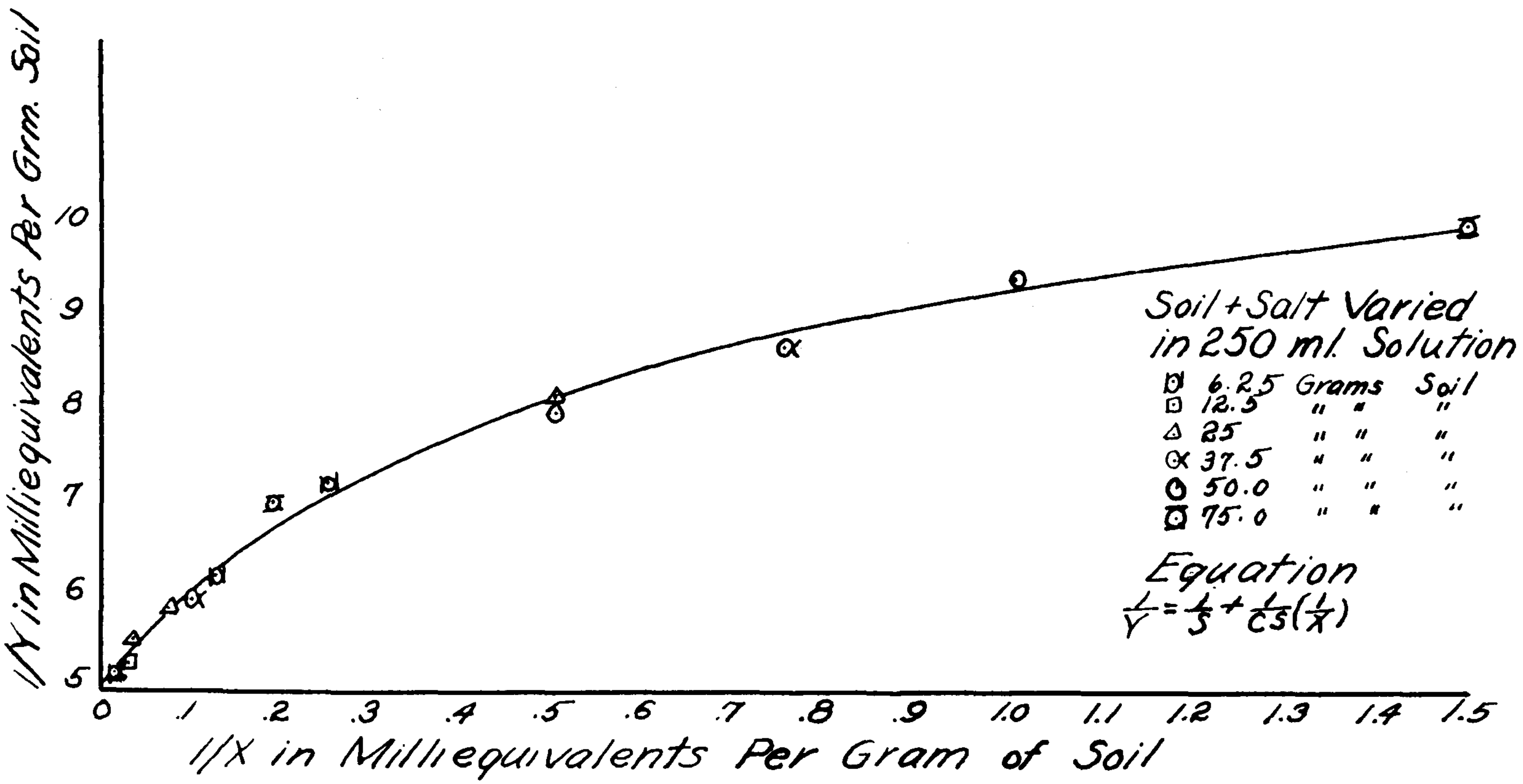

Fig. 2. Vageler's Equation Applied to Data Obtained at Constant Volume from Clarion Loam No. 1062

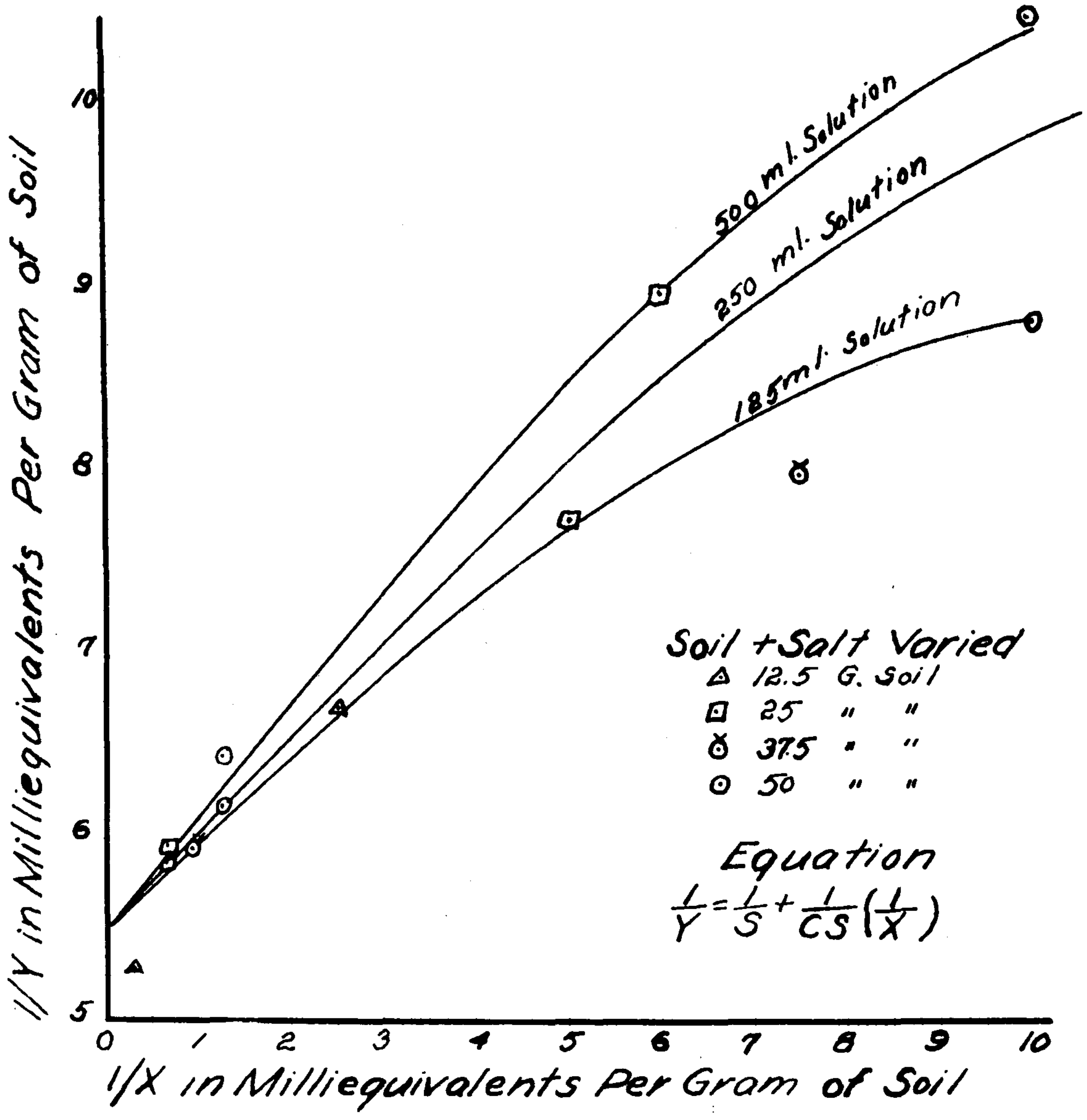

Fig. 3. Effect of Varying the Volume of Solution on Vageler's Equation

In Fig. 4 the equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{CS}(\frac{y}{x-y})$ was used for the same soil-salt mixtures shown in Fig. 2. This equation differs from Vageler's only in the last term which takes into account the effect of the displaced cations y on the equilibrium and expresses the amount of displacing ion present at equilibrium x-y, rather than the amount originally added. Again a smooth curve was obtained, but the change in the slope of the curve was less, this being the case for each different volume of solution.

This partial straightening of the curve by substituting $\frac{y}{x-y}$ for $\frac{1}{x}$ suggested that the term $\frac{y^2}{x-y}$ plotted against $\frac{1}{y}$ might produce a straight line. It can be seen in Fig. 5 that the points fall approximately on a straight line when varying amounts of soil are allowed to reach equilibrium in 250 ml. of solution containing 50 and 400 m.e. ammonium acetate. The same statement can be made concerning varying amounts of soil in 125 and 500 ml. of solution, but the slope of the curve was not the same in the three cases. This meant that the term C in the equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{y^2}{x-y})$ was constant for cases in which the same volume of solution was involved, but not for all conditions.

There was no apparent reason for squaring the y term in the numerator. When the terms $\frac{1}{x}$ or $\frac{y}{x-y}$ were plotted against $\frac{1}{y}$, as in Fig. 1 to 4 inclusive, it was noted that the slope of the curve became increasingly smaller as the

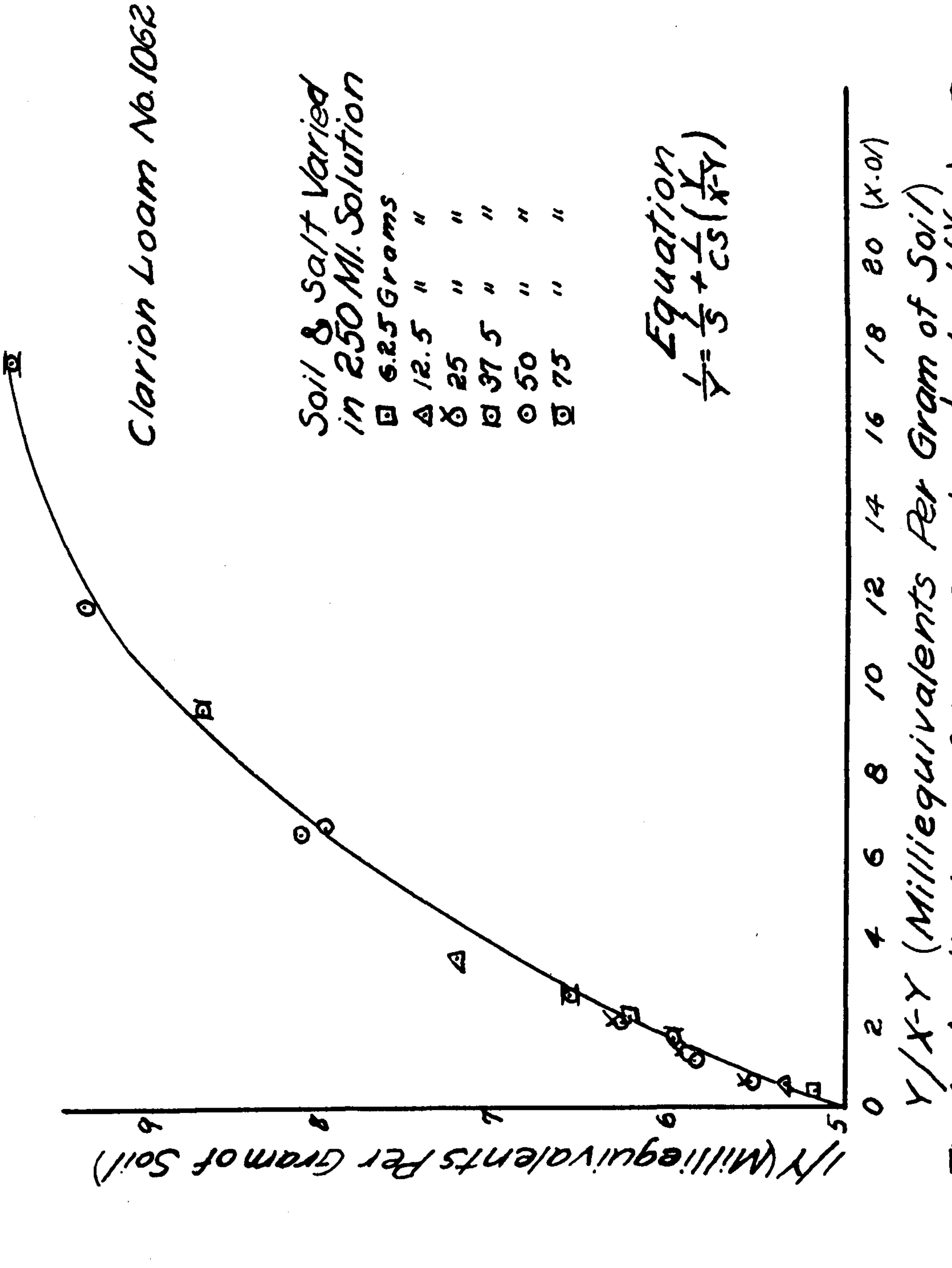

Fig. 4. Application of the Equation $\frac{1}{Y} = \frac{1}{S} + \frac{1}{CS}\left(\frac{Y}{X-Y}\right)$ to Base Exchange

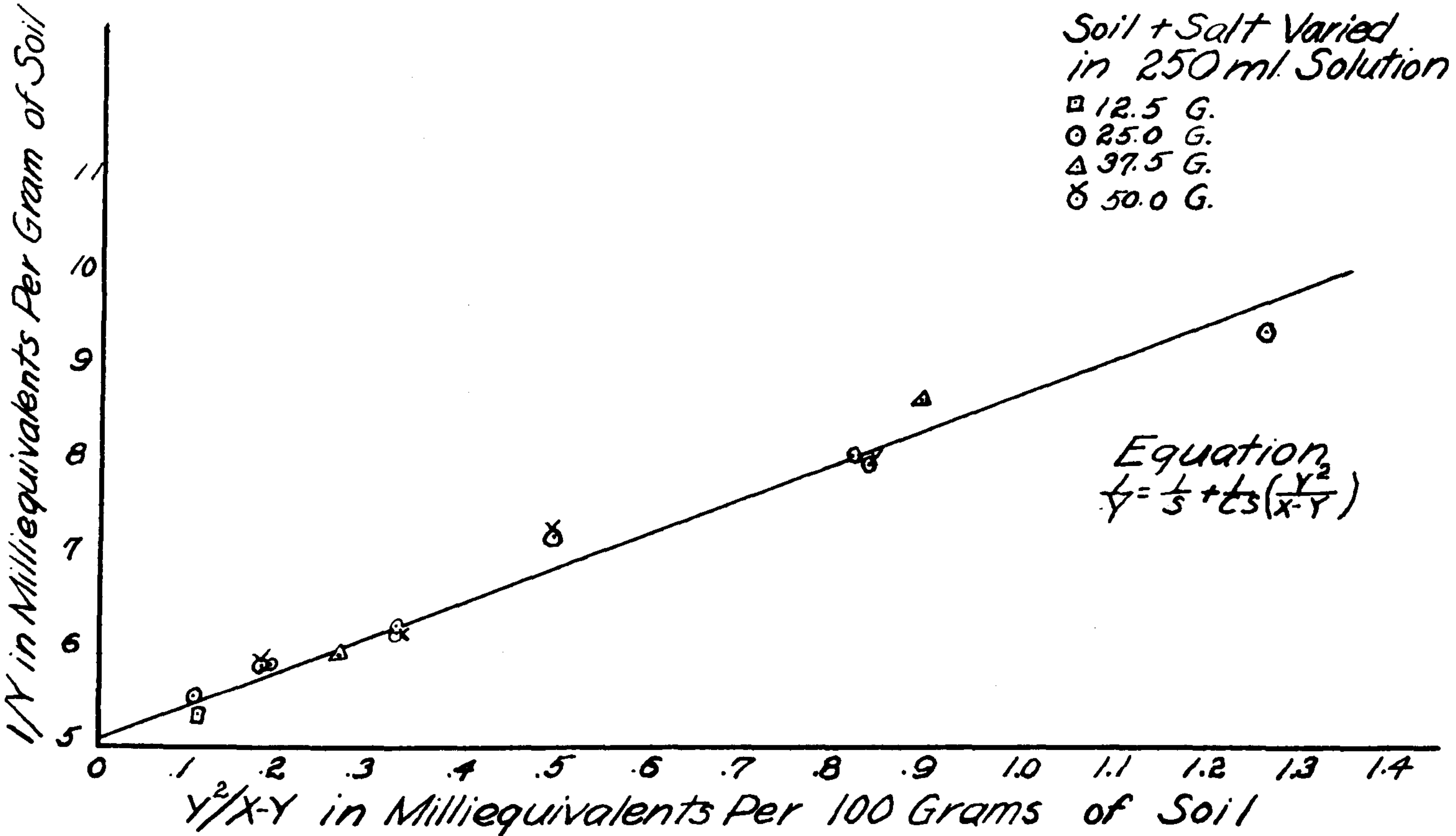

Fig. 5. Application of the Equation $\frac{1}{Y}=\frac{1}{S}+\frac{1}{CS}\left(\frac{Y^2}{X-Y}\right)$ to Base Exchange Data from Clarion Loam No. 1062

amount of salt added to the soil decreased. Evidently the amount of base liberated by small quantities of salt was too large to fit Gapon's or Vageler's equations or $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{y}{x-y})$. As Soil No. 1062 was not saturated with bases, but was studied in the base exchange state in which it existed in the field, some H^+ would also exchange for NH_4^+. A possible explanation would be that dilute ammonium acetate solutions, having a smaller buffering capacity than more concentrated ones, would have a lower pH when equilibrium was established, and therefore the capacity of the soil to hold bases would be lowered and the amount of bases released from the soil consequently increased.

Fig. 6 represents an attempt to apply Gapon's equation to the exchangeable bases from Soil No. 1062 and corresponds to Fig. 3 in which the Vageler equation was used. The points do not fall on a smooth curve, but the best line drawn through them is almost straight until the y axis is approached. The points in Fig. 6 represent the values obtained in 125, 250 and 500 ml. of solution, but there is no distinct curve representing each of the three volumes as occurred when Vageler's equation was used.

In Fig. 7 the values obtained when varying amounts of soil were placed in solutions of the same volume and concentration of displacing ion are plotted. The figure shows that straight lines were obtained, one for each

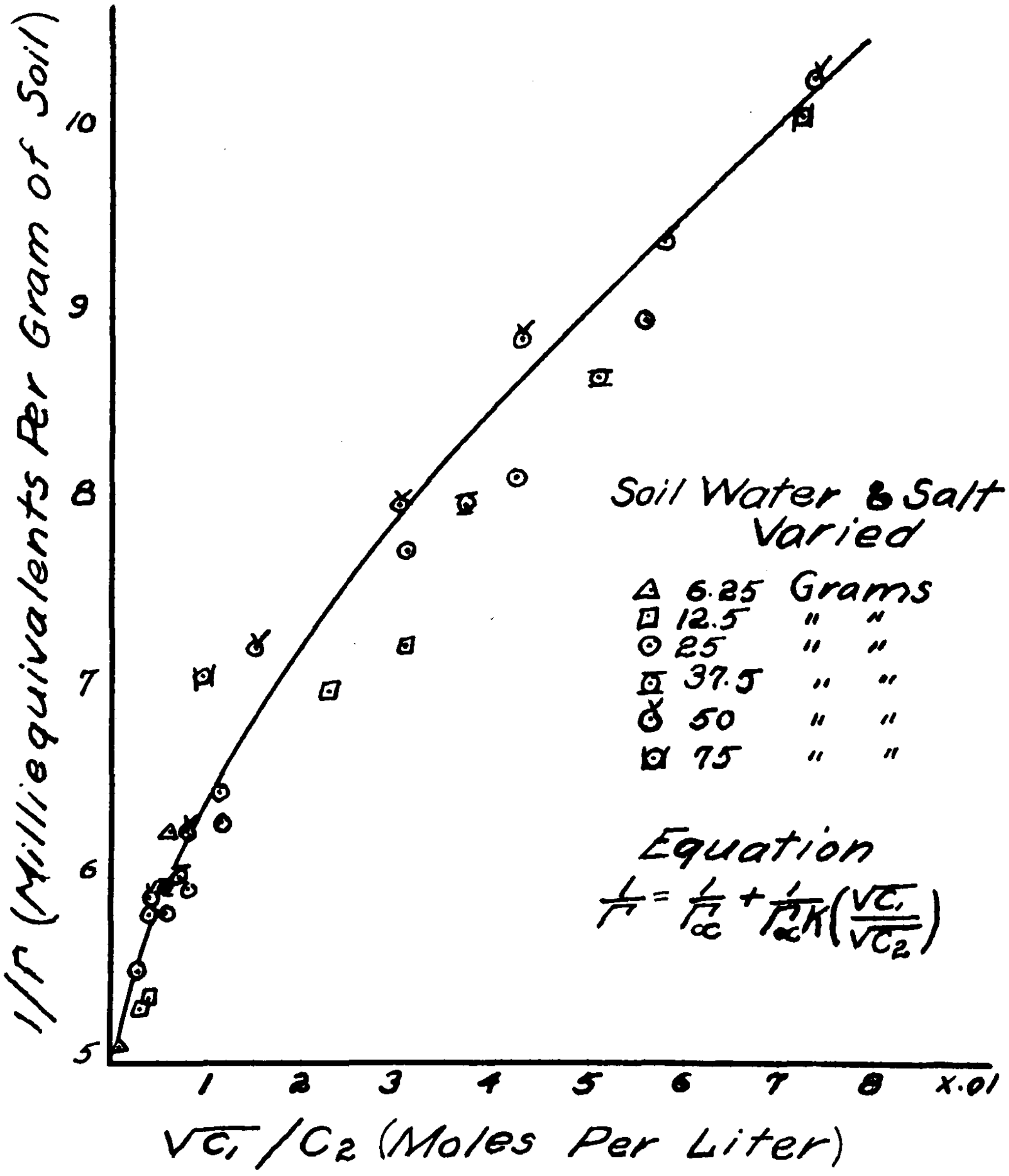

Fig. 6 Gapon's Equation Applied to Base Exchange in Clarion Loam No. 1062

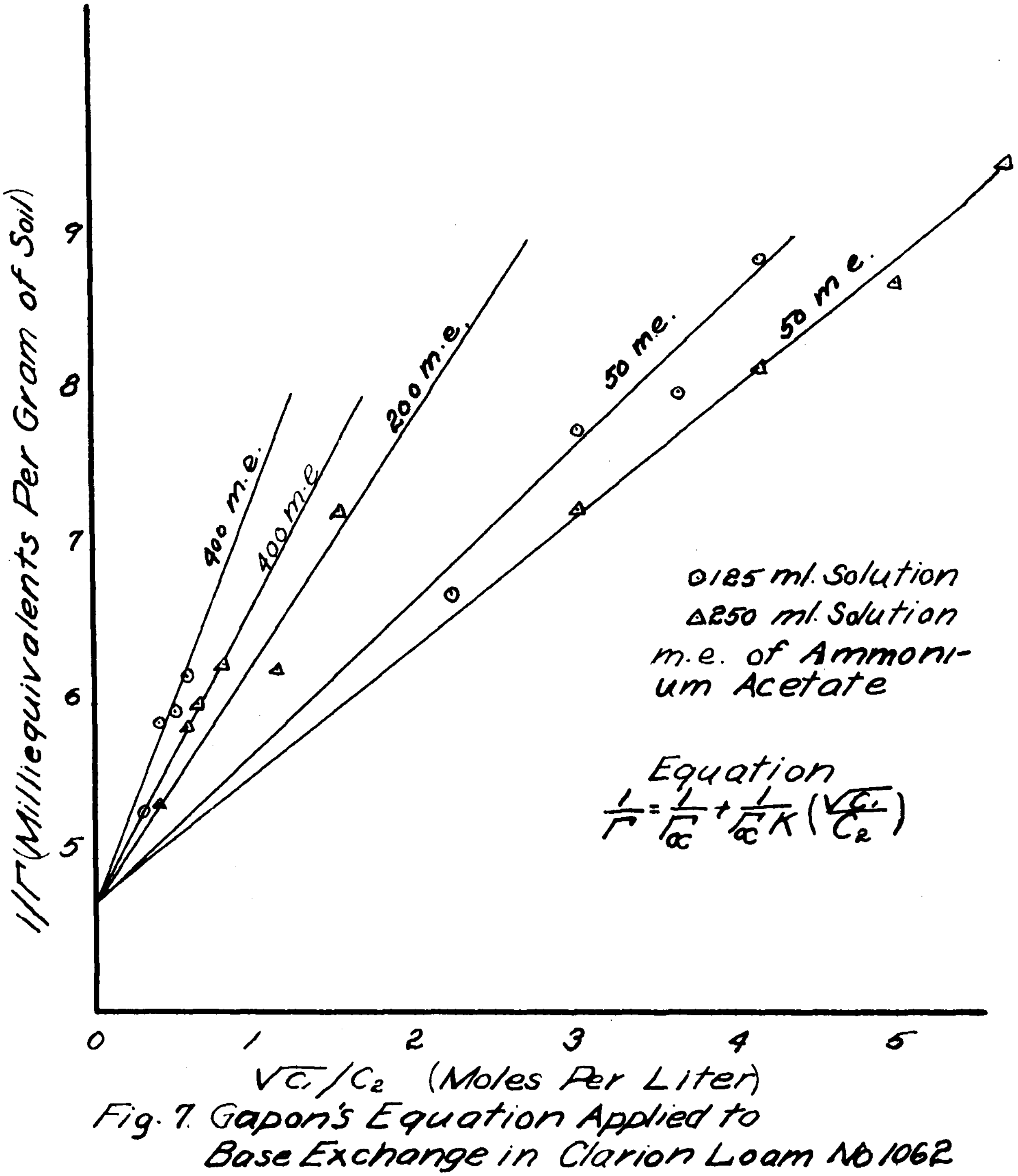

Fig. 7. Gapon's Equation Applied to Base Exchange in Clarion Loam No 1062

initial concentration of ammonium acetate used, and that the lines converge to a point on the y axis.

From an inspection of Fig. 1-7, inclusive, it was apparent that none of the equations represented accurately the base exchange phenomena for Soil No. 1062. Vageler's equation and the modified Vageler equation were definitely not satisfactory. Both equations gave a plotted value for S which agreed well with the value obtained by leaching, but the term C was not constant and would have to be determined for each individual case. The second modification of Vageler's equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{y^2}{x-y})$ gave the nearest approach to a straight line of any of the equations used, but the slope of the line changed with the volume of solution in contact with the soil. The equation derived by Gapon most nearly presented a true picture of the reaction when all factors were considered. The equation produced straight lines when varying amounts of soil were added to a solution of fixed concentration. For an explanation of the curve obtained in Fig. 6, see p. 72 and 73.

2. The effect of soil-water ratio on S as obtained by Vageler's equation.

In order to check Greene's (14) statement that S obtained by plotting $\frac{1}{y}$ against $\frac{1}{x}$ depended on the soil-water ratio, the data in Table I were recalculated in terms of soil-water, soil-salt and salt-water ratios and are presented in Table II. By inspection of Table II, it can be seen that only in those experiments in which the soil-salt ratio was constant did the value of S remain constant. If the ratio of soil to salt was constant, then the soil-water ratio could be changed fourfold without affecting the plotted value for S. Fig. 8 shows this point more clearly. The numbers given at each point are the values for S obtained when different amounts of soil were treated in 125, 250 and 500 ml. solution with 50 and 400 m.e. ammonium acetate. The numbers 1z, 2z and 4z represent salt-water ratios of 1-2.5, 1-5 and 1-10, respectively. In calculating the salt-soil and salt-water ratios, the value for salt was taken as 50 m.e. in each case. The values for S which lie on horizontal lines representing a constant salt-soil ratio were approximately constant. Soil-water and salt-water ratios were varied as much as fourfold without causing S to change. It was to be expected that a change in salt-soil ratio would give different S values since it was shown in Fig. 1 that the slope of the curve varied with the amount of salt used.

Fig. 9 shows more clearly the effect of soil-salt ratio on the calculated exchange capacity obtained by using Vageler's equation. The points fall reasonably close to a straight line and indicate a possible maximum amount of exchangeable base of 20.5 m.e. This value

TABLE II

Soil-water, Soil-salt and Salt-water Ratios for S Values on Clarion Loam

Numbers from Table I	S* Plotted Using Vageler's Equation	Soil-water	Soil-salt	Salt-water
1 & 2	20.0	1-40	1-8	1-5
3 & 4	19.4	1-10	1-4	1-2.5
5 & 6	19.6	1-20	1-4	1-5
7 & 8	18.3	1-5	1-2	1-2.5
9 & 11	18.3	1-10	1-2	1-5
13 & 14	18.2	1-20	1-2	1-10
17 & 18	17.7	1-3.75	1-1.33	1-2.5
19 & 20	17.9	1-7.5	1-1.33	1-5
21 & 22	17.3	1-2.5	1-1	1-2.5
23 & 26	17.3	1-5	1-1	1-5
28 & 29	17.2	1-10	1-1	1-10
32 & 33	15.2	1-3.3	1-0.67	1-5
34 & 35	13.5	1-2.5	1-0.5	1-5

*Values from Table I.

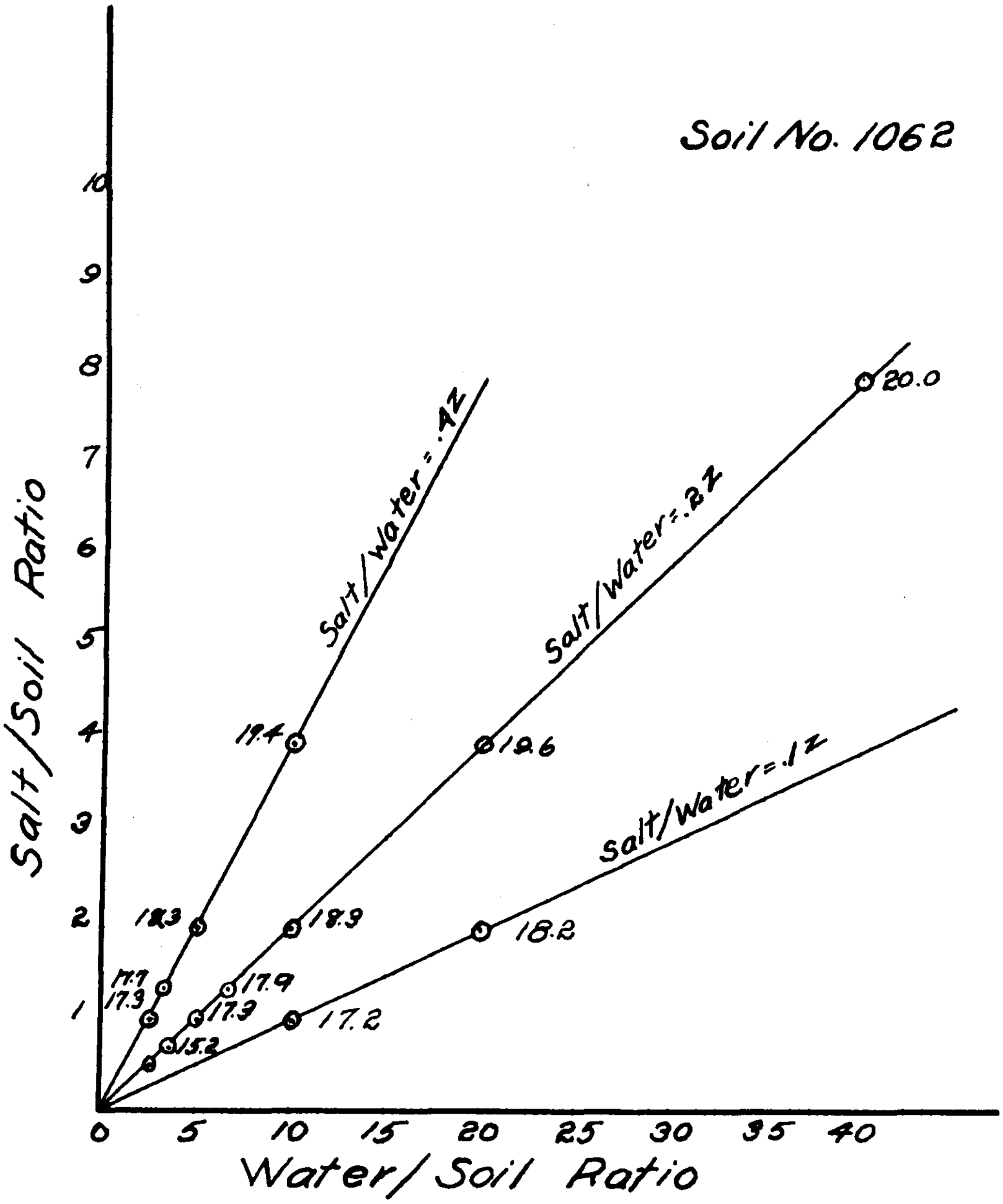

Fig. 8. Effect of Varying Salt/Soil Water/Soil and Salt/Water Ratios on S by Vageler's Equation

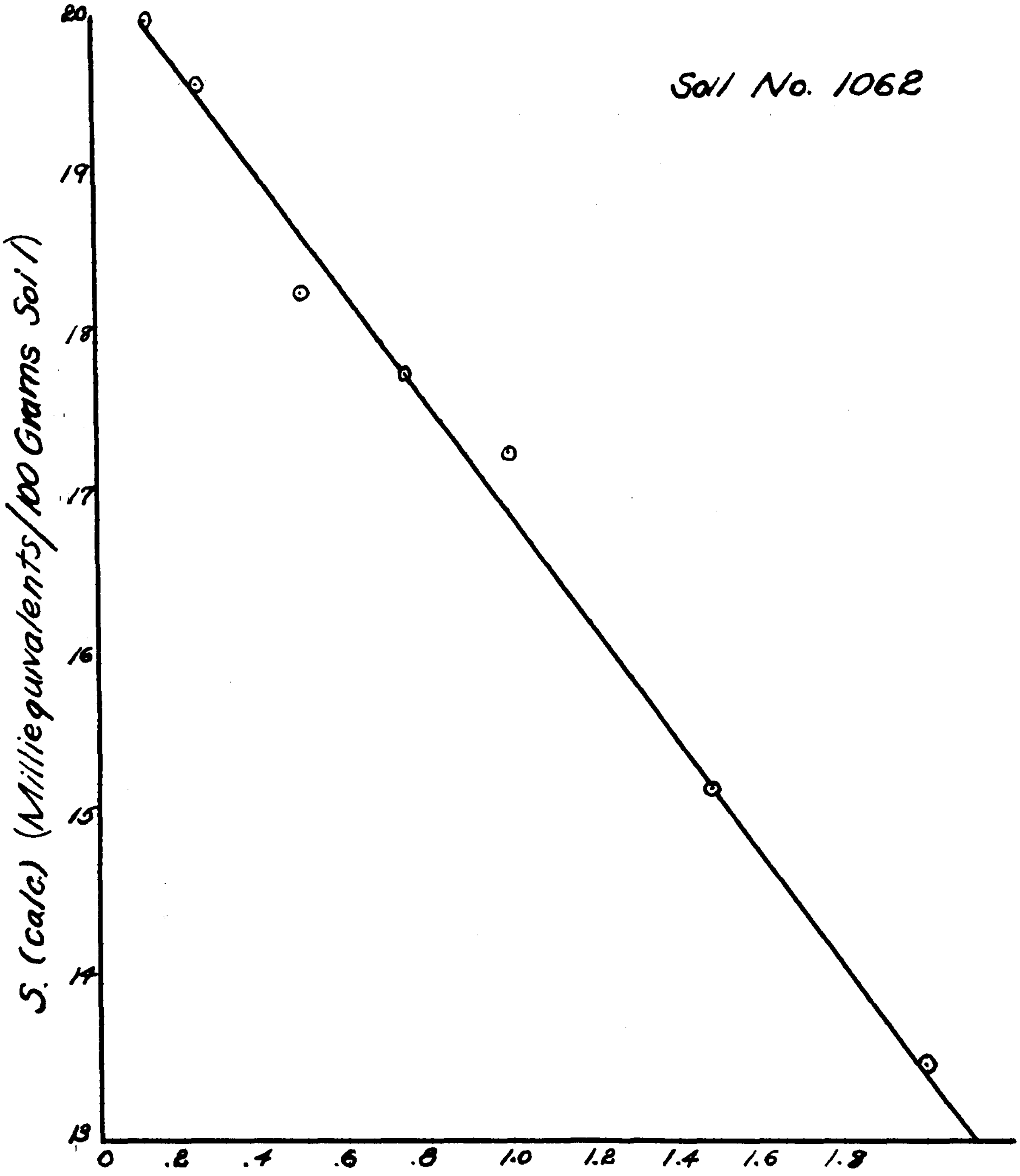

Fig. 9. Effect of Varying Soil-Water Ratio on S by Vageler's Equation

seems too high, but from the data obtained it appears that 500 ml. of 1.0N ammonium acetate was not sufficient to displace all the bases from the soil, in spite of the fact that doubling the amount of normal solution increased the bases by only 0.1 m.e. In experiment No. 2 in Table I, 400 m.e. ammonium acetate in equilibrium in 250 ml. solution with 6.25 g. soil liberated as much base per gram of soil as was obtained by leaching 25 g. soil with one liter of normal solution.

Contrary to Greene's (14) findings, Fig. 8 shows, that for Clarion loam, the values for S obtained by plotting Vageler's equation did not vary with the soil-water ratio when the soil-salt ratio was held constant. However, the slope of the curves did vary with the soil-water ratio, but the curves shifted so that they intersected the y axis at the same point.

3. Base exchange equations applied to Shelby loam.

Table III presents the data for Shelby loam, No. 17C. This soil has a moderately acid topsoil to a depth of about 30 inches and a basic to weakly acid C horizon from 30 to 60 inches. Twenty-five grams of soil was treated with four different amounts of ammonium acetate in 250 ml. of solution and the displaced bases were measured. The data obtained were plotted in Fig. 10, and curves similar to those obtained for Soil No. 1062 (Fig. 1) were obtained.

TABLE III

Base Exchange from Shelby Loam No. 17c

Soil No. 17c

No.	g. Soil	ml. Sol'n.	m.e. NH_4^+ Added	y	$\frac{1}{y}$	$\frac{1}{x}$	$\frac{\sqrt{C_1}}{C_2}$	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$	S* obtained by plotting: Vageler's	Gapon's	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$
1	12.5	125	50	11.4	8.75	.25	.194	.029	.335	13.3	13.1	13.3	13.2
2	12.5	125	400	13.0	7.77	.031	.025	.004	.053				
3	25	250	50	9.4	10.60	.50	.360	.049	.465				
4	25	250	100	10.9	9.17	.25	.190	.028	.31	13.0	13.1	13.3	13.6
5	25	250	400	12.4	8.05	.063	.050	.0078	.097	13.9	14.0	14.0	14.3
6	25	250	800	13.5	7.40	.031	.026	.004	.058				
7	50	125	50	10.2	9.61	1.00	.396	.116	1.18	13.2	13.9	13.2	13.3
8	50	125	400	12.7	7.87	.125	.051	.016	.204				
9	50	250	50	8.9	11.20	1.00	.515	.098	.87	12.7	12.8	12.9	13.4
10	50	250	400	12.1	8.27	.125	.070	.015	.185				
11	50	500	50	8.7	11.50	1.00	.725	.095	.835	12.4	12.5	12.7	13.0
12	50	500	400	11.8	8.50	.125	.098	.015	.178				
13	75	250	50	8.9	11.20	1.50	.666	.154	1.38	12.2	12.6	12.5	12.6
14	75	250	400	11.7	8.60	.19	.133	.022	.245				

*S by leaching = 14.1, 14.2, 14.0, 13.8; ave. = 14.0.

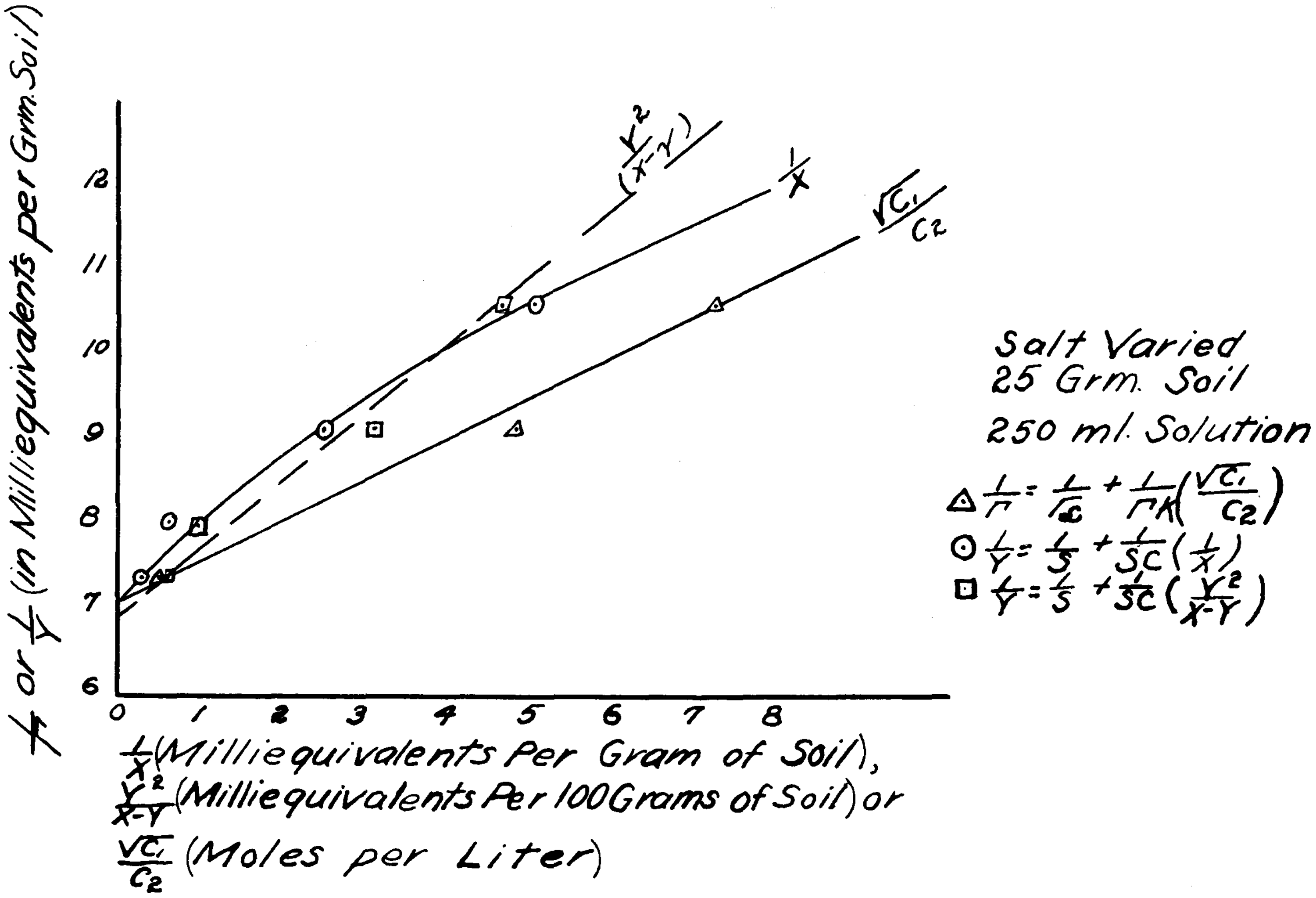

Fig. 10. Equations Applied to Base Exchange in Shelby Loam No. 17c

The value $\frac{1}{y}$ plotted against $\frac{1}{x}$ and $\frac{\sqrt{C_1}}{C_2}$ produced curved lines, but when plotted against $\frac{y^2}{x-y}$ the best line through the points was a straight line that intercepted the y axis at 7.1 (S = 14.1 m.e./100 g. soil).

This soil shows some decrease in S by plotting when wider soil-water ratios are used. Fifty grams of soil in 125, 250 and 500 ml. solution containing 50 and 400 m.e. ammonium acetate gave values for S of 13.2, 12.7 and 12.4, respectively. These values represent a constant soil-salt ratio, and Soil No. 17C is unlike No. 1062 in that the same value for S was not obtained when the soil-salt ratio was held constant.

The soil-water ratio was held constant and the soil-salt ratio varied in the experiments involving 12.5 g. soil in 125 ml. solution, 25 g. soil in 250 ml. and 50 g. soil in 500 ml. solution. The value for S decreased as the soil-salt ratio increased in a manner similar to that observed for Soil No. 1062.

4. Base exchange equations applied to Tama silt loam.

Tama silt loam, No. 19C, is a highly developed and productive soil of eastern and east-central Iowa. It is moderately acid to a depth of 36 inches or more and remains slightly acid to a depth of at least 60 inches.

A series of determinations were made on Tama silt loam, No. 19C, involving from 6.25 to 75 g. of soil.

Fifty and 400 m.e. ammonium acetate in 250 ml. of solution were used for each weight of soil. The results are presented in Table IV and Fig. 11 through 14.

Fig. 11 shows that $\frac{1}{y}$ plotted against $\frac{1}{x}$ again produced a curve whose slope was fairly constant until it approached the y axis.

When $\frac{1}{y}$ was plotted against $\frac{\sqrt{C_1}}{C_2}$, two straight lines were obtained which intercepted the y axis at the same point. This is shown in Fig. 12. Although it was not so apparent for Soils No. 1062 and No. 17C, the same type of curve resulted.

Fig. 13 and 14 show the curves for $\frac{y}{x-y}$ and $\frac{y^2}{x-y}$, respectively. The equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{y^2}{x-y})$ again seemed to give the most nearly straight line of the four equations tested. The best straight line drawn through the points gave a value for S of about 17.0 against a value by leaching of 17.2.

5. Base exchange equations applied to Conover silt loam, Fayette silt loam, Lindley fine sandy loam, Millsdale loam and a second Clarion loam.

Conover and Lindley series have moderately acid A and B horizons and a weakly acid C horizon. Fayette silt loam has medium to highly acid A and B horizons and a medium to weakly acid C horizon, whereas Millsdale loam, derived from limestone, has weakly acid, shallow topsoil overlying the parent material.

TABLE IV

Bases Exchanged from Tama Silt Loam No. 19c

Soil No. 19c

No.	g. Soil	ml. Sol'n.	m.e. NH_4^+ Added	y	$\frac{1}{y}$	$\frac{1}{x}$	$\frac{\sqrt{C_1}}{C_2}$	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$	S* obtained by plotting Vageler's	Gapon's	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$
1	6.25	250	50	14.4	6.95	.125	.218	.018	.262	17.4	17.4	17.4	17.5
2	6.25	250	400	16.9	5.90	.016	.029	.003	.045				
3	12.5	250	50	12.6	7.95	.25	.298	.032	.41	17.2	17.2	17.4	17.6
4	12.5	250	400	16.4	6.10	.031	.040	.005	.085				
5	25	250	50	11.2	8.95	.50	.396	.060	.67	16.1	16.2	16.5	17.0
6	25	250	400	15.3	6.55	.063	.055	.010	.15				
7	37.5	250	50	10.9	9.20	.75	.49	.089	.97	16.0	16.1	16.3	17.1
8	37.5	250	400	15.2	6.60	.094	.063	.014	.22				
9	50	250	50	9.9	10.10	1.00	.550	.110	.109	15.4	15.5	15.8	16.8
10	50	250	400	14.4	6.95	.125	.076	.018	.264				
11	75	250	50	9.1	11.00	1.50	.675	.158	1.44	15.1	15.3	15.7	17.3
12	75	250	400	14.0	7.15	.19	.093	.027	.378				

*S by leaching = 17.2.

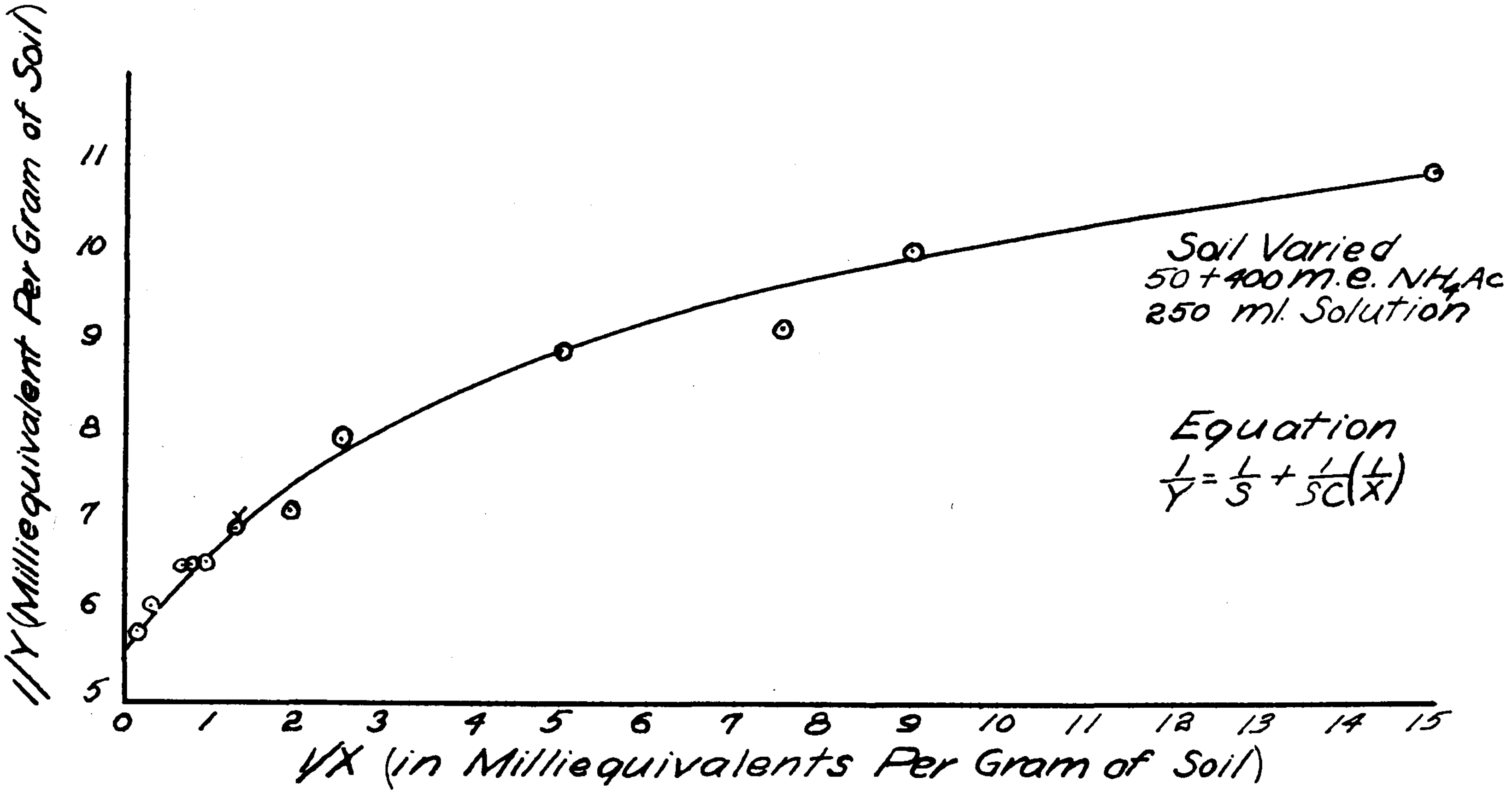

Fig. 11. Vageler's Equation Applied to Base Exchange in Tama Silt Loam No. 19c

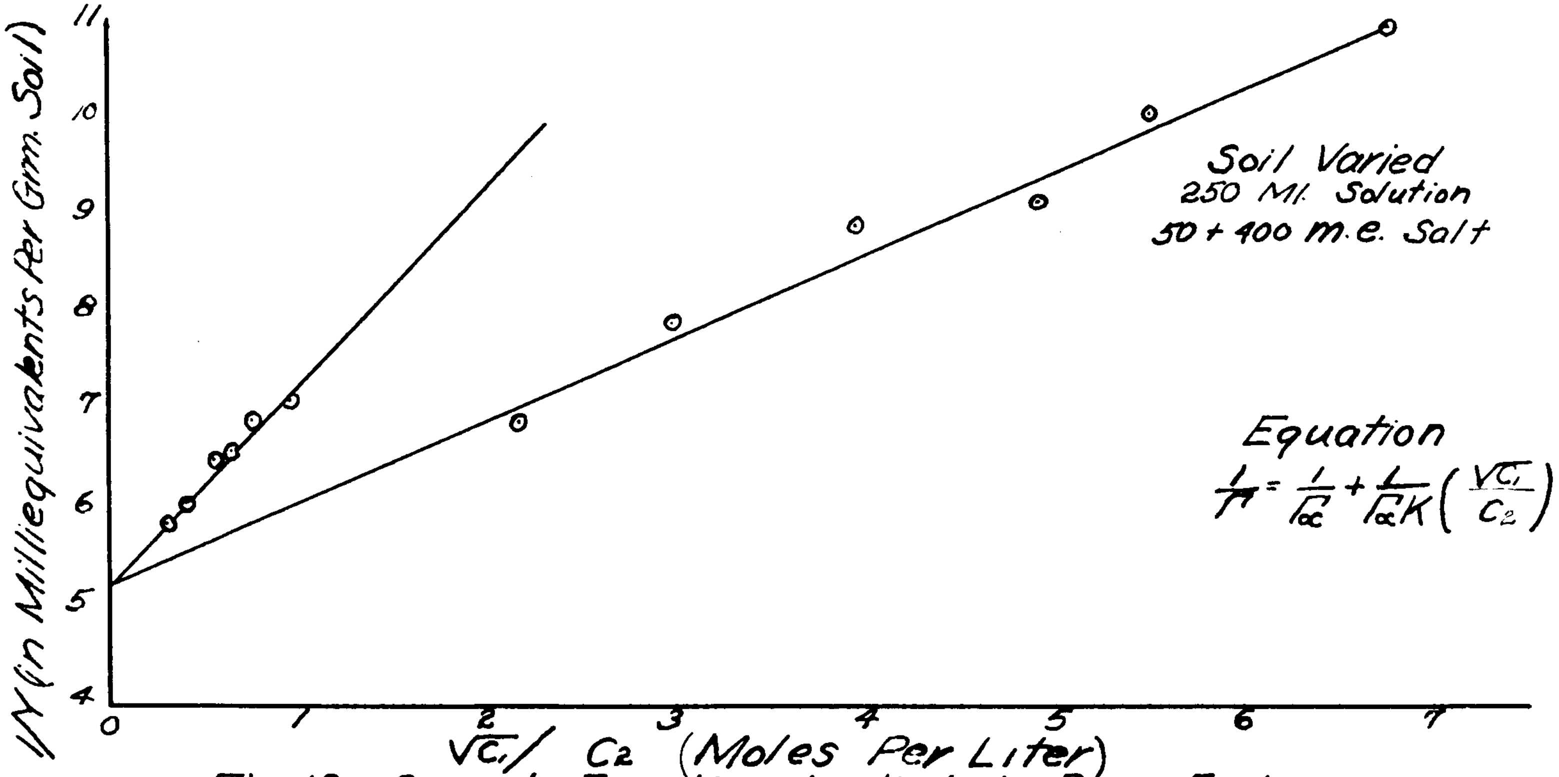

Fig. 12 Gapon's Equation Applied to Base Exchange in Tama Silt Loam No. 19c

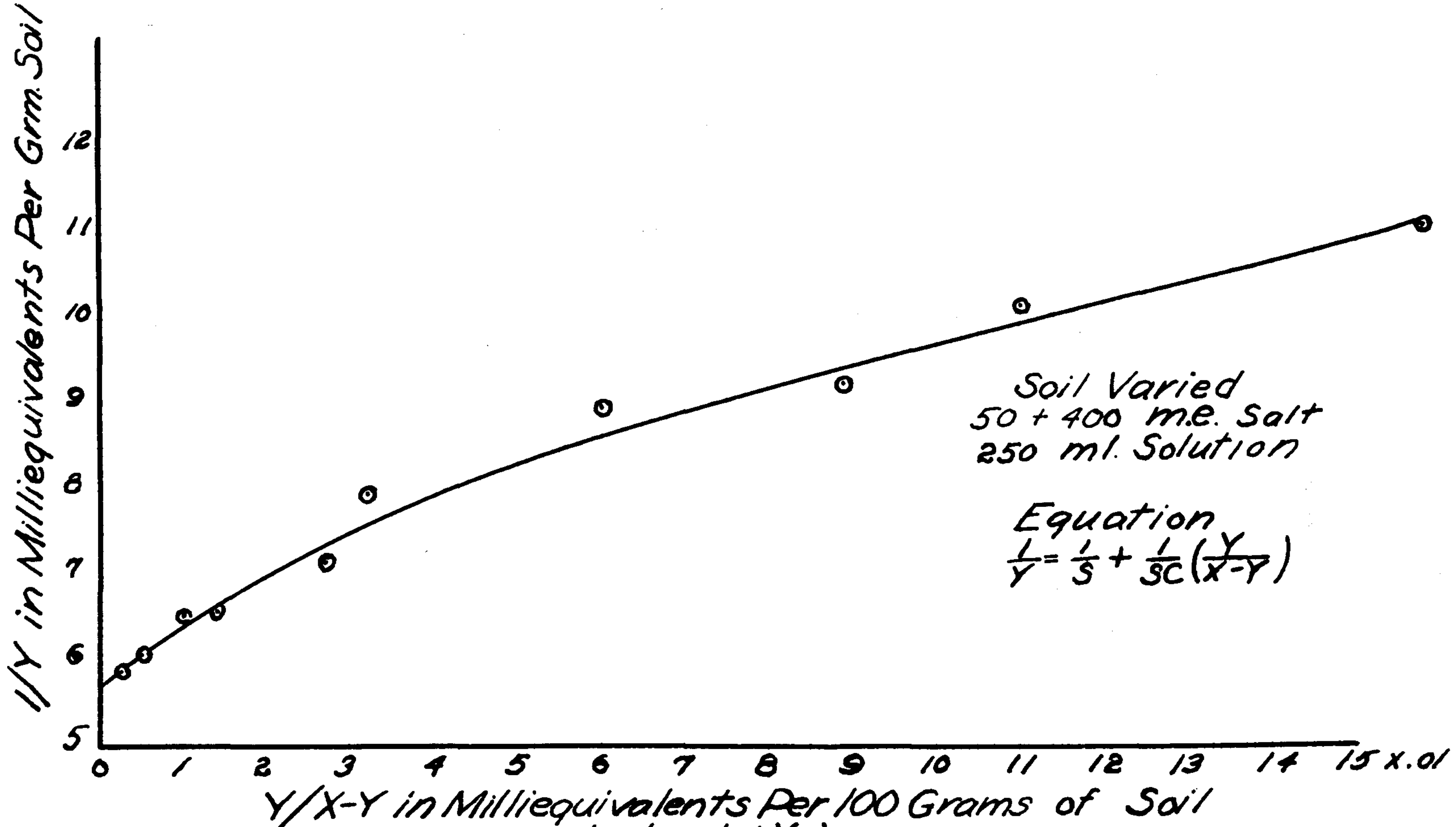

Fig. 13 The Equation $\frac{1}{Y} = \frac{1}{S} + \frac{1}{SC}\left(\frac{Y}{X-Y}\right)$ to Base Exchange in Tama Silt No 19c

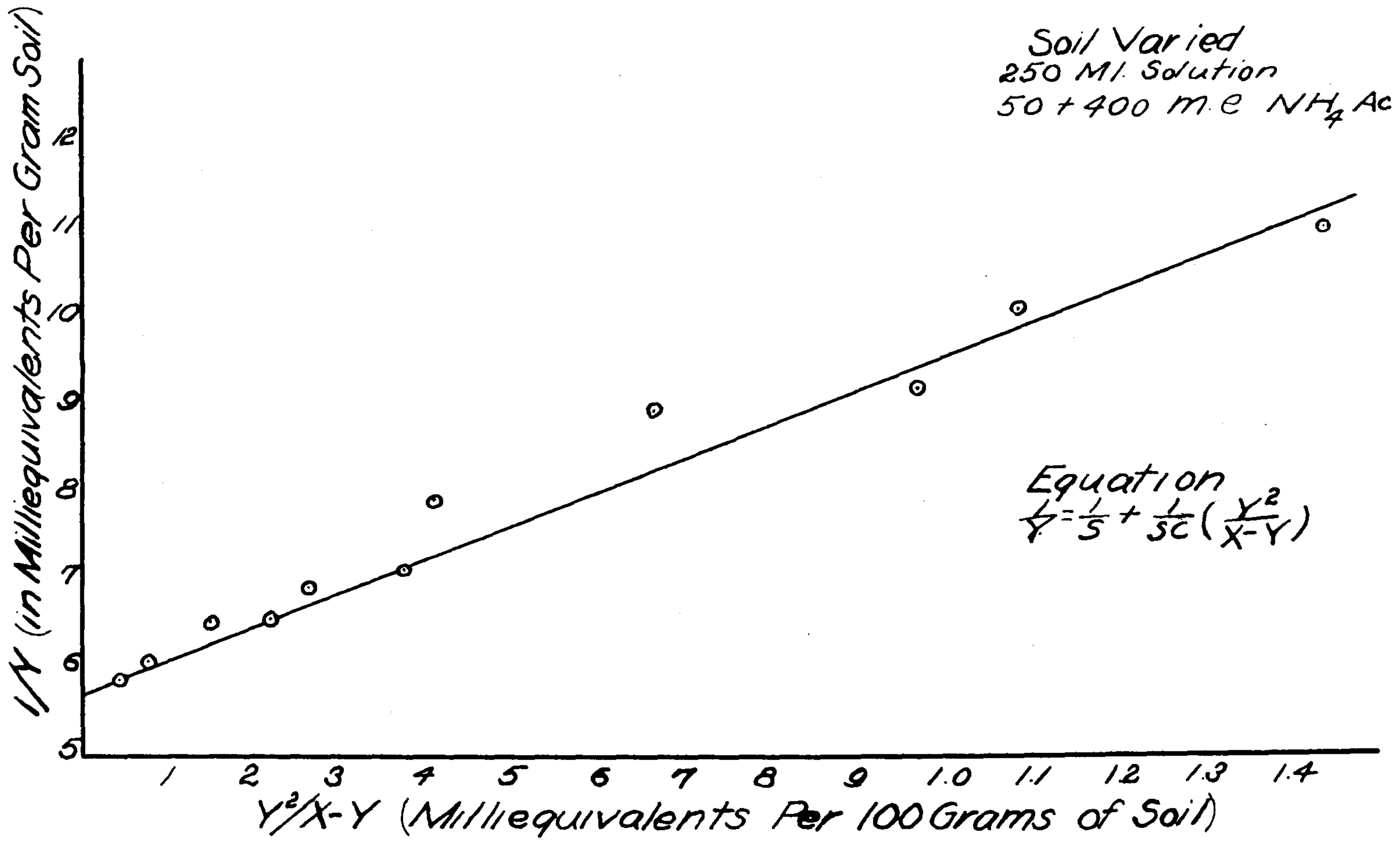

Fig. 14. The Equation $\frac{1}{Y} = \frac{1}{S} + \frac{1}{SC}\left(\frac{Y^2}{X-Y}\right)$ Applied to Base Exchange in Tama Silt

Tables V and VI present the values obtained for S by the four equations for the five soils. Fifty grams of each soil was placed in 250 ml. solution containing 50 and 400 m.e. ammonium acetate. In addition to this, three points were obtained for Soil No. 7C and S determined for 25 g. of No. 11C. (See Table V.)

Quite good agreement was obtained between S by plotting $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}\left(\frac{y^2}{x-y}\right)$ and S by leaching. The largest deviation was for No. 11C on 50 g. soil where a difference of 0.3 m.e./100 g. soil was obtained.

Soil No. 4C, a second Clarion loam soil, was the only soil tested in which S by plotting Vageler's and Gapon's equations agreed with S obtained by leaching. The same type of curves resulted when the data were plotted, but when the best curve was drawn through the points and extrapolated the intercept was about 5.15 (S = 19.4 m.e./ 100 g. soil). This corresponded to the value for S obtained by leaching Clarion loam Soil No. 1062.

6. Application of Vageler's and Gapon's equations to exchangeable H^+ in hydrogen saturated Clarion loam, No. 1062.

The following experiments were performed to determine if Vageler's and Gapon's equations could be applied to the exchangeable hydrogen in the soil.

An H^+ saturated Clarion loam, No. 1062, was obtained by intermittent leaching of 100 g. of the soil with 50 ml.

TABLE V

Bases Exchanged from Conover Silt Loam, No. 7C; Fayette Silt Loam, No. 9C; Lindley Fine Sandy Loam, No. 11C; and Millsdale Loam, No. 12C

No.	g. Soil	m.e. NH_4^+ Added	y in m.e./100 g. Soil	S by Plotting*			
				Vageler's	Gapon's	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$
			(Soil No. 7C**)				
1	50	50	8.1				
2	50	200	10.6	11.9	12.0	12.2	12.8
3	50	400	11.3				
			(Soil No. 9C**)				
1	50	50	6.97	11.2	11.4	11.7	12.5
2	50	400	10.48				
			(Soil No. 11C**)				
1	25	50	8.0	11.3	11.5	11.6	12.0
2	25	400	10.8				
3	50	50	6.89	10.7	10.8	10.9	11.7
4	50	400	10.0				
			(Soil No. 12C**)				
1	50	50	6.35	9.35	9.45	9.5	10.0
2	50	400	8.87				

*Volume of solution = 250 ml.

**Soil No.	S by leaching	Ave.
7C	13.0, 12.96, 13.14, 12.85	13.0
9C	12.7, 12.4, 12.7	12.6
11C	12.2, 12.24, 12.17	12.2
12C	10.0, 10.0	10.0

TABLE VI

Bases Exchanged from Clarion Loam, No. 4C

No.	g. Soil**	m.e. Base Added	y in m.e./100g. Soil	S from Plotting*			
				Vageler's	Gapon's	$\frac{y}{x-y}$	$\frac{y^2}{x-y}$
1	12.5	25	13.1				
2	12.5	100	16.3	18.9	18.9	19.2	19.8
3	12.5	200	17.8				
4	25	25	12.5	18.8	18.9	19.2	20.2
5	25	200	17.7				
6	50	50	12.2	18.5	18.7	18.7	20.0
7	50	400	17.4				

*S by leaching = 18.8, 18.8, 18.8; ave. = 18.8.

**Volume of solution was 125 ml. in experiments 1 to 5, inclusive, and 250 ml. in 6 and 7.

of normal HCl until the pH of the leachate was constant. This required about 1.5 liters of solution. The H^+ saturated soil was then leached with two 50-ml. portions of 95% alcohol and dried overnight in an oven at 105-110°C. The pH of the H^+ saturated soil was 3.74 when determined in a 1 to 5 water suspension by a glass electrode.

Ten grams of H^+ saturated No. 1062 was allowed to stand for twenty-four hours in 100-ml. solutions of NaCl containing from 10 to 400 m.e. Na^+. The solutions were shaken four or five times during the first twelve hours and then allowed to stand overnight. Fifty milliliters of the supernatant liquid was pipetted from the solution, the pH determined by the glass electrode method, and the H^+ liberated determined by titrating the solution with 0.2N NaOH to the end point of methyl orange.

The same experiment was carried out using $CaCl_2$ in place of NaCl. The data for these experiments are shown in Table VII. Fig. 15 and 16 show that Vageler's equation was much more satisfactory than Gapon's for exchangeable H^+. Since the Na^+ and H^+ are both monovalent, the reaction is $XH + Na^+ \rightleftharpoons XNa + H^+$ and Gapon's equation becomes $\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}(\frac{C_1}{C_2})$.

It can be seen from Table VII that Ca^{++} was more effective than Na^+ in displacing H^+ from the soil. This was especially true in the most dilute solution where

TABLE VII

H^+ Exchanged from Hydrogen Saturated Clarion Loam

m.e. Salt/ 10g. Soil*	y in m.e. H^+/ 10g. Soil	$\frac{1}{y}$	$\frac{1}{x}$	$\frac{C_1}{C_2}$	$\frac{C_1}{\sqrt{C_2}}$	pH**
(NaCl on H^+ Sat. No. 1062)						
10	.212	4.72	1.00	.0217	-----	3.27
20	.317	3.16	.50	.0161	-----	3.25
40	.472	2.12	.25	.0119	-----	3.22
80	.590	1.70	.125	.0073	-----	3.18
120	.720	1.39	.083	.0060	-----	3.10
200	.741	1.35	.050	.0037	-----	3.01
300	.732	1.36	.033	.0024	-----	2.91
400	.770	1.30	.025	.0019	-----	2.83
($CaCl_2$ on H^+ Sat. No. 1062)						
10	.445	2.24	1.00	.093	.0203	----
20	.565	1.77	.50	.058	.0181	----
40	.657	1.52	.25	.033	.0148	----
80	.705	1.42	.125	.018	.0112	----
120	.770	1.30	.083	.013	.0100	----
200	.813	1.23	.050	.0082	.0081	----
400	.835	1.20	.025	.0042	.0059	----

*10 g. soil in 100 ml. solution in each case.
**pH of H^+ sat. soil = 3.74.

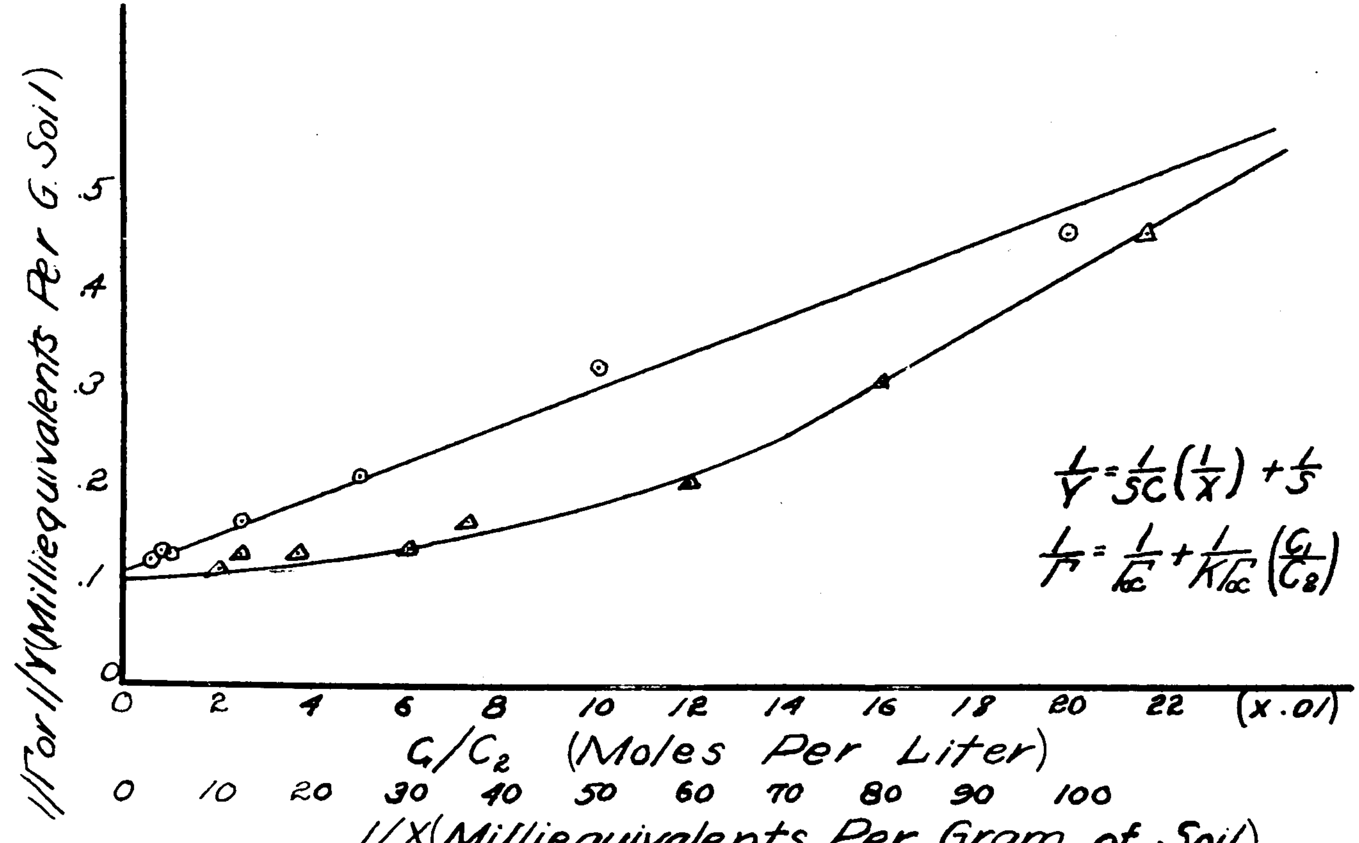

Fig. 15. Vageler's & Gapon's Equations Applied to $H^{\pm}$-Saturated
• Soil No. 1062

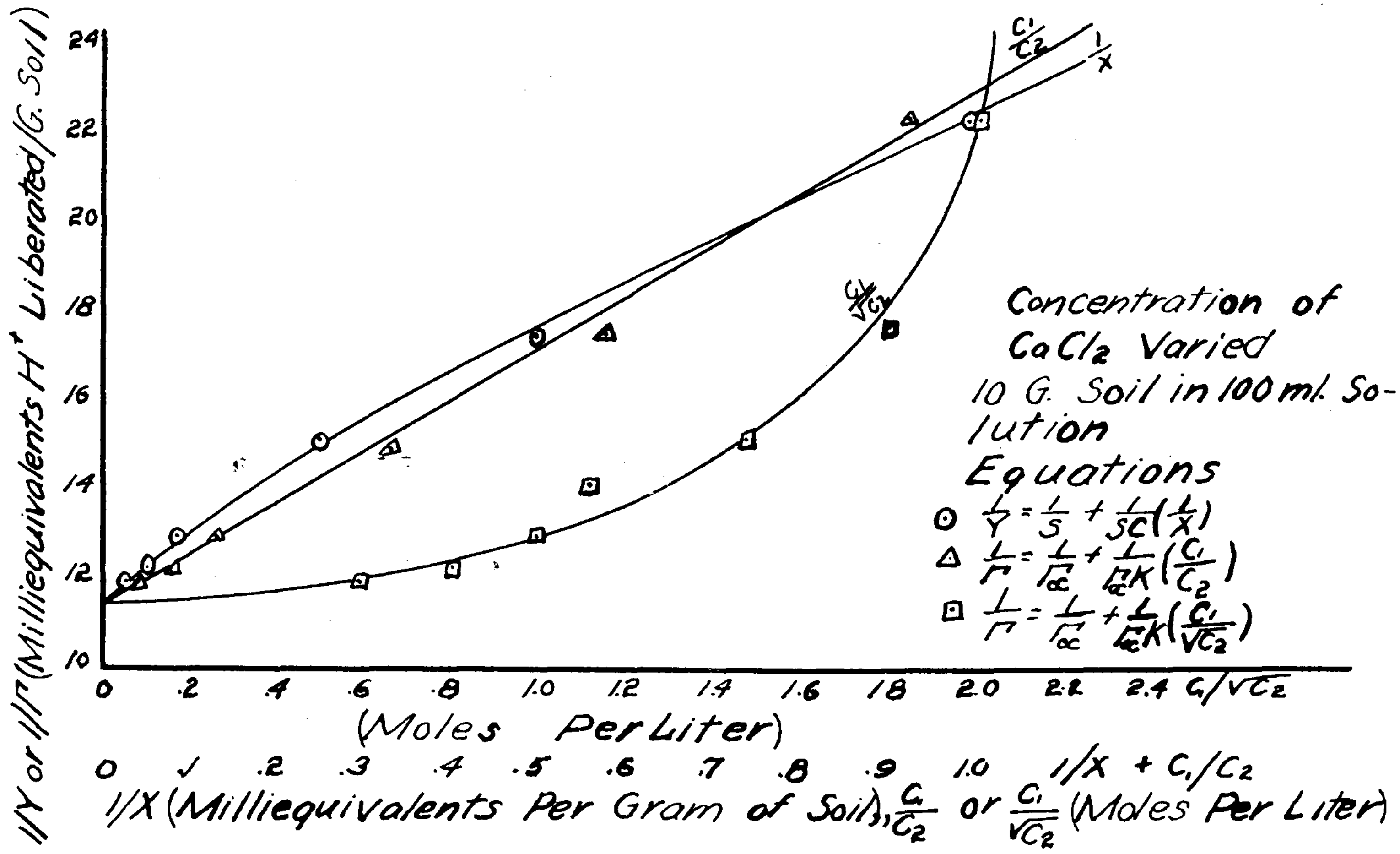

Fig. 16 Equations Applied to Exchanged H$^+$ from H$^+$-Saturated Clarion Loam No. 1062

10 m.e. Ca^{++} displaced more than twice as much H^+ as the 10 m.e. Na^+.

Fig. 15 shows that Vageler's equation was satisfactory for the data obtained by NaCl on the H^+ saturated soil. Gapon's equation did not give a straight line but curved to intercept the y axis at about the same point as Vageler's.

In Fig. 16 Vageler's and Gapon's equations were applied to the data for Ca^{++} on H^+ saturated Clarion loam. The terms x and y in Vageler's equation represent the milliequivalents Ca^{++} added and the milliequivalents H^+ exchanged in 100 g. of soil, respectively. The reaction, according to Gapon, should be written $XH + \frac{1}{2}Ca^{++} \rightleftarrows XCa_{\frac{1}{2}} + H^+$ and the equation should be $\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}(\frac{C_1}{\sqrt{C_2}})$. Since this equation produced such a sharply curved line, the equation $\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}(\frac{C_1}{C_2})$, the same as used for Na^+ on H^+ saturated soil, was tried and found to be much better than the equation using $\frac{C_1}{\sqrt{C_2}}$. In these equations, Γ represented the milliequivalents H^+ exchanged, and C_1 and C_2 represented the equilibrium concentrations of H^+ and Ca^{++}, respectively. Vageler's equation gave a line which curved slightly as it approached the y axis, whereas Gapon's equation $\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}(\frac{C_1}{\sqrt{C_2}})$ produced a curve whose change in slope became smaller as it approached the y axis. Both curves extrapolated to the y axis to give a total exchange capacity for H^+ of 8.7 m.e. per 100 g. soil. This value, and also the value obtained with NaCl, agreed with the exchange capacity for Ca at approximately the same pH. (See Fig. 17.)

7. Effect of the pH of leaching solutions on the exchange capacity of Soil No. 1062.

Table VIII presents the base exchange capacities obtained when Soil No. 1062 was leached with salt solutions of varying pH's. A 100 g. sample of untreated, air-dry Clarion loam, with a pH of 5.9 in a 5:1 solution and exchangeable bases by leaching of 19.1 m.e. per 100 g. soil, was placed in a Büchner funnel and leached with 1N $CaCl_2$

TABLE VIII

Base Exchange Capacity of Soil No. 1062 When Saturated by Leaching with Solutions at Different pH's

Leaching Solution*	pH of Leachate at Equilibrium	m.e. Cation Held by Soil**
1N $CaCl_2$	7.00	22.5
1N $CaCl_2$	6.90	22.15
1N $CaCl_2$	6.65	21.4
Untreated Soil	5.90	19.1
1N $CaCl_2$	5.60	17.8
1N $CaCl_2$	2.70	8.5

*Adjusted with HCl or $Ca(OH)_2$ to give pH desired.
**100 g. soil.

whose pH had been adjusted to approximately the desired value with HCl or $Ca(OH)_2$. The intermittent leaching was continued until the pH of successive leachates was constant and this value recorded. The salt solution was washed from the soil by leaching with a small amount of distilled water followed by 95% ethanol until no positive test for calcium could be obtained.

The exchangeable Ca^{++} held by the soil was determined by leaching 25 g. of Ca^{++} saturated soil with 500 ml. of 1N ammonium acetate in 100-ml. portions and analyzing the leachate for Ca^{++} by the volumetric oxalate method. It can be seen from Table VIII that the amount of exchangeable base held by the soil decreased rapidly as the pH of the saturating solution decreased. Fig. 17 shows that there was a linear relationship between the amount of base held by the soil and the pH of the leaching solution. It is of interest to note that the amount of exchangeable base held by the untreated soil (19.1 m.e./100 g. soil) was practically the same as that which would have been retained by the soil if leached with a solution of $CaCl_2$ at pH 5.9.

8. pH and buffering capacity of ammonium acetate solutions.

Since it was shown in Table VIII that the base exchange capacity could be changed markedly by a small change in pH, the pH of the various ammonium acetate solutions

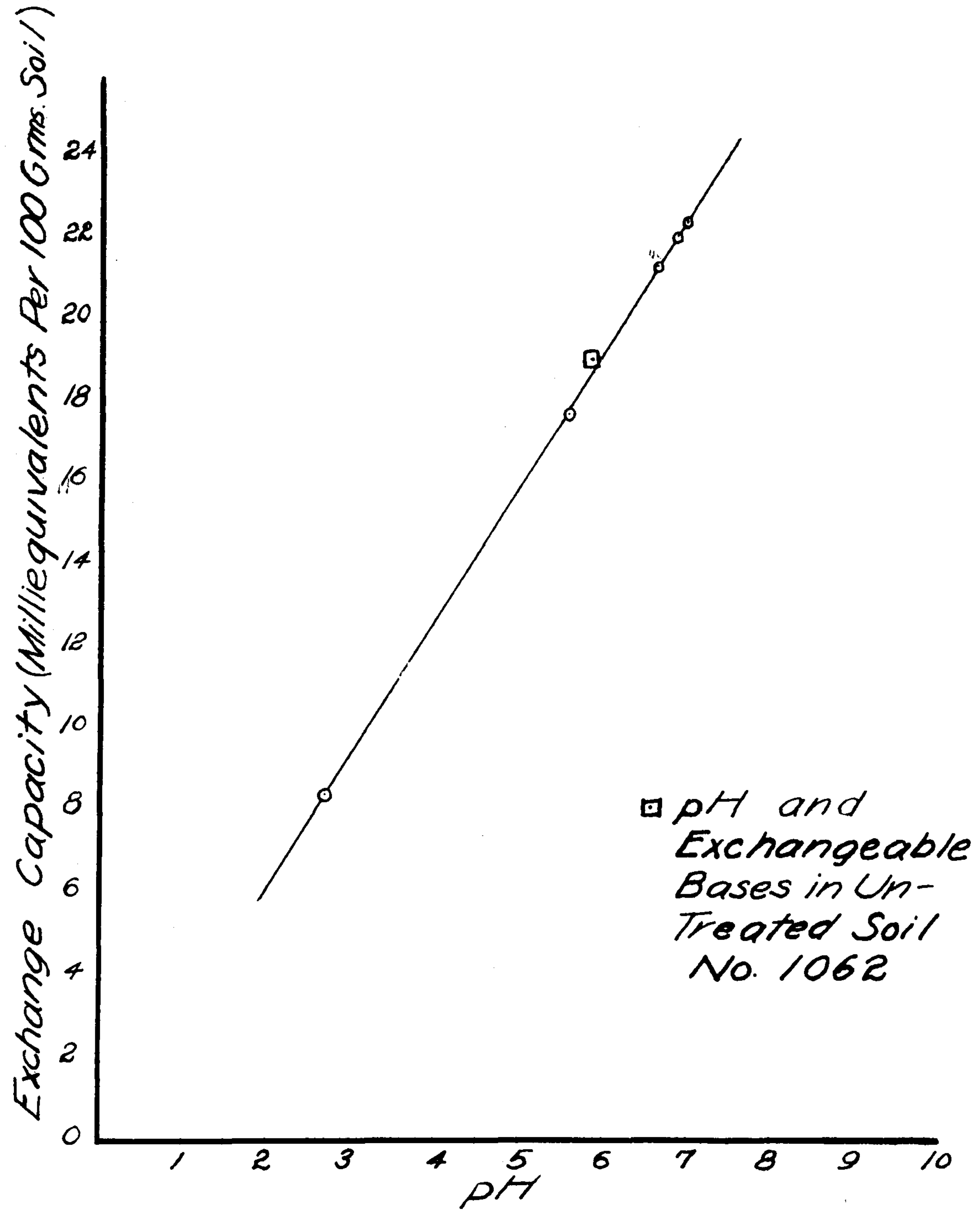

Fig. 17. Change in Exchange Capacity
of
Clarion Loam with pH

used was determined. Also, the effect of adding H^+ to each solution was noted and the data recorded in Table IX.

TABLE IX

pH of Ammonium Acetate Solutions
of Varying Concentrations with and without Acid Added

m.e. ammonium acetate	ml. sol'n.	pH	pH with 1 m.e. H^+ added	pH with 2 m.e. H^+ added
400	125	7.20	7.02	6.95
400	250	6.94	6.87	6.79
400	500	6.87	6.75	6.67
400	1000	6.82	6.67	6.60
50	125	6.82	6.38	6.10
50	250	6.76	6.28	6.04
50	500	6.70	6.25	6.00
50	1000	6.65	6.25	6.00

Eight solutions with volumes and amounts of ammonium acetate indicated in the first two columns of the table were made up and their pH determined by the glass electrode. To each solution was added one milliequivalent of H^+ as HCl and the pH redetermined. This process was repeated to obtain the data in the last column.

A decrease in concentration of ammonium acetate caused a decrease in pH of the solution, and the addition of H^+

ion was more effective in reducing the pH as the dilution increased. Also, as the volume of the solution increased, the difference in pH between the solutions containing 50 and 400 m.e. ammonium acetate decreased.

IV. DISCUSSION

It has been pointed out that Vageler's and Gapon's equations differ in two respects. Vageler's equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{1}{x})$ does not take into account the effect of the displaced ion on the equilibrium or the effect of dilution. The $\frac{\sqrt{C_1}}{C_2}$ term in Gapon's equation is conditioned by these two factors. Theoretically Gapon's equation is preferable and actually does give slightly better values for S and more nearly straight lines when graphed.

Vageler's omission of a term corresponding to C_1 in Gapon's equation did not seem to be too important when large amounts of salt were used, that is, when C_1 was small as compared with C_2. However, the failure to express the displacing ion in terms of concentration caused a considerable difference between Gapon's and Vageler's equations. Dilution caused the slope of a line drawn between any two points to decrease slightly when $\frac{\sqrt{C_1}}{C_2}$ was plotted against $(\frac{1}{y})$ but the slope increased markedly when $(\frac{1}{x})$ replaced $\frac{\sqrt{C_1}}{C_2}$.

The data obtained clearly show that neither Vageler's nor Gapon's equation produced a straight line when applied to the data obtained from the unsaturated soils of Iowa. The question naturally arises as to why they fail under these conditions. The cause for the failure of the equations to produce straight lines is apparently associated with the H^+ in the soil and with the pH and buffering capacity of the various ammonium acetate solutions used.

Attention has been called to the straight lines produced by Gapon's equation when the data, obtained by treating varying amounts of soil with the same volume and concentration of solution, were plotted. The lines converged to a point on the y axis, and the higher the concentration of the solution, the greater was the slope of the curve. The substitution of activities for concentrations in Gapon's equation failed to bring the lines in Fig. 7 closer together or to straighten appreciably the curves obtained in Fig. 1.

Table IX shows that the pH of dilute ammonium acetate solutions was lower than that of more concentrated solutions, and the difference in pH between them was still greater after the same amount of acid had been added to both. The hydrogen ion was shown (Table VIII) to be very effective in reducing the base exchange capacity of the soil. Since the base exchange capacity was lowered as the pH of the solution in contact with the soil was lowered, it seemed probable that the amount of base liberated by a given amount of displacing ion would be increased as the pH of the solution was decreased. If this was true, the values obtained for $\frac{1}{y}$ in dilute solutions would become less as the pH of these solutions decreased, and the slope of the line would likewise be reduced.

A curved line resulted when Gapon's equation was applied to data obtained from experiments in which the amount of soil was held constant and the salt and water varied. As less concentrated ammonium acetate solutions were used, the pH decreased and the amount of bases liberated was too large to produce a straight line when Gapon's equation was graphed. This excess in bases exchanged from the soil might be explained by Schofield's (24) equations. The equation $\equiv SiOH \rightleftarrows \equiv SiO^- + H^+$ would be shifted to the left by a decrease in pH and the $\equiv SiO^-$ would lose its capacity to hold bases. In addition, if the positive $-\overset{+}{Al}-OH$ was formed by the reaction $H^+ + -Al{=}O \rightleftarrows -\overset{+}{Al}-OH$, it would tend to neutralize the negative $\equiv SiO^-$ and eliminate the bases from the complex.

From Fig. 1 it can be seen that Vageler's equation produced a curve that was approximately the same as Gapon's when the volume of solution and the amount of soil were held constant. Since the two equations are so similar, the explanation given for the failure of Gapon's equation to produce a straight line in this case may also be given for the curves obtained when Vageler's equation was used.

Dilution had a much greater effect on a solution containing 50 m.e. ammonium acetate than on one containing 400 m.e. Thus the slope of the line connecting points on a graph corresponding to these two amounts of salt can change markedly with only slight change in the intercept on the y axis, ($\frac{1}{S}$). When the soil-water ratio is changed by dilution, the value for S may or may not be constant, depending on the effect of dilution on the relative amount of bases liberated in the two experiments. A change in the soil-water ratio due to a variation in the amount of soil necessarily changes the value of S calculated from Vageler's equation if the amounts of salt are held constant. This happens because each different amount of soil is represented by a pair of points on a curved line.

Table IX shows that dilution caused the difference in pH between a solution containing 50 and 400 m.e. ammonium acetate to become smaller. It follows that the greater the volume of solution for the same amounts of soil and salt, the more nearly straight should be the curve. Fig. 3 shows this to be the case. Varying amounts of soil and salt in 125, 250 and 400 ml. of solution produced three separate curves whose change in slope decreased as the volume of solution increased.

When Gapon's equation was assumed to give a straight line and two points were used to determine the line, it was noted that the values for S decreased as the amount of soil added to the two solutions of different concentration increased. This was apparently due to the lower buffering capacity of the more dilute solution and the consequent decrease in pH which caused an excessive amount of bases to be exchanged.

The equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{y}{x-y})$ was but little better than Vageler's since it did not correct for dilution effects. The same objection is true for the equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{y^2}{x-y})$. Although this last equation gave the most nearly straight line for a given volume of solution, the slope of the line changed with any alteration in the volume of the solution.

Ammonium acetate was used in the experiments for the reasons given by Schollenberger (25), namely, solutions of ammonium acetate in water were nearly neutral and moreover they possessed a certain buffering capacity which tended to keep the pH of the solutions approximately the same as that of the soils tested. However, it appeared that the buffering capacity of ammonium acetate was not great enough to overcome the effect of change in pH on the base exchange capacity of soils tested.

In order to apply Gapon's equation to base exchange in the field, the amount of moisture must be known so that C_1 and C_2 may be calculated. Instead of C_1 and C_2

in moles per liter, the terms $\frac{y}{M}$ and $\frac{x-y}{M}$ may be used, where y is the milliequivalents of base exchange per 100 g. soil, x is the milliequivalents of displacing ion added to 100 g. soil, and M is the per cent moisture in the soil. If C_1 is a divalent ion, $\sqrt{\frac{y}{2M}}$ may be used, and the equation becomes

$$\frac{1}{\Gamma} \text{ or } \frac{1}{y} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}\left(\frac{\sqrt{\frac{y}{2M}}}{\frac{x-y}{M}}\right).$$

If y is small compared with x, then the equation may be written

$$\frac{1}{y} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}\left(\frac{\sqrt{\frac{y}{2M}}}{\frac{x}{M}}\right),$$

but the determination of y when x is known involves the solution of a cubic equation. When the amount of displacing ion needed to liberate a given amount of base is calculated, the equation is again cumbersome since the value of K changes with the concentration of the displacing ion. Calculations by Vageler's equation are simple but lack the accuracy that Gapon's equation is capable of giving.

V. SUMMARY

1. Vageler's (29) equation for base exchange $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{1}{x})$ was tested on some Iowa soils. The data obtained did not produce a straight line on plotting when this equation was used. Although the same value for S was obtained when complete curves were drawn, the slope of the curves varied with the soil-water ratio.

2. Gapon's (11) equation for base exchange $\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{K\Gamma_\infty}(\frac{\sqrt{C_1}}{C_2})$ was tested and found to produce straight lines only when the same concentration of the displacing ion was used. Straight lines with increasing slopes were obtained as the concentrations were increased.

3. The equation $\frac{1}{y} = \frac{1}{S} + \frac{1}{SC}(\frac{y^2}{x-y})$ produced a straight line for each soil-water ratio when x and y were expressed in milliequivalents per 100 g. soil.

4. Changes in soil-water ratio may or may not change the value of S obtained by plotting Vageler's equation when the equation is assumed to produce a straight line and only two points are chosen to locate the line.

5. The pH of leaching solutions had a marked effect on the base holding capacity of Clarion loam and the decrease in holding capacity was a linear function of the pH.

6. Vageler's equation proved satisfactory for exchangeable H^+ from hydrogen saturated soil when a single soil-water ratio was used.

7. The failure of Gapon's equation to produce straight lines at various concentrations of displacing ion was attributed to the differences in pH and buffering power of the solutions and the consequent change in base exchange capacity.

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PART II: ACID OXIDATION METHOD FOR DETERMINING SOIL CARBON

I. INTRODUCTION

The use of a wet oxidation method for the determination of carbon in organic substances was attempted as early as 1848 by Rogers and Rogers (27). Since that time many and varied methods have been tried with varying success. The wet oxidation method was not satisfactorily applied to soils until 1914 when Ames and Gaither (5) reported a method using chromic-sulfuric acid. Several workers had previously tried chromic-sulfuric acid oxidation but failed to obtain complete oxidation, apparently due to insufficient heating of the reaction mixture.

Since 1914 a number of methods have been devised, both for complete oxidation to CO_2 and for partial oxidation. The latter methods require the use of a factor to convert the amount of oxidation obtained to that which would have been obtained had the reaction gone to completion. The complete oxidation methods meet with the objections that they are too time consuming or require too complicated an apparatus. The factor used in the partial oxidation methods is not constant. It may vary for different soils or for different horizons of the same soil.

Although the dry combustion method for determining carbon in soils is without doubt the most accurate, the apparatus is expensive and the procedure time consuming.

The dry combustion method is not readily applicable to the determination of carbon in soil extracts.

With the objections to the existing methods in mind, it seemed advisable to attempt to devise a wet oxidation method which would completely oxidize the soil carbon and measure the CO_2 liberated in a relatively short time and in a simple, inexpensive apparatus.

II. HISTORICAL

A successful wet oxidation method for the determination of carbon was reported by Rogers and Rogers (27) in 1848. Graphite samples were oxidized in a sulfuric acid, potassium dichromate solution after they had been ground with 30-35 times their weight of silica. If the grinding was efficient the sample could be oxidized completely in thirty to forty minutes. Heat was applied directly to the reaction mixture with a lamp and the CO_2 liberated was absorbed by KOH in a Liebig tube and determined gravimetrically.

Warrington and Peake (36) attempted to apply a similar method to the determination of soil carbon but came to the conclusion that complete oxidation could not be obtained. Their procedure differed in two points from Rogers and Rogers, both of which would tend to decrease the efficiency of the oxidation. Warrington and Peake used a 3-2 sulfuric acid - water solution and heated the reaction mixture only to the temperature of a water bath. They carried out the digestion for four to five hours or "as long as there was any action," but only 72-83% of the carbon was liberated by this treatment.

Another fairly early attempt to apply wet oxidation to soils was made by Cameron and Breazeale (9). Their procedure called for the use of concentrated sulfuric acid and for application of heat for ten minutes after fuming started. Low results were obtained, probably due to lack of sufficient digestion and to the decomposition of chromic acid which occurs in hot concentrated sulfuric acid. If carbonates were present they were removed by treating with a 1:6 H_2SO_4 solution. It was their opinion that the values for carbon obtained by wet oxidation were more representative of the carbon held as humus than dry combustion values.

There have been several wet combustion methods described which liberate and measure all the carbon present in the soil. Ames and Gaither (5) were the first to show that complete oxidation of soil carbon could be obtained by a chromic-sulfuric acid solution. The method proposed by Adams (1) determined the total amount of carbon present by means of a fairly simple, easily made apparatus, but the time necessary to make a determination was from forty minutes to one hour. However, the apparatus was such that a series of ten or twelve determinations could be run simultaneously.

Alper (4) introduced the use of an evacuated absorption flask for the collection of the liberated carbon dioxide. She found that complete absorption was not obtained in a tower unless the rate of aspiration was slow. The substitution of the evacuated absorption flask for the absorption tower made it possible to carry out the oxidation more rapidly. Alper's apparatus and procedure are more complicated than Adams' since they include the use of a hot combustion unit and a manometer. Alper was able to carry out the digestion of the sample and absorption of the CO_2 in thirty minutes. Both methods of analysis apparently give results that are as accurate as standard methods for sampling soils.

Christensen, Simkins and Hiatt (10) reported a wet oxidation method for soil samples of approximately 0.25 g. which required twenty minutes to complete, but the results obtained were in error by as much as 10%. The carbon dioxide liberated was absorbed in standard barium hydroxide solution, and the excess barium hydroxide was titrated with standard acid using thymol blue indicator. They found that the addition of 5 ml. of acetone sharpened the end point of the indicator.

In addition to the chromic-sulfuric acid oxidation, several other methods of determining total carbon in soil have been employed. Robinson, McLean and Williams (26) absorbed the SO_2 from a Kjeldahl digestion in a standard iodine solution and titrated the excess iodine. Each atom of carbon present was equivalent to two molecules of SO_2 or four atoms of iodine. They found that unless the soils were ground to pass a 100-mesh sieve, low results were obtained. One point in favor of the method is that carbonates do not interfere with the reaction. Both acid and alkaline $KMnO_4$ oxidations have been tried. Puri (24) reported an alkaline $KMnO_4$ oxidation method in which the excess permanganate was titrated after the reaction mixture had been boiled for ten minutes. Incomplete oxidation was obtained necessitating the use of a factor to convert the per cent carbon obtained to the per cent present as shown by dry combustion. Nostitz (21) was not able to obtain complete oxidation of soil carbon by $KMnO_4$ in an acid solution when the solution was boiled for fifteen minutes.

Hardy (18) and Cross and Bevan (11) reported gasometric methods for the determination of soil carbon. The volume of gas collected was the same whether complete oxidation to CO_2 was obtained or whether some of the gas remained in the form of CO. Both methods used chromic acid as an oxidizing agent in sulfuric acid solutions, but they failed to give results that were as high as those obtained by dry combustion.

The earlier methods used either concentrated sulfuric acid or sulfuric acid diluted with varying amounts of water. Since chromic acid decomposes in hot concentrated sulfuric acid, it was found advisable to dilute the acid. If the chromic acid decomposed, the sulfuric acid acted as the oxidizing agent and liberated SO_2. Schollenberger (28) found that SO_2 prevented the complete absorption of CO_2

in barium hydroxide in a bead tower absorption. He suggested the dilution of sulfuric acid with phosphoric acid in order to maintain a high boiling point and still prevent the decomposition of chromic acid.

Since both SO_2 and SO_3 act to neutralize the absorbing solution, they must either be prevented from forming, separated from the CO_2 before it reaches the absorbing unit, or corrected for by precipitation and double titration. Schollenberger (28) pointed out that the dilution of sulfuric acid with phosphoric minimized the formation of fumes during the digestion of the sample. Tiurin (32), White and Holben (37) and Cameron and Breazeale (9) passed the gases through concentrated sulfuric acid in order to remove both SO_2 and SO_3. Adams (1) led the gases through glass wool saturated with constant boiling sulfuric acid. A dry U-tube absorption of SO_2 and SO_3 was effected by Heck (19) by saturating pumice with constant boiling sulfuric acid. Alper (4) corrected for the absorption of SO_2 and SO_3 by the following procedure. The gases were allowed to be absorbed by barium hydroxide solution and the excess barium hydroxide neutralized to phenolphthalein with 0.2N HCl. Five milliliters of hydrogen peroxide was added and the solution boiled for two minutes in order to oxidize any $BaSO_3$ to $BaSO_4$. Excess 0.2N HCl was added, the solution boiled to expel CO_2 and the excess acid titrated with 0.2N NaOH to methyl red end point.

Chlorine or chromyl chloride must be prevented from reaching the absorption chamber if accurate results are to be expected from any of the wet oxidation methods. In Crowther's report (12), it was mentioned that CrO_2Cl_2 was formed when soils containing large amounts of chlorides were analyzed by Schollenberger's, Tiurin's and Walkley and Black's methods. The two most common methods for eliminating the error due to chlorides have been the addition of silver or mercury salts to the reaction flask and the absorption of chlorine gas by passing it through or over various absorbents. Tiurin (32) and Walkley (34) recommended the addition of silver sulfate to the chromic-sulfuric acid solution to prevent the liberation of chlorine. Garbarov (17) claimed that if the chloride content of the soil was above 0.2%, the addition of silver sulfate would not eliminate the error due to the presence of chlorine. Subrahmanyan, Narayanayya and Bhagvat (31) added silver sulfate, mercuric sulfate or mercuric oxide to the digestion mixture to correct for the presence of chlorides. Walkley (34), Ames and Gaither (5) and Cameron and Breazeale (9) led the CO_2 through a solution of Ag_2SO_4 in H_2SO_4 in order to remove any chlorine present. A bead tower containing $NaHSO_3$ was used by Alper (4) and a U-tube containing pumice saturated with an Ag_2SO_4 solution served to remove chlorine in Heck's (19) method. A KI absorption unit was used to remove chlorine in the method of Christensen, Simkins and Hiatt (10).

The failure to remove or correct for chlorides in the soil usually caused high results. However, Crowther (13) in the second report of the Organic Carbon Committee mentioned that he had received a report from J. M. Shewan stating that a saline soil gave low results by a wet oxidation method. The chlorine formed in the procedure was removed by passing the gases over powdered $PbCrO_4$. Walkley (34) obtained low results in both wet oxidation and dry combustion methods when increasing amounts of chloride were added. The soil samples were treated with Ag_2SO_4 in H_2SO_4 solutions before wet oxidations were run. This procedure tied up the chlorides present in samples that contained less than 2.5% chlorine.

Rogers and Rogers (27) claimed that it was necessary to wet thoroughly the silica-graphite mixture before adding sulfuric acid for the wet oxidation. In the determination of nitrogen by the Kjeldahl method, Bal (7) noted that wetting the sample before the digestion produced higher results in heavy clay soils. He attributed the low results obtained from the dry samples to the formation of aggregates due to the dehydrating effect of concentrated sulfuric acid on the silica in the soil. The aggregates were thought to protect mechanically part of the organic matter originally present in the soil. Walkley (34) was able to find very little effect due to the addition of water before digestion of the sample except in heavy alkaline soils.

The method used at the Budapest laboratory, as reported by Crowther (12), passed the gases through a hot CuO tube to insure complete oxidation to CO_2. Other workers have thought that all the carbon was not oxidized completely in wet oxidation procedures and have used a dry combustion unit. Alper (4) checked on the need of a dry combustion unit and found that only slightly higher results were obtained when it was used. Christensen, Simkins and Hiatt (10) made use of a slow combustion unit of the type used in gas analysis in order to insure the absence of any CO.

Several catalysts have been found which apparently speed up the rate of oxidation in chromic-sulfuric acid solution. The report by Crowther (12) mentioned the use of mercury at the Budapest laboratory and Ag_2SO_4 at the Leningrad laboratory. Komarova (20) used $HgSO_4$ as a catalyst and Alper (4) used a mixture of 10 parts selenium to 100 parts K_2SO_4 to aid the potassium dichromate oxidation.

Instead of sweeping the system with CO_2-free air, Adams (1) used a stream of oxygen to flush the carbon dioxide into the absorbent and to aid in the oxidation. Degtjareff (14) added H_2O_2 to aid the chromic-sulfuric acid oxidation. He claimed complete oxidation in one minute of vigorous swirling in this mixture. In this method the excess chromic acid was titrated with standard $FeSO_4$ solution using diphenylamine indicator. He realized that the H_2O_2 decomposed the chromic acid and consequently subtracted a blank from the titration values for soils. Walkley and Black (35) stated that the reaction between H_2O_2 and chromic acid was different in the presence of soil than in pure solutions. Since the presence of H_2O_2 decomposed and weakened the concentration of the chromic acid, Walkley and Black considered that the only function of the H_2O_2 was the addition of water which would generate heat when mixed with the concentrated sulfuric acid solution.

It is often desirable to distinguish between carbonate carbon and organic carbon in soils. The chromic-sulfuric acid wet oxidation methods decompose the carbonates with the liberation of CO_2. In such methods it is necessary either to destroy the carbonates before oxidation or correct the final results for the carbonates present. In Crowther's (12) report two methods for correcting for carbonates were given. In one method the carbonate carbon was determined by boiling the soil in an HCl solution containing $FeCl_2$ at a reduced pressure. The other method decomposed the carbonates by aëration in dilute sulfuric acid for forty-five minutes or by boiling in dilute sulfuric acid for five minutes at a pressure of 5-6 cm. Hg. Schollenberger, in Crowther's (13) second report, stated that sulfurous acid was the only one satisfactory for the removal of carbonates because it was a reducing agent and prevented oxidation by manganese oxides. Tiurin (32) aerated the soil with 1:1 H_2SO_4 for thirty minutes to remove carbonates before adding $K_2Cr_2O_7$ and Ag_2SO_4. A 1:6 H_2SO_4 solution was used to remove carbonates by Cameron and Breazeale (9), but Subrahmanyan (30) claimed that H_3PO_4 was better than H_2SO_4 for the decomposition of carbonates. The official A.O.A.C. method (6) calls for the use of $SnCl_2$ in HCl for the determination of carbonates in the soil.

The two most common methods used to determine the CO_2 in wet oxidations have been absorption and weighing, and absorption and titration of the excess absorbing agent. Of the titration methods, the absorption of CO_2 in standard $Ba(OH)_2$ and titration of the excess $Ba(OH)_2$ is the simplest method. Adams (1) used phenolphthalein indicator for this titration whereas Christensen, Simkins and Hiatt (10) preferred thymol blue indicator. Although Alper (4) did not use standard $Ba(OH)_2$, she absorbed the CO_2 in $Ba(OH)_2$ and neutralized the excess using thymolphthalein. Ames and Gaither (5) absorbed the CO_2 in 4% NaOH and determined the amount of CO_2 by a double titration using phenolphthalein and methyl orange. Adams (1) compared the double titration method using NaOH with the single titration method using $Ba(OH)_2$ and found both to be satisfactory. Friedman and Kendall (15) absorbed the CO_2 in NaOH, precipitated the carbonate with $BaCl_2$ and titrated the excess NaOH with standard HCl using phenolphthalein indicator. The titration was modified by Alper (4) to correct for the presence of any absorbed SO_2. This was done by neutralizing the excess $Ba(OH)_2$ to thymolphthalein, adding 5 ml. of H_2O_2 and boiling for two minutes to insure oxidation of $BaSO_3$ to $BaSO_4$. Methyl red indicator was then added, a measured amount of standard HCl was added in excess, the solution was boiled to expel CO_2 and the excess HCl titrated with NaOH. Alper stated that thymol blue could be used instead of thymolphthalein in the titration just described. The $BaCO_3$ precipitate was allowed to settle four hours and an aliquot of the supernatant liquid pipetted for analysis in the official A.O.A.C. method (6). The simple, direct titration of the excess $Ba(OH)_2$ with HCl, using phenolphthalein indicator, was concluded by Partridge and Schroeder (23) to be the best means of determining CO_2. Other methods tested were NaOH or KOH using a double titration, NaOH plus $BaCl_2$ in a single titration, freezing out the CO_2 and a conductimetric method in which the reduction in conductivity of a $Ba(OH)_2$ solution was measured.

Probably the most used rapid titration method for determining soil carbon is the Walkley-Black method. Browning (8) tested the Walkley-Black method on 50 samples and found that the per cent carbon ranged from 92.9 to 110.1 as compared to dry combustion data. Twenty-three of the samples gave values that were within 3% of the dry combustion data, 39 were within 5% and 45 were within 6%. Nineteen samples tested by Walkley (34) ranged in per cent oxidation from 60 to 86 with an average of 75.8. In Crowther's (12) report it was noted that the range of values obtained by the Walkley-Black titration could be lowered from 91-110% to 97-106% by applying heat to the reaction. Purvis and Higson (25) made a time-temperature study of the chromic acid oxidation of soil organic matter and found that decomposition of the chromic acid occurred when held at 140°C. or above for a period of ten minutes. They recommended the use of an electric oven and heating the samples to 175°C. for three minutes. Another modification of the Walkley-Black procedure, used by Novak and Pelisek (22), was to allow the sample to stand for one hour before the addition of Mohr's salt and titration with standard $K_2Cr_2O_7$.

The rapid titration methods which require some heating of the digestion mixture are really modifications of Schollenberger's (29) method published in 1927. This method called for heating 0.5 g. soil to 175°C. for ninety seconds in concentrated H_2SO_4 saturated with $K_2Cr_2O_7$. The reaction mixture was then cooled, diluted and the excess $K_2Cr_2O_7$ titrated. Allison (3) proposed a slight modification in Schollenberger's method in which 0.1961 g. of $K_2Cr_2O_7$ was added to 10 ml. of concentrated H_2SO_4 rather than using a saturated solution of the dichromate.

The investigation of the Organic Carbon Committee of the International Congress of Soil Science in a report by Crowther (12) showed that a method proposed by Tiurin was superior to both the Walkley-Black and Schollenberger methods. This method required that 0.1 to 0.5 g. of soil be boiled for five minutes in a 1:1 H_2SO_4 solution containing enough $K_2Cr_2O_7$ to make it approximately 0.4N. Garbarov (16) made a comparison of several methods and concluded that Tiurin's method was the best for mass analyses where only moderately accurate results were desired.

Crowther's (12) report summarizes the investigation of the rapid titration methods by giving the per cent range obtained for each method when the values were compared with those found by dry combustion. The ranges for the per cent carbon were as follows: Walkley-Black, 91-110; Schollenberger, 97-108; Tiurin, 95-107; Walkley-Black plus heat, 97-106; and a method similar to Tiurin's in which 3:2 H_2SO_4 containing Ag_2SO_4 was used, 99-103.

A rapid titration method which used $KMnO_4$ as oxidizing agent gave results which ranged from 92 to 108% carbon.

Allison (3) made a study of deviation in per cent carbon between alternate soil samples taken from the same plot. Twenty-eight samples were taken and the difference in per cent carbon between alternate samples was less than 2% in 19 cases, between 2 and 3% in 6 cases and greater than 3% in 3 cases. The deviations are based on results obtained by his modification of Schollenberger's method. If Allison's values for per cent carbon were correct, the degree of accuracy of a method should be at least 2% and probably 1% in order to keep the error in the analysis less than the deviation between samples.

The rapid methods thus far mentioned require the use of a factor to convert the values obtained by titration to the per cent carbon obtained by dry combustion. Degtjareff (14) proposed a rapid titration method in which he claimed to oxidize completely the carbon in one minute by the addition of H_2O_2 to the chromic-sulfuric acid solution. Walkley and Black (35) and Allison (3) were not able to obtain satisfactory results with Degtjareff's method and pointed out that the reaction between H_2CrO_4 and H_2O_2 was not the same in the presence of soil as in the absence of soil. Since the results obtained by Degtjareff's method had to be corrected for the effect of H_2O_2 on the H_2CrO_4 by running a blank, an error was introduced because the reaction in the blank and actual determination was not the same.

Christensen, Simkins and Hiatt (10) compared KIO_3 with $K_2Cr_2O_7$ as an oxidizing agent and were able to obtain slightly better results with the KIO_3.

The recent trend has been to report the results as per cent carbon rather than as organic matter. Alexander and Byers (2) were not able to find a satisfactory method for determining organic matter in the soil and came to the conclusion that the factor 1.728 for converting per cent carbon to organic matter was not reliable.

The work described in the following section was undertaken in an attempt to develop a method for determining soil carbon by wet oxidation. A procedure was desired which would be more accurate than the rapid titration methods and more rapid than the present methods which give complete oxidation of the soil carbon.

III. EXPERIMENTAL

A. Apparatus

The apparatus is shown in Fig. 1. Two 6-inch absorption towers A were filled with ascarite held in place by loose plugs of cotton. These towers were connected to the second dropping funnel C by a rubber tubing. The addition of the acid through dropping funnel B eliminated the removal of the rubber stopper in C and thus gave no opportunity for the stopper to come in contact with the concentrated sulfuric-phosphoric acid solution. The stem of C was bent at an angle of about 30° and was long enough to reach to the bottom of the digestion flask. Digestion flask D, which was heated with a semi-micro burner, was a 50-ml. side arm distilling flask and was tipped at such an angle that the condensate in tube G would drain back into the flask. The side arm, bent through an angle of approximately 75°, was connected to the heavy walled rubber tube E and made air tight by placing a copper wire tourniquet on E. This allowed the flask D to be shaken gently when necessary. An asbestos sheet F about three inches square was allowed to rest on E in order to deflect the heat from the burner and keep the tube G from becoming too hot. It was advisable to have a small bulb in G in order to prevent water from being carried into the reservoir. The reservoir H was connected to G and K by means of short pieces of rubber tubing. A glass-to-glass connection inside the rubber tubes connecting G to H and D was desirable.

The reservoir had a three-way stopcock at the top (which was at first turned to open G to H), a two-way stopcock at the bottom, and was joined to the leveling bottle I by means of a rubber tubing. The capacity of the reservoir H was about 200 ml. and the leveling bottle I about 250 ml. The reservoir was filled with a confining liquid of a 3:1 glycerin-water solution.

The absorption flask K was a 500-ml. Erlenmeyer flask fitted with a two-hole rubber stopper. Through one hole was placed a glass tube which was connected to H. A glass plug closed the second hole but was replaced by an ascarite tube or by the tip of a burette as required. The screw clamp J was used to hold a vacuum in K while it was being connected to the reservoir.

The stopcocks in the two dropping funnels B and C were lubricated with the H_2SO_4-H_3PO_4 solution and those in the reservoir H with glycerin. The stopcock in C remained open. The upper stopcock in H was turned to connect H and D except during the transfer of the gas to K. The stopcock in B was open only when adding acid to the digestion flask.

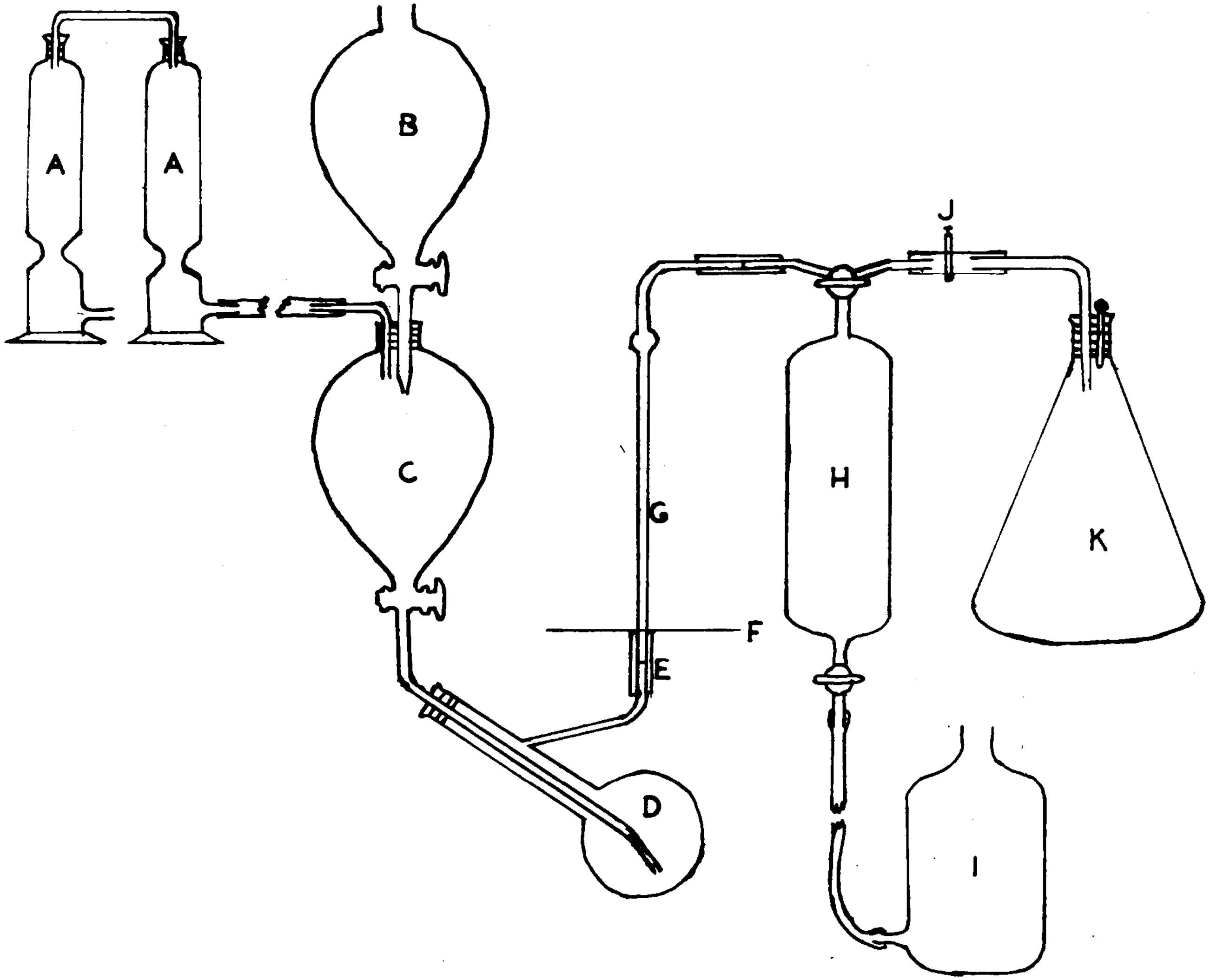
A
A
B
J
C
G
H
K
F
E
D
I

Fig. 1. Apparatus for Carbon Determination

B. Procedure

After the apparatus was assembled, the digestion flask D was disconnected and an air-dry soil sample containing between 10 and 30 mg. of carbon (usually from 0.5 to 2.0 g. of soil) was placed in the flask. One to two grams of powdered, reagent grade $K_2Cr_2O_7$ was added and the two solids washed into the bottom of the flask with 2 or 3 ml. of distilled water.

The digestion flask was connected to the apparatus and 25 ml. of a 60:40 sulfuric-phosphoric acid mixture (60 ml. of conc. sulfuric acid plus 40 ml. of 85% phosphoric acid) added to the top dropping funnel B. The stopcock in B was opened and the acid drawn into the digestion flask by opening the lower stopcock in H and allowing the confining liquid to drain slowly from the reservoir into the leveling bottle. The stopcock in B was then closed.

Heat was now applied quite rapidly to the contents of the digestion flask and the lower stopcock in H was adjusted so that two bubbles per second of CO_2-free air from the ascarite towers were sucked through the digestion mixture. The contents of the flask were shaken for one to two minutes during the initial vigorous action. Strong heating was continued until the digestion mixture began to froth and this temperature was maintained until approximately 25 ml. of glycerin solution remained in the reservoir. The source of heat was then removed, but air was sucked through the system until the glycerin was all but drained from the reservoir. The lower stopcock in H was then closed.

Before the absorption flask K was attached to the apparatus, approximately 5 ml. of acetone was added and the flask (including the screw clamp J) connected to a water aspirator at J. A calcium chloride tube (filled with ascarite held in place by loose cotton plugs) was inserted in the stopper, and a slow current of CO_2-free air was drawn through the flask for about five minutes. The suction was stopped, the calcium chloride tube removed, and in its place the $Ba(OH)_2$ burette inserted so that the tip protruded below the stopper. Fifty milliliters of standard $Ba(OH)_2$, approximately 0.2N, was added and the glass plug placed in the hole. The flask K was now evacuated by the water pump until the acetone-$Ba(OH)_2$ solution boiled vigorously; the screw clamp J was then closed. To conserve time, the charging and evacuation of the absorption flask were carried out during the first part of the digestion.

The evacuated Erlenmeyer K was joined to the reservoir at J. The upper stopcock in H was turned to connect H and K, the screw clamp J opened and the lower stopcock in H turned to allow the confining liquid to be drawn into the reservoir. When the reservoir was almost filled with the glycerin solution, the lower stopcock was closed, the screw clamp J closed and the upper stopcock turned to connect the digestion flask and the reservoir. Heat was applied as before and air drawn in by draining the glycerin from H. The system was swept with the CO_2-free air at the rate of 4 to 6 bubbles per second until the reservoir was once more almost filled with gas. The gas was transferred to the absorption flask in the manner already described. After the reservoir had been completely filled with the confining liquid the absorption flask was brought to room pressure by slowly turning the upper stopcock in H to connect H with the digestion flask D. To insure complete absorption of CO_2 the upper stopcock in H was closed, flask K shaken and then the stopcock opened to connect K with the digestion flask. If the CO_2 had not been completely absorbed, air was seen to bubble through the digestion mixture, in which case the procedure was repeated until no more absorption occurred. After insuring complete absorption, the flask K was disconnected, the glass plug removed, 4 or 5 drops of thymol blue indicator (0.2% solution in 50% alcohol) added by means of a medicine dropper, and the tip of the acid burette was inserted. The excess $Ba(OH)_2$ was titrated with standard 0.2N HCl until the indicator color changed from blue to yellow.

The procedure as described, including the weighing of the sample and the titration, required about twenty-five minutes. The following catalysts were used in an attempt to find one which would accelerate the reaction: Hg_2SO_4, Hg, Ag_2SO_4, Se, and H_2F_2. None of these had any marked effect on the time required to make a determination on soil. It was noted that low results were obtained if the delivery tube of the dropping funnel C did not extend below the surface of the acid in the digestion flask. It was thought that the O_2 in the air might be aiding the reaction since Adams (1) used a stream of O_2 to speed up the oxidation. Since H_2O_2 reacts with H_2CrO_4 to liberate oxygen, it was decided to add H_2O_2 to the reaction mixture. Three milliliters of 5% H_2O_2 was added to the top dropping funnel B and allowed to enter the digestion flask at the rate of one drop every two seconds during the collection of the second reservoir of gas. This procedure allowed the determination to be completed in less than twenty minutes. When H_2O_2 was used, the rate at which CO_2-free air was drawn through the apparatus was increased to 3 to 4 and 8 to 10 bubbles per second for the first and second parts of the digestion, respectively.

A blank run was made by adding well ignited non-calcareous soil and carrying out the procedure as described. The ignited soil was used because it was found that the temperature of the reaction mixture was not as high when soil particles were present, and the blank was consequently lower. When pure organic substances were determined by this procedure, the blank was run without the addition of ignited soil.

C. Results

1. Determination of total carbon.

In order to show that the method was applicable to different types of soil, several soils were analyzed and the data compared with those obtained by dry combustion. The values obtained are reported in Table I. Soil No. P50-10 was a calcareous subsoil, whereas the rest of the soils were non-calcareous topsoils. The data presented show that the per cent error for a single determination was less than the probable error due to sampling.

A series of determinations were made on Soil No. 1062 in order to determine the precision of the method. The results obtained were 2.70, 2.70, 2.71, 2.69, 2.70, 2.70, 2.71, 2.68, 2.69, 2.70, 2.73, and 2.68 per cent carbon.

Samples of pure organic compounds were analyzed for carbon as a further check on the accuracy of the method. Benzoic acid was used in order to determine if there was a possibility of volatilization of organic acids before complete oxidation by the chromic acid. Sucrose was analyzed to determine whether or not the procedure would

TABLE I

Total Carbon in Soils*

Soil No.	Per Cent Carbon**		
	Wet Oxidation		Dry Combustion
		Ave.	
P4-1	3.74 3.68	3.71	3.72
P26-1	2.50 2.50 2.52	2.51	2.52
P28-1	2.29 2.27	2.28	2.27
P30-1	3.40 3.38 3.38 3.36	3.38	3.38
P31-1	1.36 1.33	1.35	1.33
P50-10	0.79	0.79	0.80
P51-1	2.17 2.14 2.14	2.15	2.16

*Samples and dry combustion data supplied by Dr. Roy W. Simonson of the Department of Agronomy, Iowa State College, Ames, Iowa.

**All data given on the dry weight basis.

be satisfactory for a compound which carbonized upon contact with the oxidizing solution. Determinations were made on thiourea since it contained sulfur which would interfere if it escaped from the reaction mixture before being converted to the sulfate. It will be seen in Table II that the method is capable of analyzing all three types of compounds.

It was desired to determine the efficiency of the method on extremely stable material such as coal and charcoal. It can be seen from Table II that the method as described will not liberate all the carbon in coal and charcoal but will oxidize enough of the carbon so that any charcoal in burnt-over timberland soils will be at least 90-95% oxidized.

Table III presents the values obtained when the amount of soil, $K_2Cr_2O_7$ and chromic-sulfuric acid solution was varied. As the amount of soil was increased, the amount of both acid and $K_2Cr_2O_7$ had to be increased. It should be noted that too much water may be added to the digestion mixture as was the case in the third experiment using 0.5 g. of soil. Although 15 ml. of acid and one gram of $K_2Cr_2O_7$ are theoretically more than enough to oxidize one gram of soil, complete oxidation could not be obtained when these amounts were used. The low results may be attributed either to some carbon remaining in the

TABLE II

The Determination of Carbon in Pure Organic Compounds and Coal

Substance	Catalyst	Per Cent Carbon		
		Wet Oxidation	Ave.	Theoretical or Dry Combustion
Benzoic acid	None	68.7 69.0	68.9	68.8*
Sucrose	None	41.8 42.0 42.1	42.0	42.1*
Thiourea	None	15.8 15.7	15.75	15.8*
Coal No.**				
1	None	79.4 75.4	77.4	80.5
1	30 mg. Hg_2SO_4	79.8 79.4 78.6	79.3	
3	None	76.4 73.7 72.4	74.2	75.5
3	30 mg. Hg_2SO_4	75.3 76.1 75.7	75.7	
4	None	80.8 79.5	80.2	82.5
4	30 mg. HgO 30 mg. HgO 200 mg. HgO	81.3 80.9 81.6	81.3	
Charcoal	H_2O_2	86.0	86.0	95.2***

*Theoretical values.

**When no catalyst was added a 1000-ml. absorption flask was used for coal analyses.

***Per cent ignition loss.

TABLE III

Effect of Varying the Amount of Soil, Acid, $K_2Cr_2O_7$ and Water

Soil No.	Sample wt. in g.*	ml. H_2O	ml. 60:40 acid	g. $K_2Cr_2O_7$	% Carbon**
			Soil		
1062	0.500	3	15	1	2.72,2.65,2.63
1062	0.500	3	20	1	2.70,2.70
1062	0.500	8	20	1	2.47
1062	1.000	3	25	2	2.70(ave. of 12)
1062	2.000	3	25	4	2.62,2.63,2.68
1062	2.000	3	30	4	2.71,2.70
			Acid and $K_2Cr_2O_7$		
P26-1	1.000	3	15	1	2.36
P26-1	1.000	3	15	2	2.42
P26-1	1.000	3	20	1	2.40
P26-1	1.000	3	20	2	2.52
P26-1	1.000	3	25	1	2.46
P26-1	1.000	3	25	2	2.54,2.50
1062	1.000	3	15	1	2.58
1062	1.000	3	15	2	2.42
1062	1.000	3	20	1	2.52
1062	1.000	3	20	2	2.70
1062	1.000	3	25	1	2.68
1062	1.000	3	25	2	2.70(ave. of 12)

TABLE III (Cont'd.)

Soil No.	Sample wt. in g.*	ml. H_2O	ml. 60:40 acid	g. $K_2Cr_2O_7$	% Carbon**
			Water		
1062	1.000	0	25	2	2.70,2.72
1062	1.000	3	25	2	2.70
1062	0.500	8	20	1	2.47
P51-1	0.500	3	25	2	2.15
P51-1#	0.500	3	25	2	1.97,1.97,2.03
II-C	1.000	3	25	2	1.24
II-C#	1.000	3	25	2	1.17

*All analyses were made on air-dry samples except those marked #, which were oven-dry samples.

**Results for Soils No. 1062 and II-C are on the air-dry basis; results for Soils No. P26-1 and P51-1 are on the oven-dry basis.

solution or to the volatilization of incompletely oxidized material.

2. The effect and removal of chlorides.

In the usual wet oxidation methods, chlorides cause high results unless they are either removed or the figures corrected. When large amounts of chlorides were present, red CrO_2Cl_2 fumes and deposits on the digestion flask were noted. However, these changed to pale green fumes as the temperature was increased and no red fumes were seen entering the reservoir. In the method presented here chlorine (and possibly some CrO_2Cl_2) was removed by reaction with KI in the glycerin solution. Small amounts of chloride have little effect on the determination, but the presence of large quantities cause the results to be low. Table IV shows that the decrease in per cent carbon obtained was proportional to the amount of chloride added. This effect of chlorides was not peculiar to soil but was also noted on pure organic compounds. The addition of silver and mercury salts to the reaction mixture failed to prevent the formation and liberation of chlorine.

3. Preliminary removal of carbonates.

No attempt was made in the procedure already described to separate the organic from the inorganic carbon in the soil. If the carbonates are not removed before the analysis is made, the amount of carbonate carbon must be determined by a separate experiment. By a relatively easy change in the procedure it was possible to remove the carbonates and determine the organic carbon present.

The digestion flask was separated from the rest of the apparatus and an air-dry soil sample was introduced. Three milliliters of a solution containing 5% H_2SO_4 and 5% $FeSO_4$ was added and the mixture boiled for one minute. The flask and contents were then cooled under the tap and the acid neutralized with one milliliter of saturated

TABLE IV

The Effect of Chlorides on the Determination of Carbon

Substance	mg. NaCl Added	Per Cent Carbon	
		With NaCl Added	Without NaCl Added
Soil No. 1062	2.0	2.72	2.70
"	4.0	2.67,2.70	2.70
"	8.3	2.66,2.67	2.70
"	16.5	2.64,2.66	2.70
"	33.0	2.62,2.64	2.70
"	66.0	2.62	2.70
"	106	2.60	2.70
Soil No. II-C	4.1	1.19,1.23	1.24
"	8.2	1.17,1.19	1.24
"	16.5	1.19,1.13,1.10	1.24
"	33.0	1.10	1.24
"	82.5	1.08,1.06	1.24
Benzoic acid	8.3	67.6	68.9
Sucrose	33.0	41.1	42.0

CO_2-free KOH. Potassium dichromate was added through a long stem funnel, the digestion flask connected to the apparatus and the procedure carried out as in the determination of total carbon. Neutralization of the acid by KOH may be omitted if the $K_2Cr_2O_7$ is first dissolved in the sulfuric-phosphoric acid solution.

TABLE V

Determination of Organic Carbon in Soils

Soil No.	Treatment, Boil 1 min. with	Per Cent Organic Carbon After Treatment	Per Cent Organic Carbon No Treatment*
P50-10	5% H_2SO_4	0.49	0.495
P50-10	5% H_3PO_4	0.52	0.495
1062	5% H_2SO_4	2.69	2.70
1062**	5% H_2SO_4	2.70	2.70
1062**	5% H_2SO_4 5% $FeSO_4$	2.70	2.70
1062**	5% H_3PO_4	2.74	2.70

*0.495 obtained by subtracting carbonate carbon from the total carbon by dry combustion.

**25 mg. powdered $CaCO_3$ added.

Twenty-five milligrams of powdered $CaCO_3$ was mixed with one-gram samples of non-calcareous Soil No. 1062. The soil was treated as described above using 5% H_2SO_4, 5% H_3PO_4 or 5% H_2SO_4 plus 5% $FeSO_4$. The 5% H_3PO_4 was not as effective as H_2SO_4. The reducing agent $FeSO_4$ was added to prevent oxidation of organic matter by pyrolusite or any other oxidizing agent that might be present in the soil. Soil No. P50-10 was a calcareous Webster subsoil containing 0.80% total carbon by dry combustion. The results obtained in these experiments are presented in Table V.

4. Wet oxidation with the addition of H_2O_2.

Although most of the data presented were obtained without the use of H_2O_2, Table VI shows that considerable time could have been saved by using H_2O_2 without impairing the accuracy of the analyses. Care had to be taken in adding the 5% H_2O_2 since the reaction between the H_2CrO_4 and H_2O_2 was rather vigorous. When air was drawn through the system at 8-10 bubbles per second and one drop of H_2O_2 solution added every two seconds, no difficulty was experienced in taking care of the O_2 formed.

When 5 ml. of 1% H_2O_2 was used, low results were probably caused by two factors. First, the dilution of the sulfuric-phosphoric acid was too great, and second, an insufficient amount of O_2 was liberated. The concentration of H_2CrO_4 was great enough so that the H_2O_2 did not reduce all the chromate present.

TABLE VI

The Effect of H_2O_2 on Rate of Oxidation

Substance	Amount of H_2O_2 Added	Rate of CO_2-free air through apparatus in bubbles per second: 1st Part of Digestion	2nd Part of Digestion	% Carbon*
Soil No. 1062	5 ml.-1%	3-4	12-15	2.64
1062	5 ml.-1%	3-4	8-10	2.67
1062	3 ml.-5%	3-4	8-10	2.68 2.70 2.70 2.69 2.70
1062	None	2-3	8-10	2.66 2.64
1062	None	2-3	6-8	2.68
1062	None	2-3	4-6	2.70
Coal No. 3**	3 ml.-5%	3-4	10-12	74.3 74.5
Coal No. 3**	None	2-3	4-6	72.4 73.7 (76.4)

*Soil data on air-dry basis; coal, on oven-dry basis.

**Per cent carbon by dry combustion = 75.5; 1000-ml. absorption flask was used.

IV. DISCUSSION

The apparatus shown in Fig. 1 was easily assembled and consisted of materials found in the average laboratory with the exception of the gas reservoir. However, the reservoir used may be replaced by a separatory funnel or leveling bottle by placing a three-way stopcock in the rubber stopper. The first few experiments were made with the gas being collected in an absorption tower, but a determination could not be completed in less than thirty to thirty-five minutes since the gas could not be drawn through the absorption tower more rapidly than 3 to 4 bubbles per second. When the rate of aspiration was increased, low results were obtained, presumably due to incomplete absorption in the tower. The substitution of an evacuated absorption flask for the tower made it possible to speed up the procedure by as much as ten minutes.

A 300-ml. Erlenmeyer flask was found to be too small for one-gram samples. A 500-ml. flask was found satisfactory for soil samples containing as much as 50 mg. carbon, but better results were obtained for coal when a liter absorption flask was used.

Mercury was originally used as the confining liquid in the reservoir, but it was replaced by a 3:1 glycerin solution since the latter was more easily handled, was cheaper and allowed the removal of chlorine without introducing a U-tube into the setup.

The oxidizing mixture must be prevented from coming in contact with any rubber connections. The use of a side arm distilling flask eliminated any objection to the use of a rubber stopper in the digestion flask.

During the first experiments the tube leading from the digestion flask to the reservoir was cooled by means of a water jacket, but later experiments showed this to be unnecessary if the tube was protected from the heat of the burner. It was desirable to have a bulb in this tube to prevent water from being carried into the reservoir.

The samples analyzed should contain between 10 and 30 mg. of carbon. When larger soil samples were used, the amount of potassium dichromate and sulfuric-phosphoric acid solution had to be increased (see Table II).

A 60:40 sulfuric-phosphoric acid solution was used for the analysis of soils. It was found that a 60:30 ratio liberated some SO_2 fumes on boiling and caused the results to be high. When no water was added, a 50:50 ratio was preferable since the chromic acid tended to decompose in the hot 60:40 solution. A higher temperature was obtained in the analysis of pure organic compounds and coal than in the analysis of soils; therefore, it was necessary to dilute the acid solution with 3 to 5 ml. of water in order to prevent the decomposition of chromic acid. A 50:50 sulfuric-phosphoric acid solution would no doubt have been preferable to a 60:40 solution.

A CuO combustion unit was placed between the digestion flask and reservoir and heated to dull redness over a length of approximately 3 inches. This was done to determine whether or not complete oxidation to CO_2 was being obtained. Results obtained with and without this unit were not appreciably different. It was thought that this treatment of the liberated gases might correct for the low results obtained when high percentages of chlorine were present. However, this did not take place.

The use of 2% KI in the 3:1 glycerin solution was a convenient means of removing chlorine. This solution was used rather than a U-tube absorption in order to keep the volume of the apparatus at a minimum. It was important to keep the volume of the apparatus as low as possible as the apparatus was not swept with CO_2-free air before making a determination. The CO_2 initially present in the air contained in the system was assumed to be constant and corrected for in the blank determination.

Acetone served both to sharpen the end point of thymol blue indicator and to indicate sufficient evacuation of the absorption flask by causing the solution to boil. The standard $Ba(OH)_2$ solution was protected from CO_2 in the air by an ascarite filled $CaCl_2$ tube and drawn directly into a stoppered 100-ml. burette by suction. The $Ba(OH)_2$ was not standardized, but the amount used in each experiment and in the blank was the same. The difference in amount of standard HCl required to neutralize the $Ba(OH)_2$ in a blank and actual determination was equivalent to the amount of CO_2 absorbed.

The analyses listed in Table I were made without the use of H_2O_2 and required between twenty and twenty-five minutes for complete determination. It can be seen that the agreement with dry combustion data was good. The soil samples used were chosen because of the range in carbon content which they represented.

The results obtained on analyses of pure organic compounds agreed well with the theoretical per cent carbon contained. The analyses were carried out as directed for soil samples. Coal samples were not completely oxidized in the time allotted, the results being erratic and between 5% and 10% low. When a liter absorption flask was used and the time for the digestion increased by approximately 50%, the per cent carbon obtained was still lower than the dry combustion value. Mercury salts showed a catalytic effect on the oxidation of coal. Higher results were obtained when mercury salts and a 500-ml. absorption flask were used than when a 1000-ml. absorption flask was used.

A sample of ground wood charcoal was analyzed in order to obtain an indication of the efficiency of the method in determining the charcoal present in burnt-over timberland soils. Carbon by dry combustion was not determined. Loss on ignition would be greater than the per cent carbon so that more than 90% of the charcoal carbon was oxidized to CO_2 by this procedure.

The data presented in Table IV were not the anticipated results. Since Cl_2 reacts with $Ba(OH)_2$, high results would be expected if all the chlorine formed was not removed. If the chlorine formed was efficiently removed, no change in results would be expected to take place. However, Shewan in Crowther's (13) report obtained low results on a saline soil by a wet oxidation method. In this case the chlorine was removed by passing the gases over hot powdered $PbCrO_4$. Walkley (34) obtained increasingly lower results as the amount of chloride increased by both wet oxidation and dry combustion. Neither investigator attempted any explanation of the phenomenon. The low results obtained are difficult to explain unless chlorine acts as a negative catalyst in the reaction. There is some evidence of this since low results were obtained for two or three determinations after a sample containing NaCl was analyzed. It was noted that a red gas, probably CrO_2Cl_2, was evolved during the first part of the digestion but was apparently decomposed by higher temperatures since only a pale green gas was noted entering the reservoir. When the chlorine was not removed by KI, the sensitivity of the indicator was reduced to a noticeable extent.

Although the amount of organic carbon in a soil could be obtained by determining the carbonate carbon and subtracting this value from the total amount of carbon found by wet oxidation, it was felt that some more rapid means of determining organic carbon was desirable. It was found that by boiling the soil sample for one minute in 5% H_2SO_4 in the digestion flask any added $CaCO_3$ could be decomposed without loss of organic carbon. Only one calcareous soil, No. P50-10, was analyzed, but the result agreed with the per cent organic carbon obtained by subtracting carbonate carbon from the total carbon by dry combustion. It was thought advisable to add $FeSO_4$ to the 5% H_2SO_4 to prevent oxidation by manganese oxides. Similar treatment with 5% H_3PO_4 did not remove all the carbonates from Soil No. P50-10 nor from Soil No. 1062 to which $CaCO_3$ had been added.

More rapid oxidation was obtained with some phosphoric acids than with others although the sulfuric-phosphoric acid ratio and the concentration of the acids were the same. It appeared that as the purity of the acid decreased, the rate of the oxidation increased. Two acids which gave different rates of oxidation were analyzed spectrographically, but no appreciable difference was found. It was thought that the difference might have been due to the acids containing different amounts of H_2F_2. Small amounts of H_2F_2 solution were added to the reaction flask and caused the reaction to be accelerated for a number of determinations, but the catalytic effect wore off and could not be regained until several determinations had been made without the addition of H_2F_2. This suggested that there was a catalytic effect due to the glass of the digestion flask, but this point could not be confirmed.

The use of H_2O_2 in the reaction was prompted by Degtjareff's (14) claim that complete oxidation could be obtained in one minute when H_2O_2 was added to chromic-sulfuric acid oxidizing solutions. Although Degtjareff's claim could not be substantiated, it was found that H_2O_2 did increase the rate of oxidation. The H_2O_2 decomposed upon contact with the oxidizing solution with the liberation of O_2. The liberation of O_2 in contact with the soil particles was thought to be the cause of the increased rate of oxidation. A 1% H_2O_2 solution was not effective, but a 5% solution allowed the determination to be completed in approximately five minutes less time. Degtjareff's procedure was carried out in the apparatus shown in Fig. 1 and the CO_2 measured, but the CO_2 obtained was equivalent to only 81% oxidation.

V. SUMMARY

1. A wet oxidation method is described by which the total carbon present in soils and in pure organic compounds can be determined with a high degree of accuracy in twenty minutes.

2. Oxidation of the carbon was accomplished by $K_2Cr_2O_7$ in a sulfuric-phosphoric acid solution. The CO_2 set free was absorbed by $Ba(OH)_2$ in an evacuated flask and the excess titrated with standard HCl using thymol blue indicator.

3. A glycerin solution was used in place of mercury as a confining liquid for CO_2.

4. Chlorides were the only substances found to interfere with the determination in soils. The procedure gave satisfactory results for soils containing less than 1% chlorine but gave low results for soils containing more than this amount of chlorine.

5. A solution of KI in the confining glycerin solution was found to be a convenient method for removing the chlorine liberated.

6. Carbonates were removed by boiling the soil in a solution containing 5% H_2SO_4 and 5% $FeSO_4$ without loss of organic carbon.

7. The dropwise addition of 3 ml. of 5% H_2O_2 during the second part of the digestion made it possible to carry out a complete determination in less than twenty minutes.

8. Mercury salts had a catalytic effect in the determination of carbon in coal but had no noticeable effect on soils.

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