

A STUDY OF CATION EXCHANGE IN SOUTH AFRICAN SOILS.

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INTRODUCTION.

The colloidal fraction is the vital part of a soil. These extremely minute particles determine the nature of the soil and are mainly responsible for its many and varied functions. The most important of these functions is perhaps the ability of the colloids to adsorb and exchange cations; the elements so essential to all organisms as building materials.

When pure water is passed through a non-saline soil, the leachate will contain very few dissolved cations. If, on the other hand, an electrolyte such as a weak solution of sodium chloride is passed through the same soil, the leachate will contain considerable quantities of calcium, magnesium and potassium chlorides as well as much of the original sodium chloride. The number of equivalents of the cations collected will be approximately the same as the number of equivalents of sodium ions added. Sodium ions have displaced some of the calcium, magnesium and potassium ions from the soil. This phenomenon is known as cation exchange.

Magistad, Fireman and Mabry (1) said of cation exchange "It is believed that these reactions follow chemical laws and that definite equilibria exist between the proportions of each cation on the exchange complex and the concentrations of these cations in the soil solutions."

Cation exchange is a very complex process, and even today relatively little is known of the actual mechanisms of the reactions taking place. From time to time attempts have been made to formulate equations giving the equilibrium relationships of cation exchange in soils. However, adsorption equations and equations based on the law of mass action have been applicable only to a very limited degree, and no satisfactory kinetic equation has yet been derived. This has caused great concern and

according to Krishnamoorthy and Overstreet, (2), this "lack of ionic relationships" might be due to the absence of equilibrium in the ionic exchange processes in soils. Another possible reason is that many soils are mixtures of widely different types of clays. It may also be that the theory used in developing the ionic distribution is at fault.

The colloidal fraction of a soil, both organic and inorganic, is the seat of cation exchange. Like all colloidal materials it has a very large surface area and obeys the laws of flocculation and peptisation pertaining to colloids. Therefore the adsorbed cations on these colloidal particles have a great influence in determining the nature of the soil.

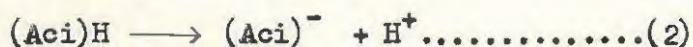
The ~~exchangeable~~ material may be considered as a weak insoluble acid. This analogy is not quite correct and it has thus been called an "acidoid."

The following equilibrium exists between exchangeable cations and the soil solutions:-

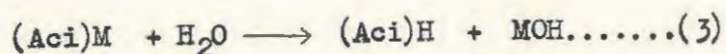


where (Aci) = exchange material and

M^+ = exchange^{able} cation. If the H^+ ion is the exchangeable cation the equation becomes



This is the same equation as for weak acids but the equilibrium constant is more obscure than with simple weak acids. The "acidoid" seems to have numerous monobasic links rather than being a polybasic acid. In addition, hydrolysis takes place i.e.



Reactions such as (2) and (3) are responsible for the pH and buffering properties of the soil. An excess of H^+ ions on the colloid favours reaction (2) and the soil becomes acidic as is the case with all base-unsaturated soils.

The monovalent ions Na^+ and K^+ are less tightly held on the colloid than Mg^{2+} and Ca^{2+} and thus in base-saturated soils, hydrolysis will be more apparent with the alkali ions than with the alkaline earth ions and consequently the pH of the former will be higher. This accounts for the excessive alkalinity of soils where Na^+ ions predominate and the less alkaline nature of soils with excess of lime.

Monovalent ions and H^+ ions have a dispersive action on the soil colloids, thus decreasing water permeability and retentivity (3). The divalent nature of Ca^{2+} and Mg^{2+} ions tends^s to have a flocculating effect on the soil colloids. Such soils usually have good water permeability and on this account, apart from any nutrient effects due to Ca^{2+} and Mg^{2+} ions, are considered desirable for good plant growth.

The proportions of the major exchange cations, Ca^{2+} , Mg^{2+} , Na^+ , K^+ and H^+ , in a soil are important because of their effect on the availability of the minor elements of the soil like Cu, Zn, Mn and Fe (4).

Other cations besides the four major ones can be adsorbed on the exchange material. Thus in certain acidic soils Mn^{2+} predominates over Mg^{2+} on the exchange material. Fe^{3+} and Al^{3+} are also common but it is doubtful whether trivalent cations exist as true exchangeable ions. Soils may also contain traces of exchangeable Cu^{2+} , Li^+ , NH_4^+ and Fe^{2+} .

The mechanism of intake of exchangeable cations by plants seems to be through an exchange equilibrium between the plant root and the soil solution, and also in certain cases a direct intake by the plant from the exchange material (5). ✓

The general effect of the exchangeable cations on plant growth and crop yield was neatly investigated on a wheat crop by Dalip Singh and Dev Rajchawla (6). ✓

They found that:-

- (a) Germination of seed was delayed in soils treated with monovalent ions.
- (b) Plant growth and crop yields were better with divalent cations. In this respect calcium was the best and sodium the worst.
- (c) The percentage of mineral matter removed was largest from potassium soils and least from calcium soils.
- (d) The plant consumed a luxurious amount of the largest available cation species. The dominant cation suppressed the adsorption of the other cations.
- (e) Crops removed a maximum amount of phosphorus from magnesium soils and least from calcium soils.

Adequate knowledge of cation exchange problems in soils is becoming of increasing importance in this age of non-humus fertilizers and dwindling food reserves. The author decided to undertake this work, on the critical study of methods of analysis used and the cation exchange properties of South African soil types, in order to augment data obtained at this laboratory by former investigators, Shirley (7) and Pienaar (8). ✓

A. REVIEW OF THE DEVELOPMENT OF CATION EXCHANGE THEORIES.

It had been known for centuries that soils have the power of decolorising and deodorising liquid manures. When it became known early in the 19th century that plants required nitrogen for growth, and with the advent of inorganic fertilizers, the way was opened for soil scientists to investigate the ammonia absorption powers of soils and hence their cation exchange properties.

The first serious investigations were carried out by Thomson (9) in 1845. Unfortunately, his experiments were not published until 1850 when Way had already submitted a much more thorough investigation on the subject.

Way was the most important investigator in this field up to 1910. His first paper, published in 1850 (10), represented the first systematic and cohesive account of cation exchange in soils. Some of his conclusions were erroneous but most of them have withstood the test of time. His most important errors were:-

- (a) In stating that the reactions were irreversible.
- (b) In assuming that neutral and basic substances were adsorbed by different mechanisms.

- (c) ^{In assuming} That the adsorption was not caused by organic matter.

His second paper, published in 1852 (11), showed that simple calcium silicates failed to adsorb ammonia, but that considerable quantities were adsorbed by complex double silicates of aluminium and sodium.

The investigations were advanced by Liebig (12), Eichhorn (13), Peters (14), Frank (15), Soloman (16), Heiden (17), and Knop (18).

The opinions of these investigators differed considerably as to whether this adsorption was a physical or a chemical phenomenon. They found that other cations, magnesium, potassium and sodium were also exchangeable but they were confused as to whether neutral and basic substances were adsorbed in the same manner. The acidic properties of soils were not attributed to the presence of H^+ ions but to the fact that anions remained in the solutions while their cations were adsorbed.

The first semblance of order was brought into the subject when Lemberg (19) showed that by treating Leucite with sodium chloride it was converted into analcite, a sodium mineral, and that the process could be reversed by treating analcite with potassium chloride. Thus by cation exchange one crystalline silicate was converted to another. This work was important in its bearing on the argument concerning the nature of the cation exchange process.

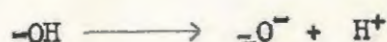
Van Bemmelen (20) published a revised paper and put forward his theory of hydrogels. These hydrogels were composed of indefinite proportions of $Al(OH)_3$, $Fe(OH)_3$, SiO_2 and humus.

He considered that, when in contact with a salt solution, these gels adsorbed the salt and that the water solution within the gel might even become more concentrated than the solution outside.

Wiegner (21) further developed this theory by assuming that the hydrogels adsorbed OH^- ions, thereby acquiring a negative charge, and thus were capable of attracting cations. He pictured the particles as being composed of (a) a kernel, (b) a layer of adsorbed anions close to the kernel, and (c) a more diffuse swarm of exchangeable cations surrounding the particle.

Mattson (22) stated that the inorganic exchange material of soil was of the nature of iso-electric precipitates. In this he was supported by the great Russian investigator Gedroiz (23) who assumed that adsorptive particles might be formed either by weathering of rocks or by the mutual precipitation of two constituents of the soil such as silicic acid and the hydroxides of iron and aluminium.

According to Mattson and Hester (24) iso-electric precipitates were not mere mechanical mixtures but chemical compounds, the union being effected by acidoid H^+ and basoid OH^- with H_2O splitting off. The remaining H^+ ions of the silicic acid were thought to be the seat of the exchange mechanism. At the iso-electric point there was no exchange power but at high pH values the residual OH^- ions of the basoid might ionise as



and the material has^s pronounced cation exchange powers.

Mattson and Csiky (25) showed that the exchange capacity of silica gel was substantially increased in the presence of aluminium and ferric hydroxides. This had a maximum, however, above which the stronger base suppressed the exchange power more rapidly than the weaker one. It appeared that silicic acid was activated when in partial combination with a base.

All these ^{investigators} ~~observers~~ assumed that the colloids were amorphous and so when Hendriks and Fry (26)² and Kelley, Dore and Brown (27), discovered that the fine grained material of the soil was crystalline, an entirely new light was cast on the subject. This discovery soon led to the identification of the specific substances that were

responsible for cation exchange in soils. They were chiefly the clay minerals, montmorillonite, beidelite, hydrous mica, kaolinite, and halloysite.

The modern concepts of crystal structure as evolved by Bragg, Goldschmidt and Pauling (28) were that this exchange was due to isomorphism in the crystal structure of certain minerals (29).

It was well established that clay minerals have a laminar plate-like appearance. This layer lattice was composed of planes of Si ions in which each Si ion was surrounded by four closely packed oxygen ions arranged in the form of a tetrahedron. The relative sizes of the oxygen and silicon ions ($\text{Si} = 0.8 \text{ \AA}$, $\text{O} = 2.7 \text{ \AA}$) made possible a very close packing. In Quartz each silicon ion was a part of adjacent tetrahedra, which were so arranged that the negative charges of the oxygen ions were just balanced by the positive charges of the silicon ions, consequently quartz was electrically neutral except on its surfaces.

In certain of the aluminosilicates such as zeolites the aluminium ions ($\text{Al} 1.1 \text{ \AA}$) were also present in the tetrahedra, being surrounded by four closely packed oxygen ions. Since the aluminium ion bore only three positive charges, these minerals should contain additional cations to balance the excess negative charge of the alumina tetrahedra. These additional cations were loosely held on the mineral and could readily be exchanged for other cations. The ferric ion could also cause isomorphisms in the tetrahedral position and in certain clays isomorphisms in the octahedral position caused cation exchange.

In the case of muscovite there was a lack of balance in the tetrahedral and octahedral planes but this excess of negative charge was

neutralised by a potassium interlayer. This potassium interlayer was a necessary part of the structure of the lattice and the potassium ions were held too strongly to take part in any exchange. Thus muscovite had very little exchangeable power, even although the inner crystal structure was electrically unbalanced.

Montmorillonites had a similar structure to the electrically neutral pyrophyllite and muscovite. It, however, swelled in water, had pronounced cation exchange powers and the crystals were thin, platy and irregular. The crystals were electrically unbalanced due mostly to isomorphisms in the octahedral planes. This was balanced by cations on the surface of the crystals, which were responsible for the exchange properties of the mineral.

The cation exchange capacity of clays, especially hydrous mica varied with pH. This variation has been attributed to the ionisation of the H^+ from the OH^- groups in the mineral. Mitra and Rajacopalan (30) considered that the negative (surface) charge of a clay crystal, which was responsible for its base exchange or base combining capacity, has a definite limiting value and is caused partly by isomorphous replacement of cations within the lattice and partly by dissociation of the available $-OH$ groups of the crystal.

The organic fraction also contributed, to a varying degree, to the total cation exchange power of a soil, but it was mostly restricted to the very top of the soil. Weight for weight these organic colloids have a greater exchange capacity than the mineral colloids. Not a great deal was known about the organic colloids. They are generally referred to as humus, humic acids, or uronic acids. In soils they appeared as ~~in~~

insoluble acids with soluble cations attached to them. They were remarkably similar in elemental constituency, even although produced under widely differing conditions. They seemed to be mixtures of lignin from plant sources and proteins from microbial synthesis (31). They also formed complexes with inorganic colloids and experimental evidence obtained by Allison, Sherman and Pink (32) showed that the nature of the inorganic colloids present influenced the formation of this humus.

The organic colloids were usually more lyophilic than the mineral colloids and they were more easily synthesised or decomposed than the mineral particles. Thus they were very important in the improvement or deterioration of a soil.

B. A REVIEW OF THE METHODS OF DETERMINING EXCHANGEABLE CATIONS IN SOILS.

The quantitative determination of exchangeable cations depends on the fulfilment of three conditions (33):-

- (a) Complete replacement of all exchangeable cations by some cation not present in the sample.
- (b) Accurate analysis of the solutions obtained.
- (c) Determination of, and suitable corrections for the cations that pass into solution.

- (i) From soluble substances.
- (ii) By decomposition of some substances in the sample e.g. calcium carbonate.

The exchangeable cations can be removed from the soil either by electrodialysis or by leaching with a suitable electrolyte.

Electrodialysis is accomplished by applying an electric potential to a soil mixed with a certain volume of water and situated in the central compartment of an electrodialyzing machine like the Loddesol apparatus (7). The soil compartment is separated from the anode and cathode compartments by semi-permeable membranes. The exchangeable cations are collected in the cathode compartment.

Electrodialysis has the advantage that analysis can be done without the separation of a leaching agent, but it is a rather cumbersome and tedious process compared with leaching methods.

Under leaching conditions, a soil is brought into contact with such a large excess of the cations of the leaching solution that the equilibrium is displaced and all the exchangeable cations are replaced by the leaching cations. This is called exhaustive leaching and it is in

great contrast to the equilibrium conditions used by early workers such as Way (10), Liebig (12) and Peters (14).

Since cation exchange is a reversible process, complete exchange can only be brought about if the replaced ions are removed from the sphere of action. Equilibrium between the soil and the displacing solution is set up very rapidly but usually considerable time is required to allow the solution to diffuse into the crystal structures of minerals such as montmorillonite.

Leaching is accomplished by passing the leaching solution slowly through a column of soil so that fresh liquid is always replacing that drawn off and thus constantly removing the exchanged cations from the sphere of action. The shaking of the soil with aliquots of the solution and filtering by centrifuge, has also come into practice especially for impermeable saline soils.

The leachate is analysed for the individual cations, calcium, magnesium, potassium and sodium. The quantity of cations adsorbed by the soil from the solution is known as the base exchange capacity of the soil and the exchangeable hydrogen is determined by subtracting the total of the cations found in the soil from its base exchange capacity, or it can be found by a titration of the leachate.

Pienaar (8) gave a very good review of the various leaching methods used and their application to special problems encountered in certain soils.

Leaching agents are chosen to be electrolytes which are easily destroyed or volatilised and do not interfere in the subsequent analysis. The following leaching agents have been used:-

(a) Weak solutions of strong acids such as hydrochloric acid (34).

Here the H^+ ion served as the replacing cation. Unfortunately the strong acid appeared to decompose the exchangeable material and it has a great solvent action on calcareous materials.

(b) Strong solutions of weak acids have been used and formerly a great deal was done on citric acid extracts but these results did not correspond to the exchangeable cations and they might be considered empirical.

[A 0.5N solution of acetic acid (35) is useful for leaching sandy soils but incomplete replacement of calcium occurs in some heavy clay soils.

(c) Ammonium chloride solutions have been widely adopted (36). Gedroiz

(34) showed that a normal solution of ammonium chloride has good replacing powers. In addition the ammonium ion can easily be removed by volatilisation and it is easy to find the quantity of NH_4^+ ions adsorbed by the soil using ^{the} Kjeldahl method. Unfortunately ammonium chloride peptises alumina and silica in soils and it has an appreciable solvent action on calcareous materials.

(d) Today the most widely adopted leaching agent is ammonium acetate and more will be said about it in the next chapter.

(e) Sodium chloride has been used as a leaching agent, notably by Hissink (37),

~~(37)~~ ^{while} ~~Thus~~ the exchangeable sodium has to be ^{determined} ~~found~~ by some other method.

This sodium chloride method was evolved mainly for leaching calcareous soils but it was found by Kelly and Chapman (38) to dissolve appreciable quantities of calcium carbonate in the presence of carbon dioxide.

Moreover, all the calcium ions were not easily displaced by the sodium ions in heavy clays.

(f) For the determination of exchangeable calcium in a calcareous soil Puri (39) leached the soil with 0.1 N sodium carbonate solution or with ammonium carbonate solution. The loss in carbon dioxide was considered equivalent to the exchangeable calcium present.

(g) For leaching non-calcareous soils, Puri (40) also used a solution of 0.1 N oxalic acid in normal ammonium acetate, and he considered the loss of oxalic acid to be equivalent to the exchangeable calcium. ✓

(h) A 0.3-N cupric nitrate solution was used by Fieger, Gray and Reed (41). The base exchange capacity was determined by the decrease in the copper content of the leachate. Copper was determined from the leachate by an electro-deposition method which leaves a copper free solution, for the analysis of the usual cations.

(i) From time to time barium salts have been suggested but they seem to be adsorbed strongly without displacing equivalent amounts of other cations. They also present the analytical difficulty of separating barium from calcium.

Mehlich (42) proposed a new method for the rapid determination of exchangeable cations using barium chloride - triethanolamine chloride as the buffered leaching agent. Calcium was determined volumetrically and magnesium, sodium and potassium colorimetrically. The base exchange capacity was obtained by replacing the barium ions with calcium chloride. ✓

These leaching methods were applicable to soils without excess soluble salts. Saline soils present even greater problems than calcareous soils, since the presence of excess soluble salts, caused the base status of the soils to vary with soil moisture (43). ✓

Gedroiz (34) proposed leaching out the salts with water and

determining the cations in the usual way. Unfortunately, as was pointed out by Kelley and Brown (43), this preliminary leaching might alter the proportion of cations in the soil.

Kelley and Brown determined soluble sodium and potassium in 1 to 5 water extracts of the soil and again in extracts obtained by leaching a sample with normal ammonium acetate. The water soluble amounts were subtracted from the ammonium acetate extracts and the difference was considered to be exchangeable sodium and potassium. The ammonia adsorbed, less the sum of the exchangeable potassium and sodium, was considered to be the exchangeable calcium and magnesium. The great difficulty in this method was that errors were introduced in finding the exchangeable sodium and potassium.

Reitemeier (44) determined the soluble calcium, magnesium, potassium and sodium at any moisture concentration. Exchangeable sodium was determined by an ammonium acetate method and the cation exchange capacity by an ammonia adsorption method. Exchangeable calcium, magnesium and potassium were determined by empirical factors.

Certain investigators attempted to use ^{higher} temperatures to facilitate the leaching methods but the exchange reaction was only accelerated slightly by any rise in temperature. The increase in solubility of certain constituents, plus the danger of decomposing some exchange material, more than counter-balanced the advantages obtained by more rapid leaching. ✓

The determination of exchangeable cations, as with other "available" constituents, was not accurate in a strict analytical sense. The results varied considerably between the methods and even between replications of the same method. This lack of reproducibility was a grave drawback when

the nature of the phenomenon was being investigated and in the formation of suitable reaction equations, but it did not seriously interfere in soil studies pertaining to the state of the soil and its suitability for plant growth, as here only rough indications were necessary.

C. PREVIOUS WORK ON THE AMMONIUM ACETATE LEACHING METHOD.

Ammonium acetate has been widely adopted as a leaching agent in cation exchange studies. The first investigator to use it was Priianishnikov (45) in 1913 but his work was overlooked until 1930, when Schollenberger and Dreibelbis (46) published a paper on the advantages of ammonium acetate as a leaching agent.

Ammonium acetate is a neutral salt, and it has pronounced buffering properties around pH 7, as may be expected from the fact that the dissociation constants of both acid and base are small and nearly equal, being about 1.8×10^{-5} at 25° C. ✓

This buffering is very important because it means that the H^+ ions of the solution are not increased to any considerable extent by the accumulated products of the exchange reactions. A maximum of NH_4^+ ions will be adsorbed and a single treatment will suffice for the extraction of all the cations and for the determination of exchange capacity as well.

Ammonium acetate is readily soluble in alcohol. Therefore, in preparation for the determination of the total exchange capacity, alcohol is employed to remove excess ammonium acetate from the residue of soil.

Ammonium acetate is more easily destroyed by evaporation than ammonium chloride. It does not 'bump' or creep up the sides of the dish during evaporation. Being a salt of a fatty acid, it has a wetting action which is useful for leaching purposes.

At a normal concentration it does not disperse clay soils but difficulty was experienced by the author with certain organic soil colloids. Aluminium acetate is slightly soluble in ammonium acetate but it does not peptise flocculated alumina colloids.

Golden, Gammon and Thomas (47) found that solutions of ammonium salts of organic acids displaced more cations from a soil than did solutions of barium, cupric, manganous or potassium salts. They also found that acetate anions gave the highest and most consistent results for anions. Thus it was shown that ammonium acetate should be a most efficient leaching agent.

Shirley (7) compared the results obtained by electrodialysis with the results obtained by various leaching agents like normal ammonium acetate, 0.5 N acetic acid, N ammonium chloride and 0.1 N oxalic acid in normal ammonium acetate. He found the N ammonium acetate gave the most reliable and consistent results.

When only the total exchangeable cations are required, ammonium acetate lends itself to very rapid and reliable methods of analysis like the method of Bray and Willhite (48), whereby the acetates are evaporated and converted into carbonates by heating. The carbonates are determined by means of an acid-base titration.

Schollenberger (49) modified this method by adding a few drops of hydrogen peroxide to dissolve any oxides of manganese present and thus include exchangeable manganese in the determination.

Pienaar (8) found that this method gave low and inconsistent results probably due to the incomplete conversion of acetates to carbonates. He evolved a new method whereby the residue of acetates was heated to destroy organic matter and excess hydrochloric acid was added to convert the acetates to chlorides. The hydrochloric acid was evaporate off and the chlorides determined argentometrically.

Pienaar used this method to investigate the reproducibility of results obtained by ammonium acetate leachings on 12 different South African soil samples. He found that in 12 leachings for each soil the percentage standard deviations from the mean varied from 0.3 % to 4.7 %. He did not use any calcareous or saline soil samples. He attributed this variation in reproducibilities^y to the difficulty of leaching out all the exchangeable calcium in some soils and to the conversion of non-exchange-
able magnesium to exchangeable forms in certain cases.

He did his final hydrochloric^{acid} evaporation on a hotplate kept approximately at 180° C. an interesting feature was that when the ratio of exchangeable calcium to exchangeable magnesium in the soil fell below 4 : 1, the chloride figures were considerably lower than those obtained from the sum of the individual analysis of the cations.

The analysis of standard samples of calcium and magnesium mixtures confirmed this and Pienaar concluded that it was due to the hydrolysis of $MgCl_2 \cdot 6H_2O$, but that the hydrolysis became negligible when the Ca : Mg ratio was more than 4 : 1. He suspected that a calcium-magnesium chloride double salt was responsible for this behaviour and he overcame the difficulty of hydrolysis by adding a calculated quantity of calcium to the aliquots to bring the Ca : Mg ratio above 4 : 1.

Ammonium acetate as a leaching agent has the following disadvantages:-

- (a) It has an appreciable solvent action on calcareous materials and some organic substances in soils.
- (b) It is difficult to titrate an excess of acid or base in the large volume of saline-buffered solution.

(c) The leachate is very vulnerable to microbial attack which causes it to decompose quickly.

(d) Ammonium acetate, when heated, produces a small quantity of acetamide which has a very unpleasant smell.

(e) As with all leaching processes, there is a slowness in the attainment of equilibrium between the soil and the leaching ^{solution} which increases the possibility of the exchange material recovering, that is, converting non-exchangeable cations to exchangeable forms and thus giving high results. ✓

Pienaar, however, found no significant differences between the exchange values of soil samples leached for four hours and those leached for sixteen hours.

In spite of these disadvantages ammonium acetate seems the most suitable leaching agent for universal adoption. ~~and~~ Numerous instrumental methods have been developed to find the exchangeable cations in soil more rapidly, if less accurately, using ammonium acetate as the leaching agent. ✓

M. Peech (51) described a micro-method determining exchangeable calcium volumetrically and magnesium, potassium and manganese colorimetrically using a photo-electric colorimeter to analyse the ammonium acetate ^{leachates}. ✓

In 1945 Peech (52) modified his methods so that the cation exchange capacity could be found by direct nesslerisation of the ammonia adsorbed and he used spectro-photometric methods for the analysis of the ammonium acetate leachates. ✓

Heidel (53) described a very convenient method of analysing ammonium acetate leachates by direct photo-electric spectro-chemical determinations, employing standard curves for Ca, Mg, Na, K and Mn. The leachate was evaporated and the organic matter destroyed in the usual way. The residue was dissolved in dilute hydrochloric acid. It was vaporised in a gas flame. The Mg and Mn intensities

were measured directly through monochromaters and the calcium, sodium and potassium through flame photometric filters.

The Beckman Model D.U. spectrophotometer was described by Cary and Beckman (54) in 1941. It consisted essentially of a quartz photo-electric spectrophotometer and a gas burning atomiser. It was further improved and Gilbert, Hawes and Beckman (55) gave an account of the instrument with its filters monochromaters and improved gas-burning atomiser.

Fieldes, King, Richardson and Swindale (56) gave a critical account of its use to determine cations in soils. All the cations were determined in a single analysis. The chief trouble in its use was the variability of gas pressure and the blocking of the atomiser due to traces of silica, alumina or other impurities.

Phosphate and iron were found to interfere with the calcium and magnesium determinations. The procedure adopted overcame these difficulties and permitted the estimations of exchangeable magnesium, for which, a satisfactory flame photometric procedure had not been reported previously. Determinations of sodium could be made on the same solutions as the other cations in this flame photometric method. The reliability of this procedure has been carefully checked by chemical methods and it was considerably faster and more convenient than standard volumetric methods.

The reproducibility of the results were not nearly as good as those obtained by the author using volumetric methods but this was no great disadvantage in the routine analysis of soils. It might be possible that in the near future instrumental methods might become as accurate as standard chemical procedures but volumetric methods will always be useful in the standardization of the instruments and as checks.

D. DESCRIPTION OF THE METHODS USED IN THE ANALYSIS.

a. Sampling procedure.

C.R. van der Merwe (57) classified the soils of South Africa on modern Pedological lines. The author has attempted to obtain several soil samples from each of the major soil regions as indicated on van der Merwe's soil map.

About sixty soil samples have been obtained. They were taken with the intention of getting samples that fit the descriptions of the types as classified by C.R. van der Merwe rather than samples representative of a given piece of land.

A sharp instrument was used to cut away the top inch of the soil which contains the surface mulch. A sample of a few 100 gms. soil was then collected from the first 6 inches of soil. Usually several such small samples were collected from different spots in the area until a total bulk of about a kilogram was obtained.

The samples were thoroughly mixed and spread out on trays, the bigger lumps or clods being broken up without grinding. The sample was left to air-dry for three days and then sifted through a 2 mm. round hole sieve. The coarser materials were again crushed and sieved until only primary particles and organic matter remained on the sieve. These were discarded and the sifted, air-dried, soil was kept in a clean stoppered bottle. It was thoroughly shaken each time before use as the finer material appeared to migrate to the bottom. ✓

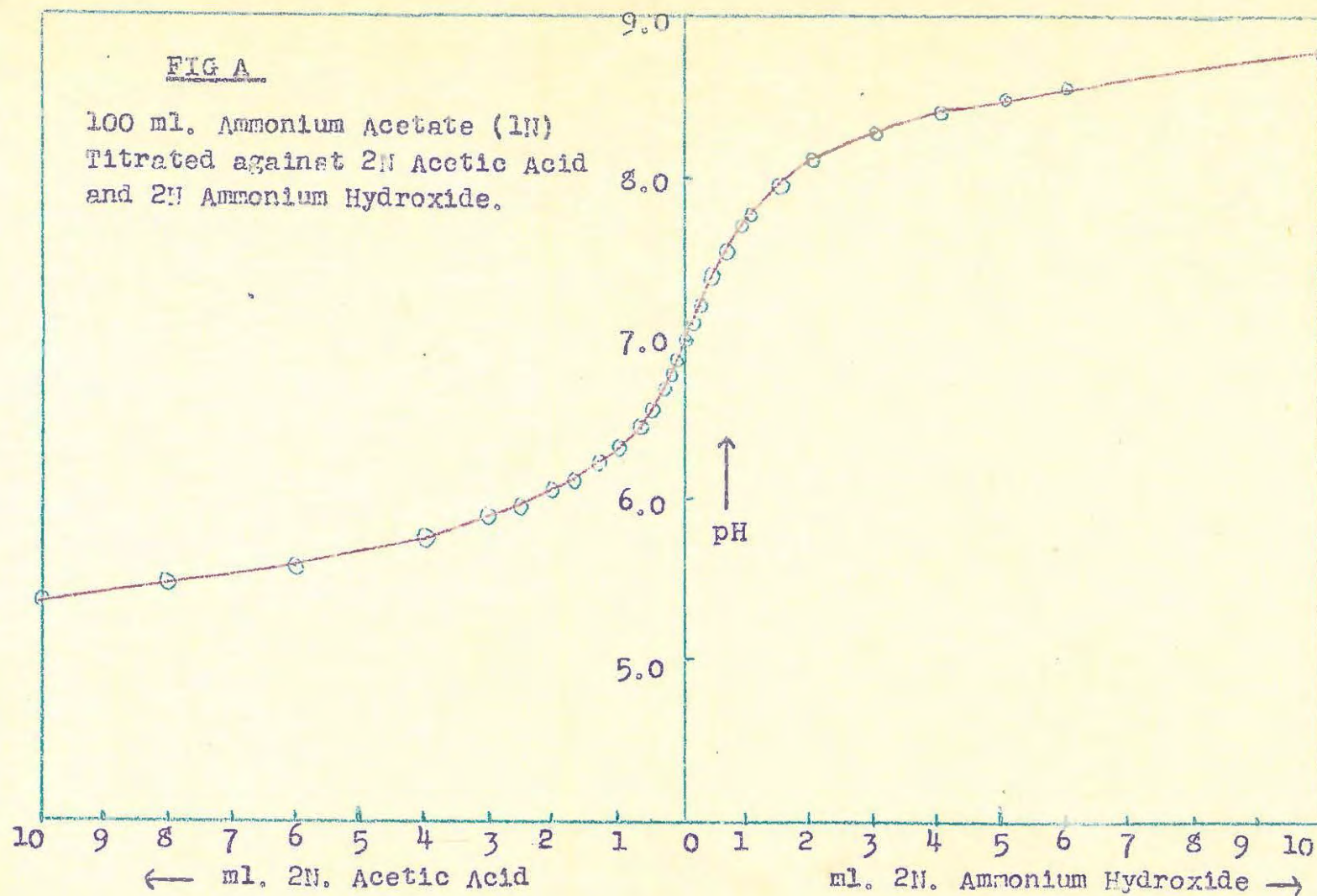
b. Leaching procedure.

(i) Preparation of the leaching agent.

The normal ammonium acetate was made up according to the method of

FIG A

100 ml. Ammonium Acetate (1N)
Titrated against 2N Acetic Acid
and 2N Ammonium Hydroxide.



Schollenberger and Dreibelbis (46) but the author modified the procedure somewhat. 10 litres of ammonium hydroxide and acetic acid were made up having normalities of just greater than 2 N. Their strengths were determined and then diluted to 2 N. Equal volumes were mixed so that the resulting ammonium acetate should be 1 normal.

Since the strength of the solution was not a critical factor, the shrinking effect, due to the addition of an acid to a base, was ignored.

100 ml. of the ammonium acetate was adjusted to have a pH of exactly 7.00. It was then titrated against 2 N ammonium hydroxide and the pH measured at various stages during the titration, employing a Marconi pH meter. Another 100 ml. sample of ammonium acetate was titrated similarly against 2 N acetic acid. A graph (fig. A) was drawn of ml. acetic acid or ammonium hydroxide versus pH. This graph was very useful for the adjustment of the pH of the stock solution of leaching agent to exactly 7.00. The pH of the stock solution was found and then the quantity of acetic acid or ammonium hydroxide required to adjust the pH to 7.00 was determined from the graph.

It was found advisable to check the pH of the ammonium acetate every few days as it tended to absorb carbon dioxide.

(ii) Method of leaching.

Apparatus.

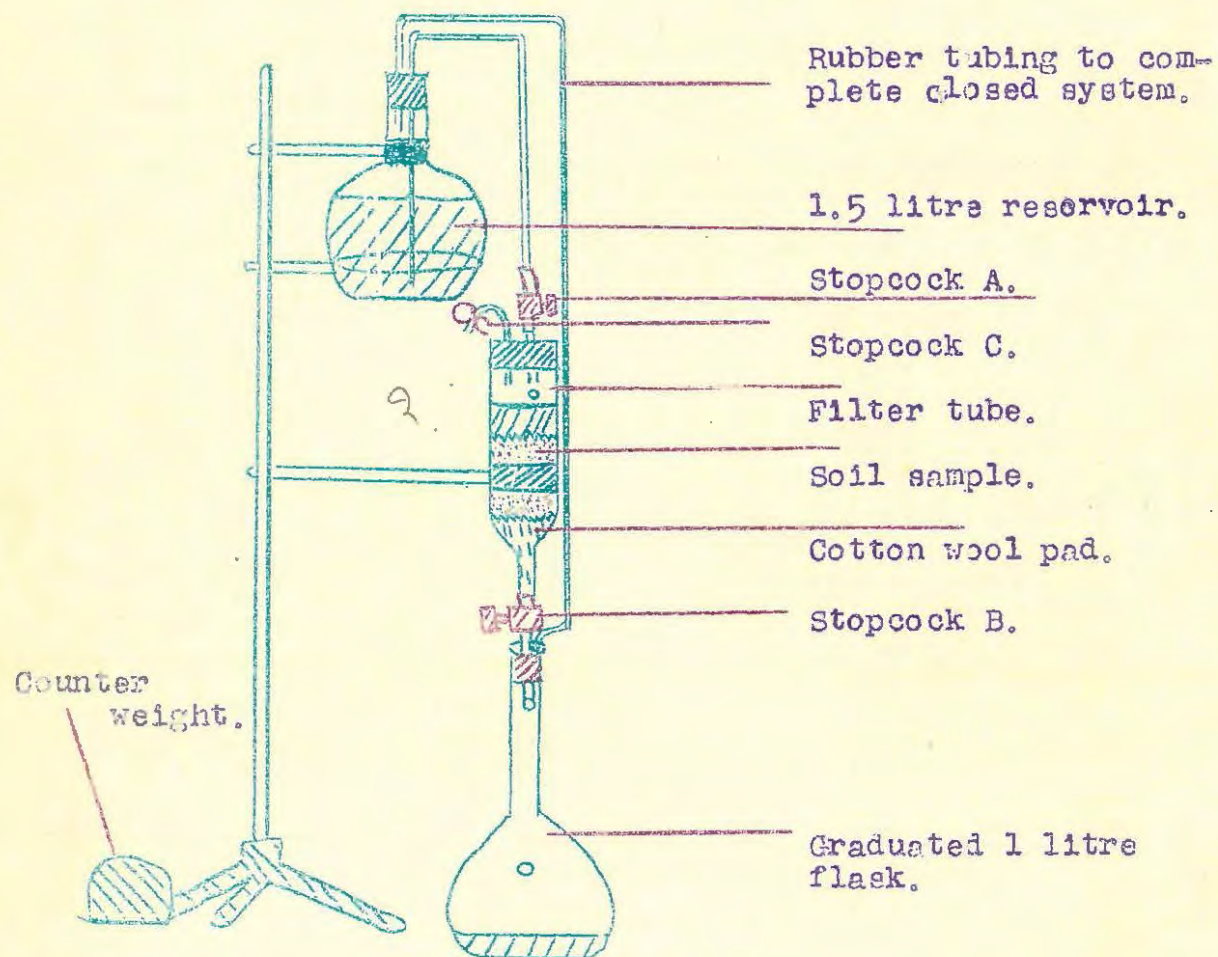
The filter tube is of 40 mm. diameter, 150 mm. height and the stem 50 mm. long. The tube easily holds 100 gms. of an average mineral soil, air-dried and sifted to pass 2 mm.

The leaching apparatus is assembled as shown in the diagram (Fig. B)

The apparatus as shown consists of a $1\frac{1}{2}$ L. flat bottom flask as the

FIG B

Diagram of Leaching Apparatus



reservoir of ammonium acetate, the filter tube and a 1,000 ml. standard flask for collecting the leachate. All the connections are made of glass and rubber tubing bent as shown, to form a closed system. Both leaching solution and leachate are thereby protected from changes in pH which may result from a loss of ammonia or the adsorption of carbon dioxide. The standard 1 litre flask is used to collect the leachate. This facilitates the accurate measurement of aliquots for analysis as exactly 1,000 ml. are collected in each case.

Procedure:-

Stuff a small pad of cotton wool into the bottom of the filter tube to prevent the passage of soil grains into the leachate. Pour some ammonium acetate through the pad to rinse it and to check on the percolation rate. Close stopcock B and pour 75 ml. of ammonium acetate into the filter tube and then add the weighed soil into the filter tube. The preliminary addition of the solution prevents the shrinking and caking of the soil and facilitates the mixing of the soil with the solution, so as to get optimum leaching conditions.

The author used 100 gram samples for soils poor in exchange cations and 40 - 80 gms. for black clays and richer soils.

Open stopcock A and apply gentle suction to stopcock C to start the flow of solution from the reservoir. Close stopcock C and regulate stopcock B so that 1,000 ml. are collected in 5 to 6 hours. See that the soil sample is kept well covered with solution as this promotes steady and even leaching. The leaching operation does not need much further attention except regulating the flow from stopcock B every hour or so.

c. Determination of individual exchangeable cations.

Collect exactly 1,000 ml. of the leachate. (Solution A). The initial separations of silicates, iron, aluminium and manganese are omitted because the first three are usually only present in minute quantities and manganese is determined together with magnesium. These separations are undesirable as they greatly increase the ammonium ion concentration and thus interfere with the magnesium phosphate separations. ✓

(i) Calcium (8) (Modified).

Take a 100 ml. aliquot of solution A and evaporate to dryness on a hotplate in a 250 ml. pyrex beaker. It is advisable to have the hot plate turned down as low as possible in order to avoid spluttering, when the residue dries. Cover the beaker with a watch glass as a further precautionary measure against bumping, spluttering or foreign matter (e.g. plaster) falling into the beaker during evaporation. ✓

When all the ammonium acetate has been driven off, wash the glass cover into the beaker and remove it. Add a little aqua regia (58) and evaporate the contents of the beaker to dryness on a waterbath.

Ignite the residue in a muffle furnace at 400°C for 10 minutes. The residue should be completely white after this treatment. A brownish colour indicates the presence of manganese.

Dissolve the residue in 5 ml. 6 N hydrochloric acid and add distilled water to bring the volume to approximately 100 ml. Heat to boiling on a hotplate and add 5 - 10 ml. of a solution containing 10 % each of oxalic and acetic acids, and with sufficient bromocresol green to produce a distinctly yellow-tint. Now add dropwise a solution of ammonium hydroxide (6 N), stirring constantly until the indicator colour is a pure green,

corresponding to a pH of approximately 4. Boil, with frequent stirring until the precipitate has coarsened appreciably. Filter through a Whatman No. 40, washing the precipitate with hot very dilute ammonium solution, and adding the first few washings to the filtrate containing magnesium. If little or no calcium oxalate is precipitated at once, digest the mixture for several hours with the occasional addition of a drop of ammonia if necessary to separate the small amount of calcium (according to Chapman) (59).

Dissolve the precipitate of calcium oxalate in 50 ml. of hot 10 % (SO_2 free) sulphuric acid and hot water by piercing the paper with a thin glass rod and washing the precipitate into the original beaker.

Titrate this solution at $55^\circ \text{C} - 60^\circ \text{C}$ with N/20 standard potassium permanganate to faint pink which does not fade after stirring thoroughly for a few seconds. Do a blank determination on 100 ml. of the N ammonium acetate leaching solution.

One millilitre of N permanganate corresponds to 1 mgm. equivalent of calcium i.e. to 0.02004 gm. calcium in the aliquot.

(ii) Magnesium (Pienaar (8), Scott (60)).

Combine the cooled filtrate and first washings from the calcium oxalate precipitate. Add 1.0 gm. of hydrated diammonium hydrophosphate, $\text{[(NH}_4)_2\text{HPO}_4 \cdot 7\text{H}_2\text{O]}$ in 10 ml. distilled water, followed by strong ammonia solution dropwise and with constant stirring. Rub the inner walls of the beaker and strike them with the stirring rod to encourage the crystallisation and adherence to the glass of precipitated $\text{Mg(NH}_4)_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

After the precipitate appears or when an excess of ammonia is clearly present, continue stirring for 2 or 3 minutes, then add one tenth by

volume of strong ammonia solution slowly and with further stirring. To prevent the escape of ammonia, cover the beaker and set aside in a cool place overnight. Filter on a Whatman No. 42 filter paper and wash well with cold water containing one tenth of its volume of strong ammonia solution; wash finally with alcohol to expedite the drying of the filter paper. The paper plus precipitate may be dried in an oven for 10 to 15 minutes at 60° C.

When the odour of ammonia can no longer be detected, transfer the precipitate and filter paper to the original beaker in which the precipitation was done.

Add a few drops of methyl-red-methylene-blue mixed indicator and an excess of standard decinormal hydrochloric acid. Warm to 90° C and leave for half an hour. Titrate back with standard 1/20 N sodium hydroxide from a microburette. In this titration tribasic phosphate is in effect titrated to monobasic phosphate and 1 ml. of normal hydrochloric acid is equivalent to 1 mgm. equivalent (or 0.01215 gm.) of magnesium in the aliquot taken. (The mixed indicator is prepared by dissolving 0.125 gm. methyl red and 0.083 gm. methylene blue in 100 gms. absolute alcohol. This indicator is green in an alkaline medium, violet blue in an acid medium and the end point corresponds to a steel gray colour.)

(iii) Potassium (method developed by Steyn (61)).

Reagents.

Sodium cobaltinitrite: Prepare an aqueous solution, containing 1.0 gm. trisodium cobaltinitrite of reagent quality per 5 ml. of solution. Filter before use, if necessary. A fresh solution should be made for each set of determinations.

Sodium bicarbonate (about saturated),

Dissolve 96 gms (C.P.) sodium bicarbonate in 1 litre of distilled water. Filter.

Potassium iodide (10 %),

Dissolve 100 gms. potassium iodide in water and dilute to one litre. Before use remove any trace of free iodine with a drop or two of thio-sulphate solution.

Sulphuric acid (50 %, SO_2 -free).

Add carefully, with stirring, 500 ml. conc. sulphuric acid to 500 ml. water. Cool and bring to faintly pink with N/20 potassium permanganate.

Starch (0.1 %).

Freshly prepared for each set of determinations.

Asbestos.

Place a suitable quantity of good asbestos in a large porcelain basin. Add a few permanganate crystals and enough 20 % sulphuric acid to cover the whole mass. Digest on a waterbath for 3 hours. Wash the brown mass with water to remove the excess potassium permanganate. Add excess oxalic acid and dilute hydrochloric acid and heat on the waterbath until the mass is white. Wash thoroughly with hot water on a Buchner funnel, until free from acids. The asbestos so prepared can be used repeatedly.

Sodium thiosulphate (N/20)

Dissolve enough $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 5 litres water to make up to 1/20 N strength. Add 1 ml. chloroform to keep the solution stable. Standardise and check the normality every fortnight.

Potassium Permanganate (N/20)

Boil and filter a normal solution of potassium permanganate and dilute to N/20. Standardise and check at regular intervals.

Analytical procedure.

Evaporate 100 ml. aliquots of solution A to dryness on a waterbath. When completely dry add a little aqua regia and evaporate ~~to~~ to dryness again. Ignite in a muffle furnace at 400°C for 10 minutes. Cool and add 1 ml. of 6 N hydrochloric acid and rinse down the side of the beaker with distilled water from a wash bottle. This is to convert all the salts to chlorides since these are very soluble in water. Again evaporate to complete dryness. The residue is now taken up in 10 ml. water and heated to incipient boiling on a hot plate. With the help of a rubber-tipped policeman transfer to a Whatman No. 40 filter and wash well with hot water, catching the filtrate in a 250 ml. beaker. Evaporate the filtrate to dryness, add 10 ml. water and 1 ml. N nitric acid (A.R.) and mix well. Bring the contents of the beaker to 20°C ; add 5 ml. sodium cobaltinitrite reagent also at 20°C , mix and leave to stand for two hours. Filter through a gooch crucible, well packed with the specially treated asbestos, using 0.01 N nitric acid in a wash bottle to complete the transfer. Wash 10 times with 2 ml. portions of the dilute acid. With the help of a glass rod transfer the asbestos with the precipitate to the original beaker. Wash the gooch with 20 ml. hot saturated sodium bicarbonate allowing the washings to drip into the beaker. (Leave the glass rod in the beaker). ^{As soon as possible} ~~Immediately~~ bring the contents of the beaker to the boil on a hot plate so as to dissolve the precipitate as quickly as possible, preventing any cobalt hydrate from forming. Dilute the resultant green solution to 50 ml. with water and cool.

Add a slight excess of N/20 potassium permanganate from a burette and slowly, 10 ml. 50 % sulphuric acid. Leave for about twenty minutes, warm to 40°C , add 5 ml. 5 % potassium iodide and immediately titrate the

liberated iodine with N/20 sodium thiosulphate, using a microburette. Add starch near the end point. The "flashing back" of the blue colour after the end point has been reached, is considerably retarded, owing to the carbon dioxide atmosphere present.

$$\text{Potassium} = (0.1818 \times \text{ml. KMnO}_4) \times (\text{Normality of KMnO}_4) \text{ m.e.}$$

(iv) Sodium (Barber and Kolthoff (62)).

Reagents.

(1) A.	Uranyl acetate (2 H ₂ O).....	10 gms.
	Acetic acid 30 %	6 gms.
	water to make	65 gms.
B.	Zinc acetate (2 H ₂ O).....	30 gms.
	Acetic acid 30 %	3 gms.
	water to make	65 gms.

*Insert in
adverted
columns*

After the salts A and B are dissolved by warming, the solutions are mixed and allowed to stand for 24 hours. The precipitate of uranyl zinc sodium acetate is filtered off and a solution is obtained which is saturated with the triple salt due to the sodium contained in the chemicals which go to make up the reagent. If kept in pyrex glass the reagent does not become turbid, after long standing.

(2) 95 % Ethyl alcohol saturated with the "triple acetate".

(3) Anhydrous ether.

Analytical procedure.

Take another 100 ml. aliquot from solution A and evaporate it to dryness. Treat it with a few drops of aqua regia and evaporate it to dryness again. Ignite in a muffle furnace at 400° C for 10 mins., add 1 ml. of 6 N hydrochloric acid and again evaporate to complete dryness.

Take up with 10 ml. water as with potassium and filter it through a Whatman 40 filter. Evaporate this filtrate to 1 ml., cool to 20° C and add 10 ml. of the zinc uranyl acetate and mix well. Allow to stand for at least thirty minutes and filter through a tared sintered-glass crucible. Transfer the precipitate by means of a wash bottle containing the 95 % alcohol saturated with the triple salt. Wash the precipitate five times with this alcohol (2 ml. portion) and then finally with the anhydrous ether in which the precipitate is completely insoluble. Dry the precipitate at 60° C for half an hour and weigh as $\text{Na}_2\text{U}_2(\text{O}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_6(\text{H}_2\text{O})_x$.

d. The determination of the pH of the soil.

Mix 50 grams of the soil with 100 gms. water and stir intermittently for one hour. Measure the pH of the soil solution employing a T.F. 717A Marconi glass electrode.

e. Total exchangeable cations.

(i) The Bray and Willhite (48) method as modified by Schollenberger (49). (The author modified this method by igniting the residue in a muffle furnace).

Analytical procedure.

Evaporate 100 ml. of solution A in a 250 ml. beaker, to dryness, on a hot plate and ignite the residue in a muffle furnace at 550° C for 15 minutes. Cool thoroughly, then add a slight excess of 1/20 N hydrochloric acid and a few drops of 10 % hydrogen peroxide. Raise to the boil and boil for 10 seconds to expel carbon dioxide. Rub the contents against the bottom with a rubber policeman. Set aside for two hours.

Titrate the solution against standard 1/20 N sodium hydroxide using a few drops of 1 % methyl red indicator solution. Do a blank using 100

ml. of the ammonium acetate solution to correct for any impurities.

Calculate the total exchangeable cations by assuming that all the acetates have been converted to carbonates and thus the carbonates determined will be equivalent to the total cations present.

(ii) The Pienaar (8) Argentometric method as modified by the author.

Analytical Procedure.

Evaporate 100 ml. of solution A, in a 250 ml. pyrex beaker, to dryness, on a hotplate.

Add 1 ml. ~~6N~~ hydrochloric acid and again evaporate to dryness. ✓

Ignite the residue in a muffle furnace at 500° C for 15 minutes, cool and add 3 ml. ~~6N~~ hydrochloric acid. Evaporate to dryness on a waterbath to ensure complete removal of excess hydrochloric acid. Add 20 ml. of water and titrate with standard 1/20 N silver nitrate using 5 drops of 2 N potassium chromate as indicator.

E. EXPERIMENTAL STUDIES ON THE REPRODUCIBILITY OF THE VARIOUS METHODS.a. The Pienaar Argentometric method.

(i) A comparison was made between the results obtained for the total exchangeable cations by the Pienaar method and the sum of the exchangeable cations as obtained from the individual analyses, employing a standard soil sample.

Eight separate one litre leachings were made on different portions of the soil sample U 4 (a soil sample obtained from Uitenhage. It was a brown sandy loam containing much organic matter but no free lime).

Aliquots were analysed for Ca, Mg, K and Na as described ^{under (ii),} on pages ^{(i), (ii) & (v).} ~~(25, 26, 27, 30)~~ and total cations were determined by the Pienaar Argentometric method as described ^{under (i) & (v)} on pages ~~31 & 32~~, but a ~~waterbath~~ ^{water bath} heated with Fisher burners was used for the initial evaporations.

The results (Table I) show that the sum of the individual cations is greater by 1.70 m.e. per 100 gms. than the total cations obtained by the Pienaar method.

Table I (See over).

TABLE I.

m.e. per 100 gms. soil.

U 4

No. of Leachate	X Pienaar mean of 2.	Ca ²⁺ mean of 2.	Mg ²⁺ mean of 2.	K ⁺	Na ⁺	Sum = Y	Y - X
A	13.64	11.85	2.94	0.55	0.39	15.73	2.09
B	13.84	11.88	3.00	0.56	0.40	15.84	2.00
C	13.27	11.33	2.98	0.57	0.40	15.28	1.99
D	12.75	10.89	2.80	0.56	0.38	14.63	1.88
E	13.87	11.23	3.01	0.59	0.41	15.24	1.37
F	13.39	10.86	2.73	0.60	0.41	14.60	1.21
G	13.59	11.15	2.89	0.59	0.39	15.02	1.43
H	13.29	11.11	2.85	0.58	0.39	14.93	1.64
Mean	13.45	11.29	2.90	0.57	0.40	15.16	1.70

A more complete and accurate analysis was performed by mixing 5 leachings from U 4. Exchangeable Ca²⁺, Mg²⁺, K⁺, and Na⁺ were determined in the usual way. In addition, separate gravimetric determinations were done for Ca²⁺ and Mg²⁺. Total bases were determined by the Pienaar method and by the Bray and Wilhite method.

The anions, phosphate, silicates, and sulphates were also determined in the leachate. The sulphate results were extremely high (Table II) and led to the suspicion that sulphate ions might be the cause of the interference in the Pienaar and Bray and Wilhite methods. This sulphate could either ^{have} come from sulphates in the soil or from sulphur from the

TABLE II.

U 4

Individual Ions	Mean of 2 volumetric Det.	Mean of 2 Gravimetric Det.	Mean
Ca ²⁺	11.41	11.11	11.26
Mg ²⁺	2.93	2.98	2.95
Na ⁺		0.40	0.40
K ⁺	0.56		0.56
Mn ²⁺	0.07		0.07
PO ₄ ³⁻	0.2		0.2
SiO ₂		0.12	0.12
SO ₄ ²⁻ on water bath		1.77	1.77
SO ₃ ²⁻ on hot plate		0.03	0.03
X Total Bray & Willhite	13.30		13.30
^{The method} Y Pienaar (on water bath)	13.81		13.81
^{The method} Z Pienaar (on hot plate)	14.74		14.74
W Sum of individual cations			15.24
<u>Differences:</u>			
W - X			1.94
W - Y			1.43
W - Z			0.50

All figures are expressed in m.e. per 100 gms. soil.

Al³⁺ and Fe³⁺ were absent.

burners. Subsequently, aliquots of the leachate were evaporated on a hot plate and the Pienaar determinations were repeated. In this case the Pienaar method gave much higher values than previously (14.74 m.e. per 100 gms. as compared with 13.81 m.e. per 100 gms.) The sulphate value on the other hand was negligibly small (0.03 m.e. per 100 gms.)

From Table II it could be seen that the difference between Y (the Pienaar method, ~~evaporated~~ ^{when the evaporation is done} on a water bath) and the sum of the total exchangeable cations, W, was 1.43 m.e. per 100 gms. whereas the difference between Z (the Pienaar method, ~~evaporated~~ ^{when the evaporation is done} on a hot plate) and W was only 0.50 m.e. per 100 gms.

The anions, phosphate and silicates, found in the leachate added up to 0.35 m.e. per 100 gms. soil and they undoubtedly also caused interference in the Pienaar and the Bray and Willhite methods.

To test the absorption of sulphur by the leachate, 100 ml. aliquots of pure N ammonium acetate plus 10 ml. of 0.1 N potassium chloride were evaporated,

- (i) on a water bath,
- (ii) on a hot plate.

The sulphate was determined in both cases by a barium gravimetric method.

(i) The solutions evaporated on a water bath contained 1.55 m.e. SO_4^{2-} per 1 L. of solution.

(ii) The solutions evaporated on a hot plate contained 0.01 m.e. SO_4^{2-} per 1 L. of solution.

This proved that the bulk of the sulphate was introduced through the gases from the burners under the water bath. In the Pienaar method

it was therefore deemed necessary to evaporate the aliquots of the leachates on a hot plate and only to use the water bath for the very final removal of the excess hydrochloric acid, prior to the silver nitrate titration.

(ii) The effect of the temperature of ignition on the Pienaar Method.

An artificial standard soil leachate was prepared in order to investigate the effect of the temperature of ignition on the Pienaar method. This artificial standard was also useful to check the methods for the individual cation analyses.

Two litres of the artificial standard leachate were prepared by dissolving weighed amounts of calcium carbonate (AR) and magnesium turnings in slight excesses of hydrochloric acid and mixing them in a 2 litre graduated flask. Weighed quantities of potassium and sodium chlorides were also added and the flasks were made up to the mark with normal ammonium acetate. 10 ml. aliquots were analysed for Ca^{2+} , Mg^{2+} , K^+ , Na^+ and total bases according to the Pienaar method using a hot plate for the initial evaporations and heating the residue at 500°C , 400°C and 300°C successively. The results are shown in Table III. The values obtained for Ca^{2+} , Mg^{2+} , K^+ and Na^+ agreed very well with the theoretical values. The Pienaar method at 500°C and 400°C gave slightly lower values than the sum of the individual cations. At 300°C the values were slightly higher than the sum totals but there was an increase in the standard deviation among the eight replicates from ± 0.054 m.e. per 100 ml. at 400°C to ± 0.11 m.e. per 100 ml. at 300°C . This seemed to indicate that all the ammonium chloride had not been driven off at 300°C .

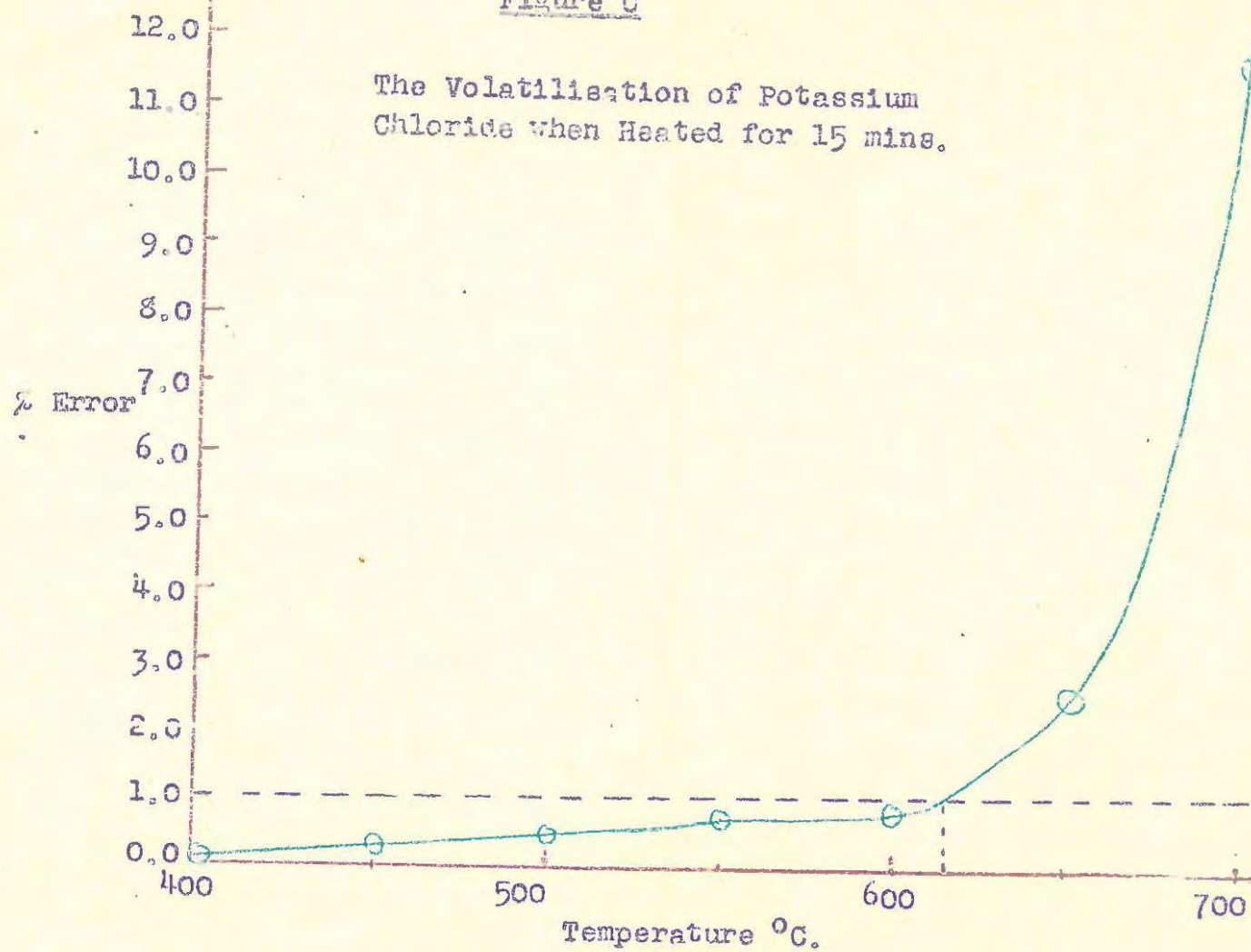
TABLE III.

m.e. / 100 ml. solution.

	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Sum Total	Total by Pienaar ignited for 10 mins. at			Difference		
						300° C	400° C	500° C	W - X	W - Y	W - Z
Theoretical	20.94	5.99	2.18	1.48	W	X	Y	Z			
1	20.94	5.99	2.18	1.48	30.59	30.59	30.59	30.59			
2	21.03	6.01	2.19	1.35		30.86	30.31	30.33			
3	21.04	5.98	2.10	1.54		30.79	30.32	30.25			
4	21.15	5.98	2.20	1.39		30.66	30.38	30.27			
5	21.12	5.99	2.08	1.37		30.66	30.32	30.21			
6	21.14	5.96	2.29	1.40		30.93	30.28	30.28			
7	21.10	6.02	2.23	1.39		30.73	30.23	30.33			
8	21.15	6.03	2.29	1.32		30.58	30.39	30.29			
8	21.07	5.94	2.22	1.30		30.79	30.27	30.32			
Mean	21.10	5.99	2.20	1.39	30.68	30.74	30.31	30.28	-0.06	0.37	0.40
(Theoretical - Mean)	-0.16	0.00	-0.02	0.09	-0.09	-0.15	0.28	0.31			
Std. Deviation	±0.048	±0.03	±0.078	±0.073		±0.11	±0.054	±0.042			
% Std. Deviation	0.2	0.5	3.5	5.0		0.38	0.17	0.14			

Figure C

The Volatilisation of Potassium
Chloride when Heated for 15 mins.



The following experiment was performed in order to find out whether the 1% difference between the sum of the individual cations and the total cations as determined by the Pienaar method was due to the loss of potassium by volatilisation.

A potassium chloride solution was made up to exactly 0.02500 N by weighing out a sample of fused potassium chloride. Aliquots of this solution were evaporated and heated at various temperatures from 400° C to 700° C for 15 minutes. They were then treated with dilute hydrochloric acid, evaporated to dryness and titrated with 1/20 N silver nitrate in the usual way to determine their normalities.

The temperature was plotted against the percentage difference between the normality obtained by titration and 0.02500 N. From Fig. C it appeared that 1% volatilisation occurred only after 600° C.

Potassium might possibly volatilise at a lower temperature in the presence of other cations. Thus aliquots of the previously prepared artificial leachates (see page 37) were similarly heated at temperatures from 300° C to 550° C for 15 minutes. The results are shown in Table IV.

TABLE IV.

Temperature °C	Heated for 15 min. Normality mean of 3 titres x	Theoretical Normality y	Difference. y - x.
300	0.3078	0.3059	-0.0019
350	0.3034	0.3059	0.0025
400	0.3032	0.3059	0.0027
500	0.3030	0.3059	0.0029
550	0.3027	0.3059	0.0032

There was a considerable difference between the normality figures obtained at 300° C and at 350° C but no corresponding decrease in the normality figures between 350° C, 400° C or 500° C as should have been the case had this difference been due to the volatilisation of potassium. It therefore appeared that the high results obtained at 300° C were due to the incomplete destruction of ammonium chloride at this temperature. There is very little difference between the results obtained at 400° C and at 500° C so it was decided to do all the ignitions at 500° C to facilitate the removal of all carbon and carbon compounds from the leachates.

A statistical comparison between the Bray and Willhite method and the Pienaar method for total exchangeable cations.

Pienaar found that ^{the} Bray and Willhite's method gave low and inconsistent results when ignited with a bunsen burner over a silica plate. He assumed that this inconsistency was caused through variability in the temperature of ignition. The author has attempted to standardise the ignition by igniting the residues in a muffle furnace at 550° C for 15 minutes.

Ten 1,000 ml. leachings were done on separate portions of the soil sample U 5 and the leachates were thoroughly mixed in a large aspirator.

16 determinations were made for total exchangeable cations using the Bray and Willhite's method, and 16 determinations were made for total exchangeable cations using the Pienaar argentometric method. In both cases the evaporations were done on a hot plate. 16 determinations were done for each of the four individual cations and the result tabulated in Table V.

TABLE V.

U 5

m.e. per 100 gms. soil.

No.	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Total	Bray & Willhite at 550° C	Pienaar at 500° C
1	52.05	6.71	1.56	0.56		57.60	60.04
2	52.53	6.30	1.69	0.50		59.29	60.33
3	52.14	6.51	1.66	0.44		59.59	60.29
4	52.24	6.45	1.61	0.50		59.29	60.15
5	52.64	6.35	1.70	0.50		59.63	60.17
6	52.60	6.43	1.59	0.58		59.61	60.19
7	52.74	6.41	1.60	0.48		59.40	60.27
8	52.27	6.43	1.59	0.60		59.19	60.25
9	52.15	6.71	1.56	0.48		59.41	60.37
10	51.89	6.71	1.61	0.52		59.38	60.13
11	52.53	6.49	1.58	0.56		58.75	60.33
12	51.87	6.65	1.60	0.58		56.44	60.41
13	51.95	6.55	1.60	0.46		58.95	60.21
14	52.14	6.55	1.58	0.49		58.34	60.65
15	52.65	6.34	1.56	0.50		58.79	60.15
16	52.60	6.51	1.63	0.47		59.39	60.27
Mean	52.33	6.50	1.61	0.51	60.95	58.94	60.27
St.Dev.	±0.30	±0.134	±0.043	±0.049		±0.85	±0.14
% St. Dev.	0.57	2.07	2.69	9.62	00.00	1.44	0.25
Diff. from Total					0.00	2.01	0.68

Phosphates mean 2 det. = 0.30 m.e./100 gms. Sulphate mean of 2 det. = 0.19 m.e./100 gms. Mn, Fe, Al = Nil

It was seen that the Pienaar results agreed much better with the sum total results than did the Bray and Willhite results. The mean of the exchangeable bases by the Pienaar method was 0.68 m.e. per 100 gms. less than the mean of the sum total. While the Bray and Willhite's mean was 2.01 m.e. per 100 gms. lower than the sum total results.

The Pienaar method was also more precise than the Bray and Willhite method having a standard deviation of 0.25 % as compared with 1.44 % for the Bray and Willhite method.

These results show that the Pienaar method was considerably better than the Bray and Willhite method both in accuracy and precision.

A similar comparison was made between the Pienaar method and individual cation determinations employing an entirely different soil sample, ^{no} Namely ✓ a light sandy soil from Venterstad (B2). The results are shown in Table VI.

From Table VI it was seen that the Pienaar method gave values which were 0.49 me. per 100 gms. less than the sum of the individual analysis. This amounted to a 6 % error. An analysis of the anions present, which would interfere with the Pienaar method, amounted to 0.32 m.e. per 100 gms. soil. Therefore it appears as if this 6 % error is mainly due to the interfering anions.

TABLE VI.

B 2. m.e. per 100 gms. soil.

No.	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Total	Pienaar at 500° C.
1	3.64	3.24	0.61	0.15		7.17
2	3.66	3.22	0.60	0.17		7.16
3	3.65	3.27	0.63	0.13		7.18
4	3.65	3.27	0.64	0.17		7.18
5	3.63	3.31	0.63	0.16		7.18
6	3.62	3.19	0.65	0.16		7.11
7	3.63	3.29	0.60	0.16		7.11
8	3.62	3.23	0.60	0.16		7.16
9	3.64	3.26	0.61	0.16		7.17
10	3.64	3.36	0.60	0.17		7.20
11	3.57	3.20	0.60	0.15		7.14
12	3.57	3.22	0.62	0.14		7.17
Mean	3.63	3.25	0.62	0.15	7.65	7.16
St. Dev.	±0.029	±0.049	±0.018	±0.016		±0.027
% St. Dev.	0.8	1.5	2.9	11.0		0.3

phosphate = 0.19 m.e. per 100 gms.
 silica = 0.04 m.e. per 100 gms.
 sulphate = 0.09 m.e. per 100 gms.

Difference 0.49

DISCUSSION OF THE PIENAAR ARGENTOMETRIC METHOD.

The Pienaar method had the following advantages over the Bray and Willhite method:-

(i) The Bray and Willhite method depended for its effectiveness on the complete conversion of acetates to carbonates or oxides. It was exceedingly sensitive to changes in temperature during ignition. The author was not in favour of igniting the residue over a bunsen burner because of the lack of control of temperature and the subsequent danger of volatilisation of potassium salts or the incomplete conversion of acetates to carbonates when the gas pressure was low. Even when ignited at 550°C for 15 minutes, the Bray and Willhite method still gave low and inconsistent results (See Table V.). On the other hand the Pienaar method was not sensitive to temperature changes during ignition as the hydrochloric acid stoichiometrically displaced the acetate ions from the residue. The residue was ignited to 500°C to volatilise ammonia and to destroy any organic matter present. A little elemental carbon did not interfere in the Pienaar method although it is undesirable as it masked the silver chromate end point and might possibly adsorb some silver ions.

(ii) The Bray and Willhite method required a back titration which complicated the experiment and increased the possibility of error since the standard acid was liable to absorb ammonia which was frequently present in soil laboratories.

(iii) The Pienaar method was much simpler and shorter than the Bray and Willhite method. The alkali and alkaline earth chlorides were readily soluble in water, whereas the carbonates had to be heated strongly before they would dissolve in the standard acid.

The Pienaar method gave very consistent and reproducible results as was seen in Tables III, V and VI. The precision was much better than the reproducibility obtained from successive leachings and as Pienaar has shown it was a good method for testing the leaching methods.

The results obtained by the Pienaar method were generally slightly lower than the sum of the individual cations. This seemed to be due in small measure to the individual estimation being slightly high and to a varying extent, to anion interference. Any non-volatile anions like phosphates or sulphates would interfere in this method. ✓

$\text{Ca}^{2+} + \text{SO}_4^{2-} + \text{Cl}^- + \text{H}^+ \longrightarrow \text{CaSO}_4 + \text{HCl}$ would occur and the cations in combination with the phosphate or sulphate ions would not be determined by the silver nitrate titration. Fortunately these anions were present in the leachate only in very small amounts and would thus not seriously upset the results except in soils that were very poor in exchangeable cations. Good examples of such soils were H 1 and P 4.

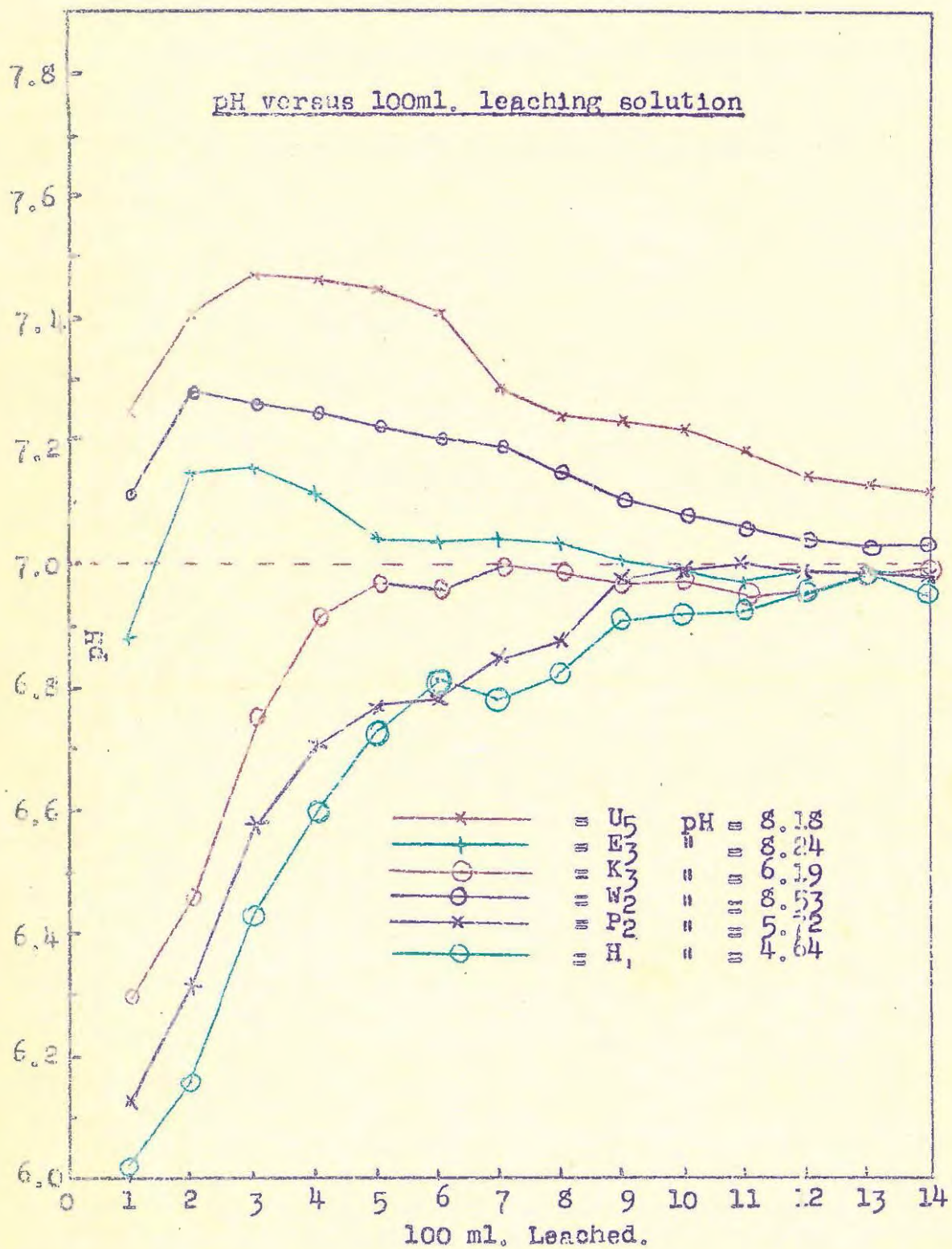
The leaching process.

The reproducibility of the leaching process was tested on various soil samples, using the Pienaar argentometric method.

Shirley (7) considered 1,000 ml. of ammonium acetate to be sufficient to leach out all the exchangeable cations in 50 gms. of soil. The author found it convenient to use from 50 to 120 gms. of soil per leaching, depending on the amount of exchangeable cations present.

Approximately 80 gms. samples of various soil types were leached and the leachates collected in 100 ml. flasks. 14 successive 100 ml. portions were collected from each sample. 50 ml. aliquots were taken and analysed for total exchangeable cations, according to the modified Pienaar method.

Graph I



The pH of the leachates were determined from the remainder of the 100 ml. portions.

Six soil types were used and in each case the leaching operation was adjusted to proceed at the rate of 1 litre per 4 hours.

The results were tabulated and Graph I was drawn of pH versus the number of 100 ml. portions leached. Graph II and Graph III were drawn of total cations versus the number of 100 ml. portions leached.

The six soil samples used were:-

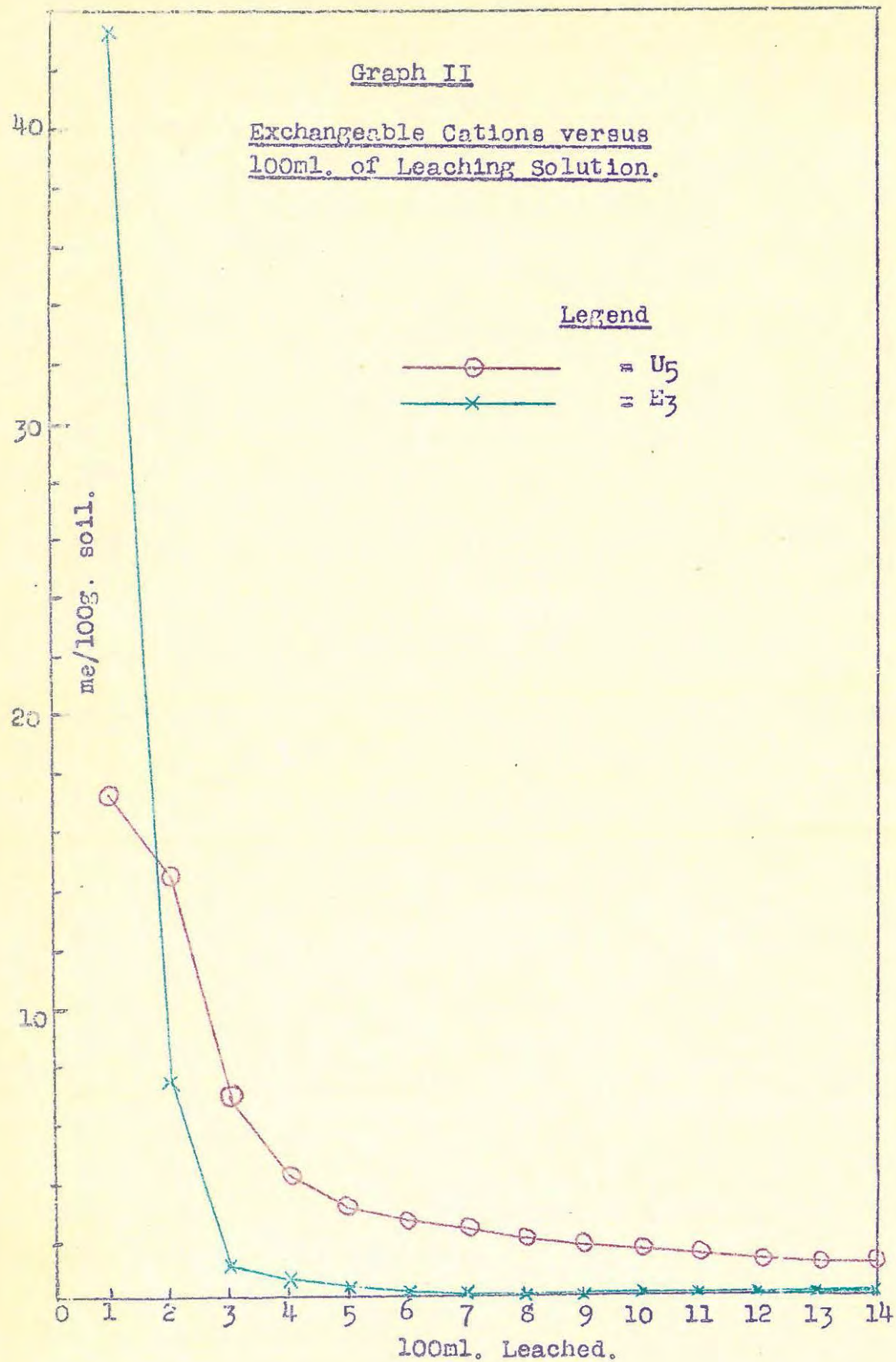
- (1) H 1, a dark brown sandy soil from De Kuilen near Lydenburg.
- (2) K 3, a grey, sandy clay podsollic soil from Harding.
- (3) P 2, from Estcourt, a dark red hard lumpy clay soil on ferruginous laterite.
- (4) E 3, from Marikana, a black clay chernozem-like soil.
- (5) W 2, from Stillbay, a sandy soil with much evidence of Aeolian deposits. It contained an appreciable quantity of free lime.
- (6) U 5, from Uitenhage, a dark brown sandy loam, containing much organic matter and calcium carbonate.

In Graph I all the pH curves have a general kind of characteristic. They can be divided into two types:

- (a) ~~Curves~~ of H 1, K 3 and P 2 were those of acid soils. The pH curve started low down and approached the line pH 7.00, asymptotically as more and more H^+ ions were exchanged by NH_4^+ ions.
- (b) ~~Curves~~ of E 3, U 5 and W 2 were the curves of alkaline soils. The pH curves started low at the first 100 ml. and then it rose to a maximum at the second or third 100 ml. It then gradually approached the pH 7.00 line.

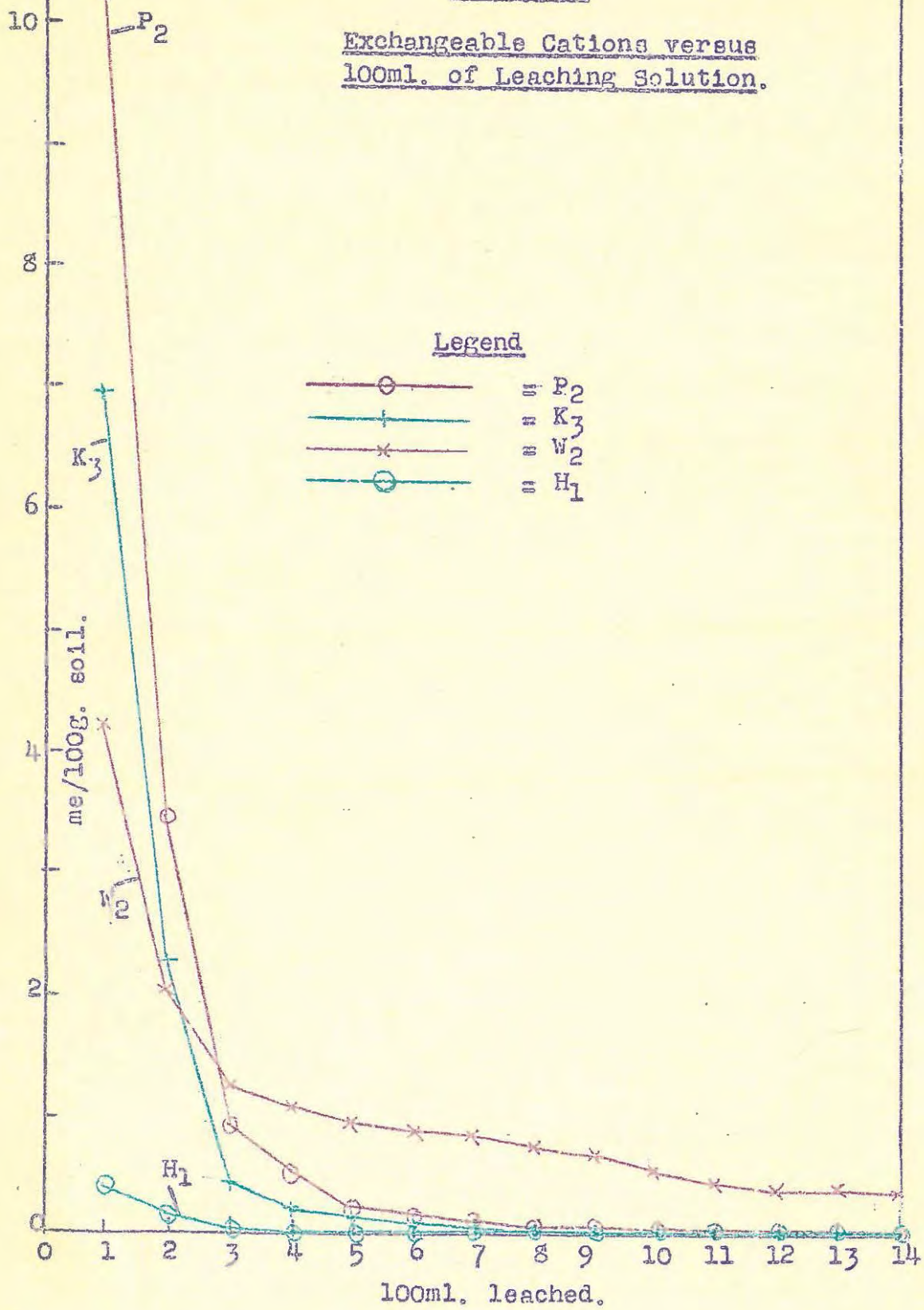
Graph II

Exchangeable Cations versus
100ml. of Leaching Solution.



Graph III

Exchangeable Cations versus
100ml. of Leaching Solution.



This seemed to indicate a preferential exchange of metallic cations with NH_4^+ ions in the first 100 ml. and then in the second and third 100 ml. the metallic cations were depleted causing H^+ ions to be adsorbed from the solution to establish an equilibrium between NH_4^+ and H^+ ions.

Graphs II and III were the curves of exchangeable cations versus 100 ml. leachates. In graph II, E 3 and U 5 had nearly equal exchangeable cation values (53.70 m.e. per 100 gms. and 60.95 m.e. per 100 gms. respectively) but their curves were very different. Note the rapid fall off in the cations leached out in E 3. By the 10th 100 ml. the E 3 value fell to 0.23 m.e. per 100 gms. while the U 5 value was still large (1.87 m.e. per 100 gms.).

An arbitrary value C is chosen so that

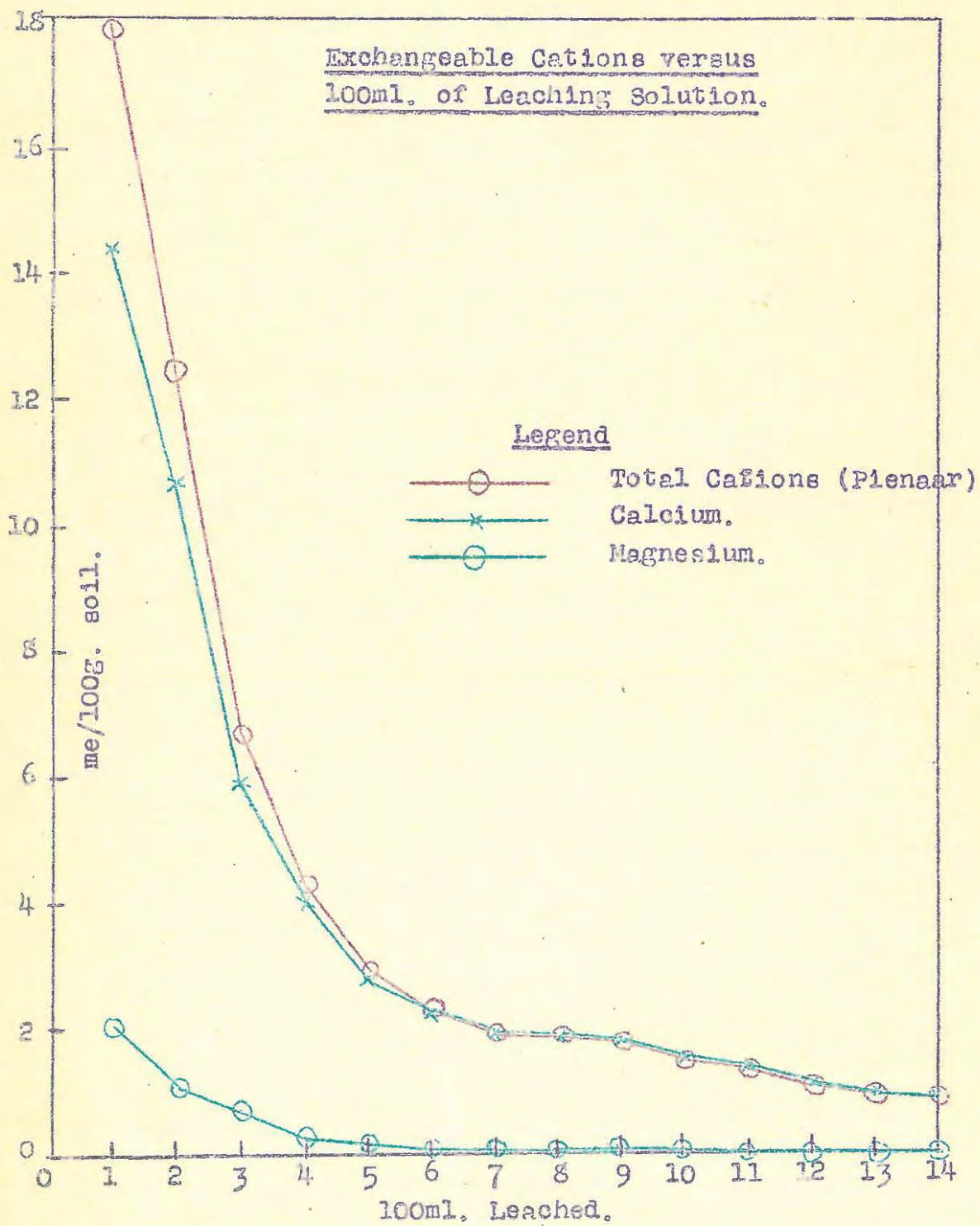
$$C = \frac{\text{cation values obtained in (11th + 12th + 13th + 14th)}}{\text{cation values obtained in (1st + 2nd + 3rd + 4th)}} \quad \begin{matrix} 100 \text{ ml.} \\ 100 \text{ ml.} \end{matrix}$$

C was a good index as to the degree of completion of leaching and if C was greater than 1 % the leaching process could not be considered complete at 1 litre and the results would not be reproducible.

$$\begin{aligned} \text{In E 3 } C_{E3} &= \frac{0.54}{52.50} = 0.01 = 1. \% \\ \text{In U 5 } C_{U5} &= \frac{5.76}{43.03} = 0.12 = 12. \% \\ \text{In P 2 } C_{P2} &= \frac{0.13}{15.16} = 0.008 = 0.8 \% \\ \text{In K 3 } C_{K3} &= \frac{0.06}{9.93} = 0.006 = 0.6 \% \\ \text{In W 2 } C_{W2} &= \frac{1.48}{8.6} = 0.15 = 15. \% \\ \text{In H 1 } C_{H1} &= \frac{0.00}{0.62} = 0.00 = 0.0 \% \end{aligned}$$

C_{E3} , C_{K3} , C_{P2} and C_{H1} were all less than 1 % showing that the soils were completely leached with 1 litre of ammonium acetate and thus their results should be reproducible.

Graph IV



C_{U_5} and C_{W_2} , on the other hand, were large showing that appreciable quantities of cations were still leached out after 1 litre. Both U_5 and W_2 contained appreciable quantities of calcium carbonates and their leachates had a very dark colour. This colour appeared to be due to lyophobic organic colloids as they were flocculated by the addition of calcium or magnesium ions.

Another series of leachings was made on U_5 and the 100 ml. portions were analysed (i) for total cations, (ii) calcium, (iii) magnesium. The results were plotted in Graph IV. The total cations, and the calcium curves converged, while the magnesium curve rapidly fell to zero. This showed that only calcium was present after the 8th 100 ml. ✓

These results showed that the ammonium acetate method of leaching 50 to 120 gms. soil samples with 1,000 ml. solutions would give reproducible results on all the types of soil except those containing large percentages of lime. In these cases the calcium figures were too high and the final results depended on the volume of leaching solution used.

If better results are required for calcareous soils, the author advises the adoption of another leaching method. The buffered barium chloride method developed by Hanna and Fielding Reed (63) is very suitable under these conditions. ✓

Has it
been tried
and - 2

F. THE ANALYSES OF THE SOIL SAMPLES.

The author analysed 56 different soil samples taken from various localities in the Union of South Africa. These samples were taken as described on page 22.

Table VII gives a short description of the soil samples and their exchangeable cation analysis figures. They were classified in accordance with the soil regions of C.R. van der Merwe's soil map of South Africa⁽⁵⁷⁾. ~~(57)~~ The colour and texture of the soils were as described by the author and the pH of the soil was determined using a 1 : 2 soil : water mixture and employing a Marconi pH meter. The analyses of the soil samples for the exchangeable cations Ca^{2+} , Mg^{2+} , K^{+} and Na^{+} were given together with the sum total figures and the total cations as determined by the Pienaar argentometric method. The difference between the sum of the individual figures and the Pienaar method was given in the column (X - Y).

Table VIII contains the total exchangeable cation figures arranged in order of magnitude together with the ratios, divalent to monovalent cations ($\text{M}^{2+}/\text{M}^{+}$) and the calcium to magnesium ($\text{Ca}^{2+}/\text{Mg}^{2+}$). Carbonates were indicated by treating the sample with dilute hydrochloric acid. Excessive effervescence was denoted by ++, while moderate effervescence was shown by +.

Discussion.

These results were seriously hampered by the lack of profile data, base saturation figures and by the inherent heterogeneous nature of soils. It was hoped that these analyses would give some indication of the chief cations/ exchange characteristics of the various soil types in the Union but as was shown by Steyn (61) sampling errors were very great even in

seemingly homogeneous plots of soil and thousands of soil samples would have to be obtained from each area before a comprehensive account could be given of its soil properties. Nevertheless the author has noticed several significant trends in the cation exchange values of the soil samples. ~~soils than for soils poor in exchangeable cations. These ratios~~

(1) From Table VIII it was seen that the pH values were higher for soils rich in exchangeable cations than for poorer soils. The pH of the semi-arid and solonchic groups A and B were not as high as would be expected from their unleached conditions. The sub-tropical black clay samples E had higher pH values than the Drakensberg black clays, while the lateritic earths and the podsollic samples had generally low pH values. This was as would be expected since they were more extensively leached by higher rainfalls than the arid types A, B, C, D, E and F. The high pH values of U and W types seemed to be caused by high free calcium ^{carbonate} contents. No soils (with the possible exception of E 2) were encountered with high pH values due to monobasic ion saturation. ~~There were no appreciable differences~~

(2) The E and I black clays had the highest cation exchange values. The Uitenhage series U had very high values but it was suspected that a large proportion of their calcium values were due to dissolved limestone. The brown forest soils F had higher values than was expected but F 2 seemed to belong rather to the sub-tropical black clays than to this group. The one sample from the Lydenburg group H, had an extremely low cation exchange value as well as being very acidic (pH 4.64).

The podsollic soil samples J, K and L were generally grey in colour and had low cation exchange values. They were difficult to leach with ammonium acetate probably due to an ~~impermeable~~ ^{deflocculated} clay fraction. The

^{7, 8 deflocculated}

lateritic earth samples also had low cation exchange values but they were more variable than the podsol. The samples from the winter fainfall areas had low cation exchange values with the exception of U and W types.

(3) The ratios of divalent to monovalent ions were greater for the richer soils than for soils poor in exchangeable cations. These ratios were also greater for saturated than for unsaturated acidic samples.

This was in accordance with the valency effect of Donnan equilibria, as explained by Mattson and Larsson. (64). ✓

(4) There did not appear to be any correlation between the ratio of Ca : Mg and cation exchange magnitude or pH. Most soil samples have a Ca : Mg ratio of between 1 and 4, only 3 samples S 1, P 2 and N 2 were found with a Ca : Mg ratio of less than 1 and the only samples with a Ca : Mg ratio bigger than 10 are the lime sands W. ✓

(5) The difference between the sum of the individual analyses and the total values by the Pienaar method was usually positive and varied from 0.16 to 1.16 m.e. per 100 gms. soil. There were no appreciable differences between the discrepancies occurring in the richer soils and those occurring in the poorer soils. This was further proof that these discrepancies were not caused by a methodical error but rather by an interference such as non-volatile acids which would affect the argentometric method but not the individual determinations.

TABLE VII.

Number	A 1	A 2	A 3	B 1	B 2
Place	Craddock	Tarka (Vlekpoort)	Steynsburg	Venterstad	
Colour	Yellow brown	Reddish brown	Yellow brown	Reddish brown	Reddish brown
Texture	Sandy loam	Sandy loam	Sandy Clay loam	Sandy loam	Sandy loam
Rainfall p/a	14"	15"	15"	17"	17"
pH 1 : 2	7.3	7.0	6.72	6.8	6.24
Group according to C.R. v.d. Merwe's					
Soil Map	Semi arid & desert soils			Solonetzic soils	
<u>Exchangeable cations in M.e. per 100 gms. soil.</u>					
Ca ²⁺	5.04	3.89	5.19	4.18	3.62
Mg ²⁺	1.93	1.93	3.34	2.79	3.25
K ⁺	0.59	0.43	0.51	0.46	0.62
Na ⁺	0.17	0.07	0.12	0.06	0.15
X Total	7.73	6.32	9.16	7.49	7.64
Y Pienaar total	8.03	5.85	8.73	7.18	7.16
Diff. X - Y	-0.30	+0.47	+0.43	+0.31	+0.48

Number	B 3	C 1	D 1	E 1	E 2
Place	Queens- town	Mahala- pye	Koffie- fontein	Bon Accord	Pienaaars River
Colour	Brown	Yellow red	Yellow brown	Brown black	Black
Texture	Sandy loam	Sand	Sandy loam	Crumbly clay	Crumbly clay
Rainfall p/a	21"	15"	14"	23"	23"
pH 1 : 2	6.68	8.04	6.96	6.79	8.6
Group	Solonetzic soil	Kalahari sand	Kalahari sand on lime	Subtropical black clay soils	
<u>Exchangeable cations in M.e. per 100 gms. soil.</u>					
Ca ²⁺	3.42	11.37	7.01	19.3	31.92
Mg ²⁺	1.67	1.84	3.05	11.14	10.2
K ⁺	0.5	1.07	0.1	0.54	1.37
Na ⁺	0.05	0.08	0.08	0.12	1.11
X Total	5.64	14.36	10.24	31.1	44.6
Y Pienaar total	5.25	13.29	9.32	29.91	44.19
Diff. X - Y	+0.39	+1.07	+0.92	+1.19	+0.41

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TABLE VII Continued.

Number	E 3	E 4	F 1	F 2	F 3
Place	Marikana	Crecy	Messina	40 miles N of Beit Bridge	Lebombo Mts.
Colour	Black	Black	Red brown	Dark brown	Choc. brown
Texture	Clay	Big hard lumpy clay	Sandy	Clay loam	Clay loam
Rainfall p/a	26"	24"	14"	13"	13"
pH 1 : 2	8.24	6.29	7.65	6.91	6.3
Group according to C.R. v.d. Merwe's Soil Map	Subtropical black clay soils		Brown Forest Soils		
<u>Exchangeable cations in M.e. per 100 gms. soil.</u>					
Ca ²⁺	36.89	23.84	10.73	18.5	13.96
Mg ²⁺	16.44	19.08	1.14	9.63	6.66
K ⁺	0.04	1.8	0.91	1.01	1.22
Na ⁺	0.33	0.77	0.07	0.09	0.22
X Total	53.7	45.49	12.85	29.23	22.06
Y Pienaar total	53.87	44.47	12.66	28.27	22.09
Diff. X - Y	-0.17	+1.02	+0.19	+0.96	-0.03

Number	G 1	H 1	I 1	I 2	I 3
Place	Nylstroom	De Kuilen	Barkly East	Basutoland near Matatiele	Maseru
Colour	Red yellow	Dark brown	Black	Brown	Black
Texture	Sandy loam	Sand	Clay	Crumbly clay	Clay
Rainfall p/a	25"	35"	23"	35"	29"
pH 1 : 2	6.78	4.64	6.78	5.98	7.7
Group	Waterberg light brown sandy	Lydenburg dark brown sand	Drakensberg Mountain black clay soils		
<u>Exchangeable cations in M.e. per 100 gms. soil.</u>					
Ca ²⁺	4.96	0.56	20.54	24.12	26.71
Mg ²⁺	0.55	0.36	9.16	10.64	9.31
K ⁺	2.42	0.01	0.5	0.03	0.97
Na ⁺	0.1	0.14	0.17	0.27	0.35
X Total	7.76	1.07	30.37	35.06	37.34
Y Pienaar total	7.72	0.33	29.72	34.00	36.42
Diff. X - Y	-0.04	+0.74	+0.65	+1.06	+0.92

TABLE VII Continued.

Number	J 1	J 2	J 3	K 1	K 2
Place	Bethal	Maseru	Witkop Jamestown	East London	Grahamstown
Colour	Brown grey	Light brown	Light brown	Grey	Grey Sandy
Texture	Sandy loam	Sandy loam	Loamy sand	Sandy loam	Clay loam
Rainfall p/a	29"	29"	25"	32"	28"
pH 1 : 2	5.38	5.49	6.7	6.54	6.49
Group according to C.R. v.d. Merwe's Soil Map	Highveld prairie (Podsolis)			Eastern Province Semi Coastal Belt (Podsolis)	
Exchangeable cations in M.e. per 100 gms. soil.					
Ca ²⁺	2.51	1.83	5.72	4.23	2.21
Mg ²⁺	1.65	0.12	1.58	0.72	0.6
K ⁺	0.43	0.34	0.08	0.5	0.14
Na ⁺	0.09	0.01	0.11	0.24	0.13
X Total	4.68	2.3	7.49	5.69	3.08
Y Pienaar total	4.23	2.26	6.62	5.23	3.22
Diff. X - Y	+0.45	+0.04	+0.87	+0.46	-0.14

Number	K 3	K 4	K 5	L 1	L 2
Place	Harding	Kingwil- liamstown.	Fort Beaufort	Durban	Pinetown
Colour	Grey	Grey	Grey brown	Red brown	Grey
Texture	Loamy sand	Loamy sand	Sandy loam	Sand	Sand
Rainfall p/a	32"	21"	21"	40"	36"
pH 1 : 2	6.19	6.12	5.88	5.18	5.81
Group	Eastern Province Semi Coastal Belt (Podsolis)			Natal coast belt (Podsolis)	
Exchangeable cations in M.e. per 100 gms. soil.					
Ca ²⁺	6.26	5.78	4.74	2.00	1.33
Mg ²⁺	3.02	1.51	0.98	0.43	2.6
K ⁺	0.65	0.8	1.49	0.27	0.21
Na ⁺	0.17	0.02	0.14	0.12	0.04
X Total	10.1	8.11	7.35	2.82	1.84
Y Pienaar total	10.17	8.2	6.89	2.45	1.64
Diff. X - Y	-0.07	-0.09	+0.46	+0.37	+0.2

TABLE VII Continued.

Number	M 1	M 2	M 3	N 1	N 2
Place	Kruger- dorp	Wychwood Germiston	Louis Trichardt	Cedara	Ixopo
Colour	Red Brown	Red brown	Red brown	Choc brown	Choc brown
Texture	Sandy clay loam	Sandy loam	Clay	Clay	Clay
Rainfall p/a	30"	31"	29"	34"	34"
pH 1 : 2	5.00	4.97	6.38	5.64	4.84
Group according to C.R. v.d. Merwe's Soil Map	Lateritic red earths			Lateritic yellow earths	
Exchangeable cations in M.e. per 100 gms. soil.					
Ca ²⁺	1.47	3.7	12.18	8.28	4.39
Mg ²⁺	0.18	0.49	4.79	8.4	1.22
K ⁺	0.01	0.00	1.55	0.21	0.09
Na ⁺	0.13	0.08	0.12	0.15	0.1
X Total	1.79	4.27	18.64	17.04	5.8
Y Pienaar total	1.11	3.4	18.27	15.88	5.64
Diff. X - Y	+0.68	+0.87	+0.37	+1.16	+0.16

Number	O 1	O 2	P 1	P 2	P 3
Place	Warmbaths	Grey	Estcourt	Estcourt	Estcourt
Colour	Choc brown	Dark red	Red	Red	Red brown
Texture	Sandy loam	Sandy clay loam	Sandy clay loam	Sandy loam	Sandy clay
Rainfall p/a	22"	24"	28"	28"	28"
Group	Grey ferruginous laterite Brown and reddish laterite				
pH 1 : 2	6.38	6.49	5.24	5.72	6.28
Exchangeable cations in m.e. per 100 gms. soil.					
Ca ²⁺	4.21	10.21	2.52	7.81	7.71
Mg ²⁺	0.6	6.96	1.15	8.17	2.82
K ⁺	0.54	0.83	0.49	0.31	0.7
Na ⁺	0.01	0.09	0.01	0.24	0.02
X Total	5.36	18.09	4.17	16.53	11.25
Y Pienaar total	5.2	18.1	3.97	15.76	10.42
Diff. X - Y	+0.16	-0.01	+0.2	+0.77	+0.83

TABLE VII Continued.

Number	P 4	R 1	R 2	R 3	S 1
Place	Pretoria	Glen	Glen	Bloemfontein	Knysna
Colour	Grey brown	Red	Brown	Brown	Brown
Texture	Sandy loam	Loamy sand	Sandy loam	Sandy loam	Sandy loam
Rainfall p/a	25"	19"	19"	20"	30"
pH 1 : 2	6.52	6.31	7.98	7.27	6.81
Group according to C.R. v.d. Merwe's Soil Map	Brown & reddish laterite	Geo ^{Neo} Gal ian sandy soil		Grey sandy and Table Mt. sandstone	
Exchangeable cations in M.e. per 100 gms. soil.					
Ca ²⁺	2.29	3.17	16.18	13.33	2.97
Mg ²⁺	0.91	1.17	6.43	4.63	4.08
K ⁺	0.04	0.51	3.17	0.44	0.2
Na ⁺	0.01	0.03	0.02	0.4	0.56
X Total	3.25	4.88	25.8	18.77	7.81
Y Pienaar total	2.87	4.3	24.81	18.37	7.26
Diff. X - Y	+0.38	+0.58	+0.99	+0.4	+0.55

Number	T 1	T 2	U 1	U 2	U 4
Place	Stellenbosch	Riversdale	Uitenhage	Coega	Uitenhage
Colour	Brown	Red buff	Brown	Brown	Brown
Texture	Sandy clay loam	Gravelly clay loam	Organic Sandy loam	Organic Sandy loam	Sandy loam
Rainfall p/a	27"	17"	17"	13"	17"
pH 1 : 2	5.68	6.82	6.69	8.51	6.81
Group	Gravelly sandy loam or clay		Sandy loams on lime and clay		
Exchangeable cations in M.e. per 100 gms. soil.					
Ca ²⁺	3.71	4.77	19.28	56.89	11.41
Mg ²⁺	0.56	3.06	2.44	32.65	2.93
K ⁺	0.26	0.52	2.81	2.06	0.56
Na ⁺	0.14	0.81	3.39	0.67	0.4
X Total	4.67	9.18	28.12	92.27	15.3
Y Pienaar total	3.93	8.08	28.14	92.7	14.74
Diff. X - Y	+0.74	+1.1	-0.02	-0.43	+0.56

TABLE VII Concluded.

Number	U 5	V 1	V 2
Place	Uitenhage	Port Alfred	Begelly Alexandria
Colour	Brown	Grey	Red brown
Texture	Organic sandy loam	Sandy loam	clay loam
Rainfall p/a	17"	25"	21"
pH 1 : 2	8.18	6.00	6.78
Group according to C.R. v.d. Merwe's Soil Map	Sandy loam on lime and clay	Red brown sandy loams	
<u>Exchangeable cations in M.e. per 100 gms. soil.</u>			
Ca ²⁺	52.33	1.88	7.46
Mg ²⁺	6.5	0.53	1.91
K +	1.61	0.24	1.78
Na +	0.51	0.01	0.04
X Total	60.95	2.66	11.19
Y Pienaar total	60.27	2.5	10.54
Diff. X - Y	+0.68	+0.16	+0.65

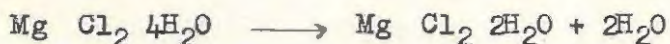
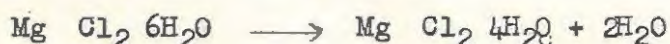
Number	W 1	W 2	W 3
Place	Stillbay	Stillbay	Cape Flats
Colour	Grey brown	Brown	White
Texture	Sandy loam	Organic sand	Sand
Rainfall p/a	15"	15"	24"
pH 1 : 2	8.25	8.25	8.18
Group	Coastal ^{Red} Coastal ^{Gal} Gal ^{ian} ian sands on lime		
<u>Exchangeable cations in M.e. per 100 gms. soil.</u>			
Ca ²⁺	23.81	13.72	9.52
Mg ²⁺	0.96	0.29	0.57
K +	0.39	0.01	0.06
Na +	0.01	0.00	0.15
X Total	25.17	14.02	10.24
Y Pienaar total	24.5	13.8	9.81
Diff. X - Y	+0.65	+0.22	+0.48

TABLE VIII.

No.	Total m.e./ 100 gm.	$\frac{m^{2+}}{m^{+}}$	$\frac{Ca^{2+}}{Mg^{2+}}$	pH	CO ₂	No.	Total m.e./ 100 gm.	$\frac{m^{2+}}{m^{+}}$	$\frac{Ca^{2+}}{Mg^{2+}}$	pH	CO ₂
U2	92.27	32.8	1.7	8.51	++	T2	9.18	6.4	1.5	6.82	
U5	60.95	27.7	8.6	8.18	++	A3	9.16	13.5	1.5	6.72	
E3	53.7	144.0	2.2	8.24	+	K4	8.11	8.8	3.8	6.17	
E4	45.49	16.7	1.2	6.29	+	S1	7.81	9.2	0.73	6.81	
E2	44.6	16.5	3.1	8.6	++	G1	7.76	2.1	8.5	6.78	
I3	37.34	27.3	2.8	7.7		A1	7.73	9.1	2.6	7.3	
I2	35.05	115.0	2.2	5.98		B2	7.64	8.9	1.1	6.24	
E1	31.1	46.2	1.6	6.79		J4	7.49	38.4	3.6	6.7	
I1	30.37	44.4	2.2	6.78		B1	7.49	13.4	1.5	6.8	
F2	29.23	14.1	1.9	6.91		K5	7.35	3.5	4.8	5.88	
U1	28.12	3.5	8.0	6.69		A2	6.32	11.6	2.0	7.00	
R2	25.8	7.4	2.5	7.98	++	N2	5.8	29.0	3.6	4.84	
W1	25.17	61.9	24.8	8.52	++	K1	5.69	6.7	5.8	6.54	
F3	22.06	14.3	2.1	6.3		B3	5.64	9.1	2.1	6.68	
R3	18.77	21.0	2.9	7.27		O1	5.36	8.7	7.0	6.38	
M3	18.64	10.0	2.5	6.38		R1	4.88	8.0	2.7	6.31	
O2	18.09	18.7	1.4	6.49		J1	4.68	8.0	1.5	5.38	
N1	17.04	47.7	0.98	5.64		T1	4.67	10.6	6.6	5.68	
P2	16.53	29.1	0.93	5.72		M2	4.27	50.2	7.6	4.97	
U4	15.3	15.0	3.9	6.81		P1	4.17	7.3	2.2	5.25	
C1	14.36	11.5	6.2	8.04		P4	3.25	60.5	2.5	6.52	
W2	14.02	774.0	25.7	8.53	++	K2	3.08	10.4	3.7	6.49	
F1	12.85	12.1	9.4	7.65	+	L1	2.82	6.2	4.6	5.18	
P3	11.25	14.6	2.7	6.28		V1	2.66	9.6	3.5	6.00	
V1	11.19	5.1	3.9	6.78		J2	2.3	5.5	15.2	5.49	
W3	10.24	48.0	16.3	8.18	++	L2	1.84	6.5	5.6	5.81	
D1	10.24	55.6	2.3	6.96		M1	1.79	11.4	8.1	5.00	
K3	10.1	11.3	2.3	6.19		H1	1.07	4.0	1.5	4.64	

G. A STUDY OF THE HYDROLYSIS OF MAGNESIUM CHLORIDE IN THE PRESENCE OF CALCIUM CHLORIDE.

When hydrated magnesium chloride was heated it lost water of crystallisation in the normal manner: ✓



But this last molecule of water was not easily removed and on further heating it caused hydrolysis, with the evolution of hydrochloric acid gas and the formation of numerous magnesium oxychlorides, the simplest of which was $\text{Mg}(\text{OH})\text{Cl}$ (50). ✓

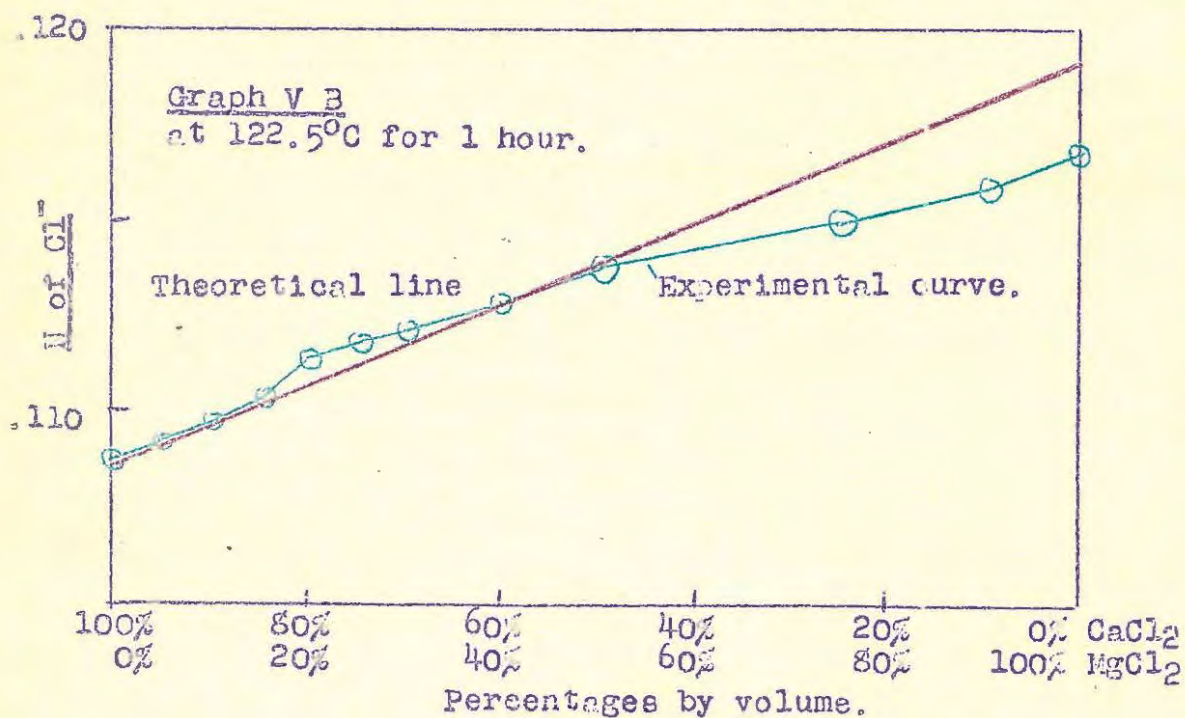
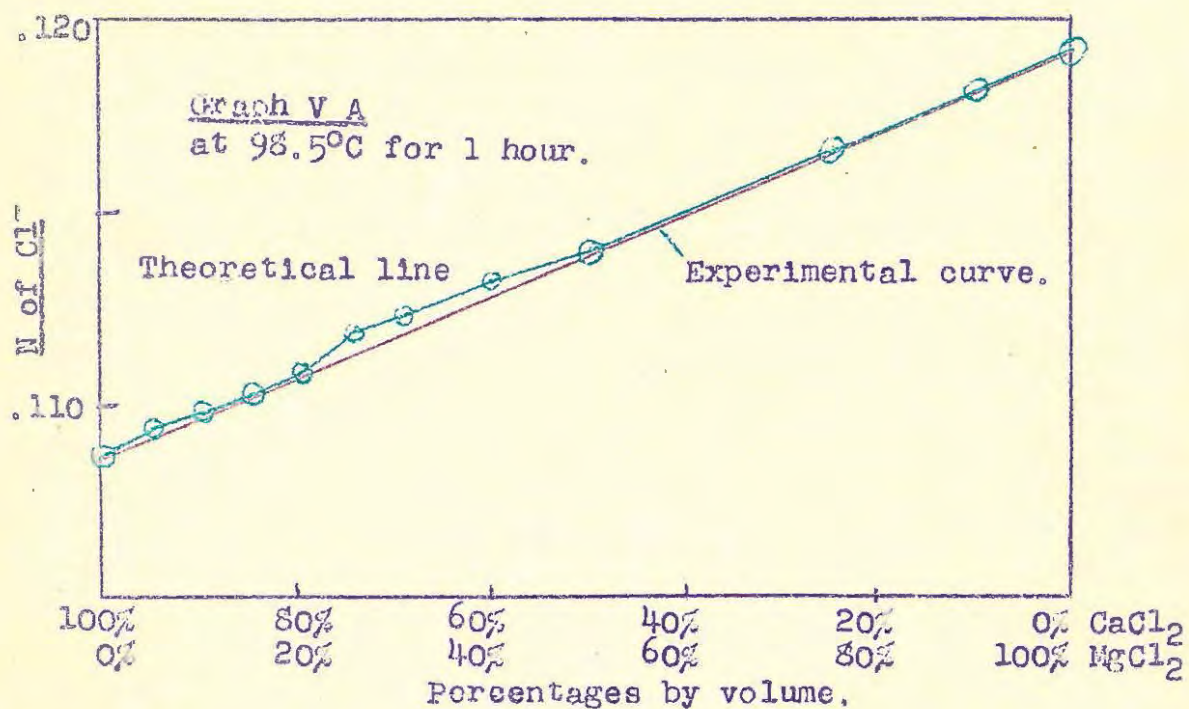
Pienaar (8) found that low results were obtained when soil residues, containing large proportions of magnesium chloride, were evaporated on a hot plate and titrated with silver nitrate. He attributed this to the hydrolysis of magnesium chloride. He subsequently found that calcium chloride affected this hydrolysis and that large ratios of calcium chloride prevented any hydrolysis taking place.

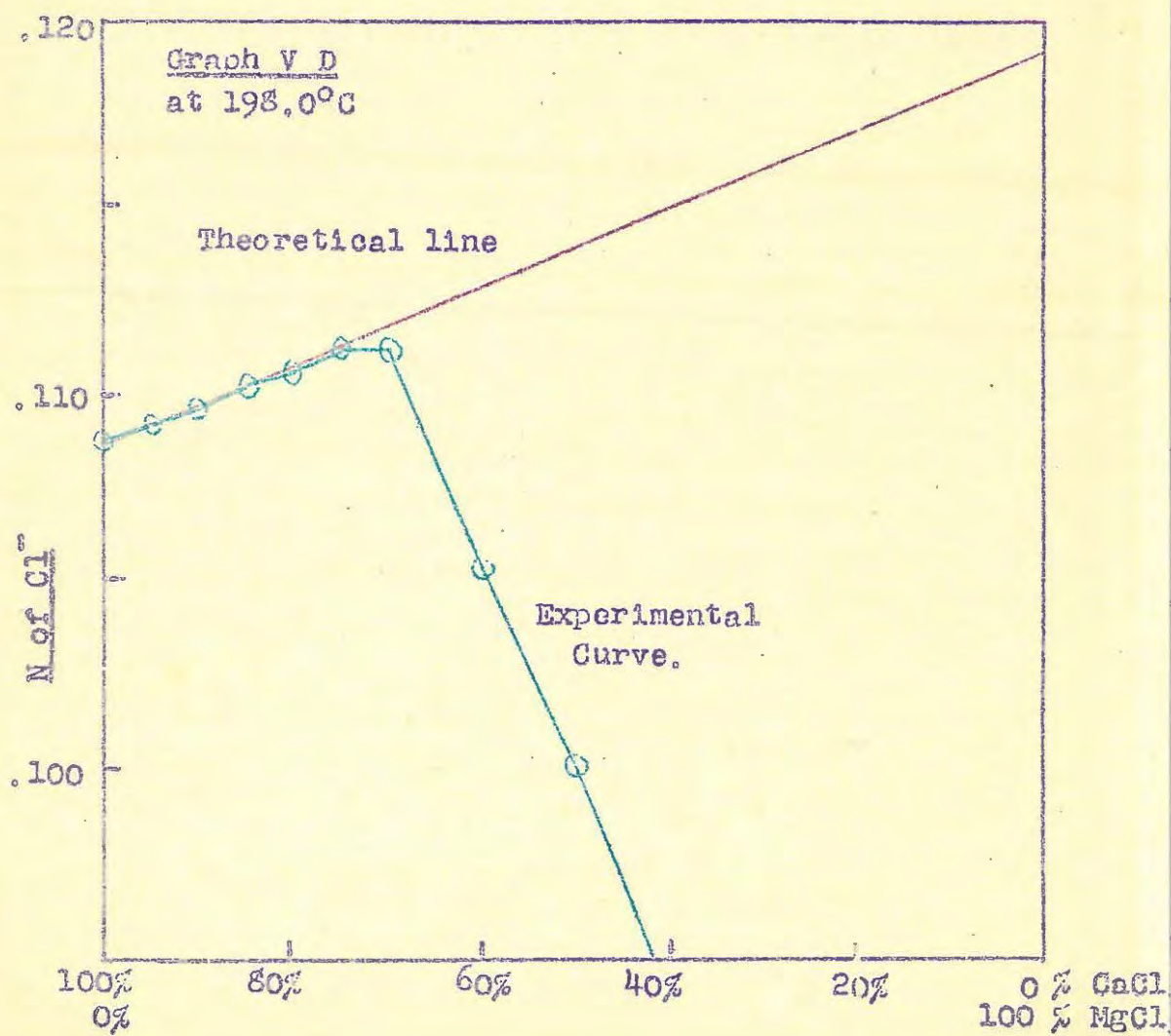
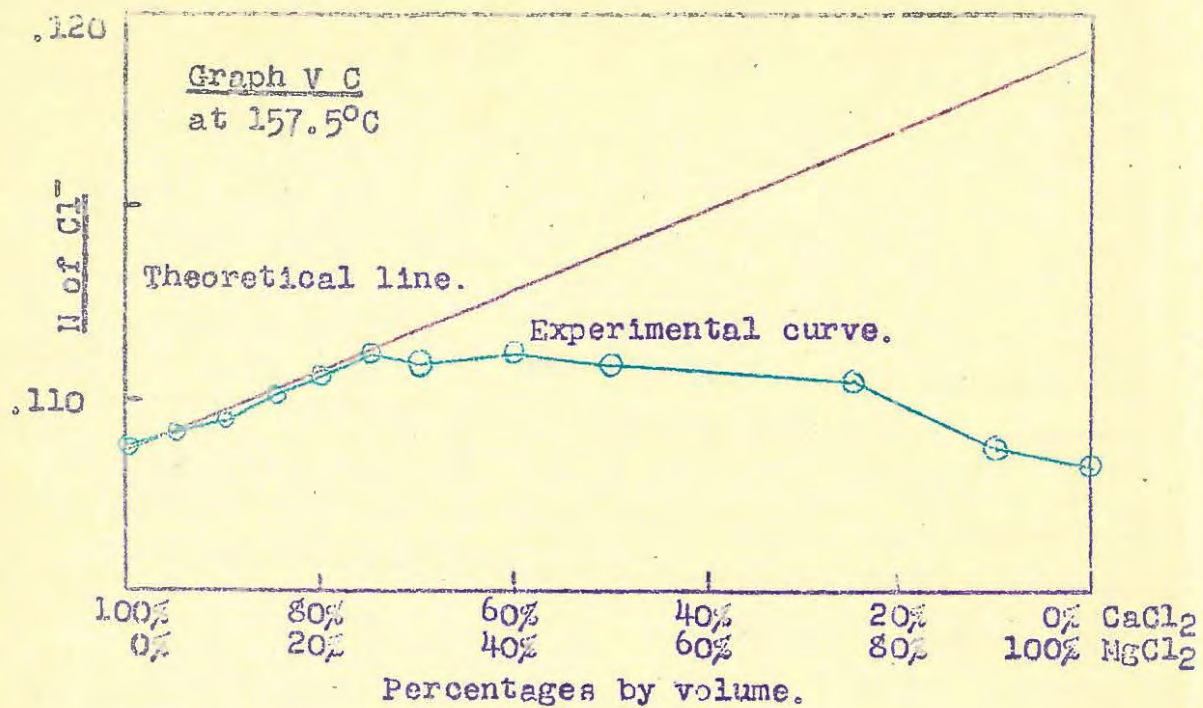
By employing standard calcium : magnesium chloride ratios he found that the hydrolysis of magnesium chloride was stopped completely when the Ca : Mg ratio was bigger than 4 to 1. He explained this by postulating a new calcium-magnesium double salt of the approximate formula $\text{Mg Cl}_2 \cdot 4\text{Ca Cl}_2 \cdot \text{XH}_2\text{O}$.

The author has found no such compound described in the literature and decided to investigate the matter more fully than Pienaar was able to do.

(A) An approximately 0.1 normal solution of calcium chloride was made up by dissolving precipitated calcium carbonate (AR) in a slight excess

The Hydrolysis of Magnesium Chloride in the
Presence of Calcium Chloride.





of hydrochloric acid. It was standardised using an oxalate-permanganate volumetric method (65). The normality was found to be 0.1086 N. of Ca :

(B) An approximately 0.1 normal solution of magnesium chloride was made up by dissolving magnesium metal turnings (AR) in a slight excess of pure hydrochloric acid. Its normality was found accurately by using a gravimetric and a volumetric acid-base phosphate method. The mean normality was found to be 0.1191 N. 0.4000 N with respect to Ca^{2+} ions,

was Varying proportions of A and B were measured out into standard flasks and diluted to known volumes. Aliquots of these solutions were evaporated to dryness in 250 ml. beakers on a water bath. They were then subjected to temperatures from 100°C to 200°C for an hour, in a well regulated oven, and then titrated against standard $1/20$ N silver nitrate solution.

(a) The normalities as indicated by the titrations, were plotted against the Ca Cl_2 : Mg Cl_2 volume ratios and compared with the theoretical line by adding 3 parts 0.4000 Ca Cl_2 to 1 part 0.4000 N Mg Cl_2 . obtained by plotting the original normalities of the calcium and magnesium

(b) 0.3200 N with respect to Ca^{2+} chloride solutions and joining them with a straight line. The results are shown in graphs V A, V B, V C and V D. at 0.4000 Mg Cl_2 .

Graph V A showed that at 98.5°C the experimental values agree very well with the theoretical line showing that no loss of HCl had occurred through hydrolysis. There was a slight bump in the experimental curve at about 75 % Ca Cl_2 . This might be due to adsorbed hydrochloric acid.

In graph V B, at 122.5°C , this bump still persisted between 75 % and 80 % Ca Cl_2 . The experimental curve dropped as hydrolysis became apparent. then heated at 200°C for 24 hours and titrated against $1/20$ N

silver. In graphs V C and V D at 158°C and 198°C respectively, the experimental curves and the theoretical lines agreed well up to 75 %

calcium chloride but after this the experimental curves dropped rapidly.

These results verified Pienaar's conclusion that at a ratio of Ca : Mg of 4 : 1 or 3 : 1 the hydrolysis of magnesium chloride was negligible. These results also proved the validity of this throughout the temperature range 98.5° C to 198.0° C.

A more extensive investigation was carried out on the Ca : Mg ratio.

A solution of Ca Cl₂, exactly 0.4000 N with respect to Ca²⁺ ions, was made up by dissolving calcium carbonate (AR) in a slight excess of hydrochloric acid. Also a solution of Mg Cl₂, exactly 0.4000 N with respect to Mg²⁺, was made up by dissolving pure magnesium turnings in a slight excess of hydrochloric acid.

From this, two solutions were prepared:

- (a) 0.3000 N with respect to Ca²⁺
0.1000 N with respect to Mg²⁺

by adding 3 parts 0.4000 Ca Cl₂ to 1 part 0.4000 N Mg Cl₂.

- (b) 0.3200 N with respect to Ca²⁺
0.0800 N with respect to Mg²⁺

by adding 4 parts 0.4000 N Ca Cl₂ to 1 part 0.4000 Mg Cl₂.

A check by volumetric analysis (Page 25) gave the following results:

- (a) 0.3006 N with respect to Ca²⁺
0.1001 N with respect to Mg²⁺
- (b) 0.3206 N with respect to Ca²⁺
0.0801 N with respect to Mg²⁺

Five, 5 ml. aliquots of (a) and (b) were buretted out with a microburette into 250 ml. beakers and evaporated in the oven at 100° C. They were then heated at 200° C for 24 hours and titrated against 1/20 N silver nitrate, to determine the amount of hydrolysis that had taken place.

The results follow:

TABLE IX.

	Ratio Ca : Mg	Normality by Weight	Normality by Analysis.	Sum X	Normality of Cl at 200° C. Y	Diff. X - Y
A	3 : 1	Ca 0.3000 N Mg 0.1000 N	0.3006 N 0.1001 N	0.4007 N	0.3972 N	0.0035 N
B	4 : 1	Ca 0.3200 N Mg 0.0800 N	0.3208 N 0.0801 N	0.4009 N	0.4006 N	0.0003 N

These results indicated that slight hydrolysis occurred in A as the difference in ($\text{Ca}^{2+} + \text{Mg}^{2+}$) and Cl normality is 0.0035 N, but hardly any hydrolysis occurred in B. Thus B was shown to be more stable than A and further investigations were restricted to the Ca : Mg ratio of 4 : 1.

Five, 10 ml. aliquots of B were buretted out with a microburette into tared weighing bottles with ground glass tops.

The aliquots were evaporated in an oven at 100° C until the residues were perfectly dry. They were then heated at various temperatures, ranging from 100° C to 200° C in the oven for 12 hours at a time, and weighed after each heating.

Great analytical care was taken to ensure that the bottles were well stoppered before cooling in a desiccator and that they were left unstoppered in the oven.

Table X shows the weight of the residues at various temperatures.

The weights of the residues became constant between 150° C and 160° C indicating that a stable compound was formed at that temperature. The weight of H_2O was found by subtracting the calculated weights of calcium chloride and magnesium chloride from the weights of the residues and hence the mols. of H_2O per mol. magnesium in the residues were determined.

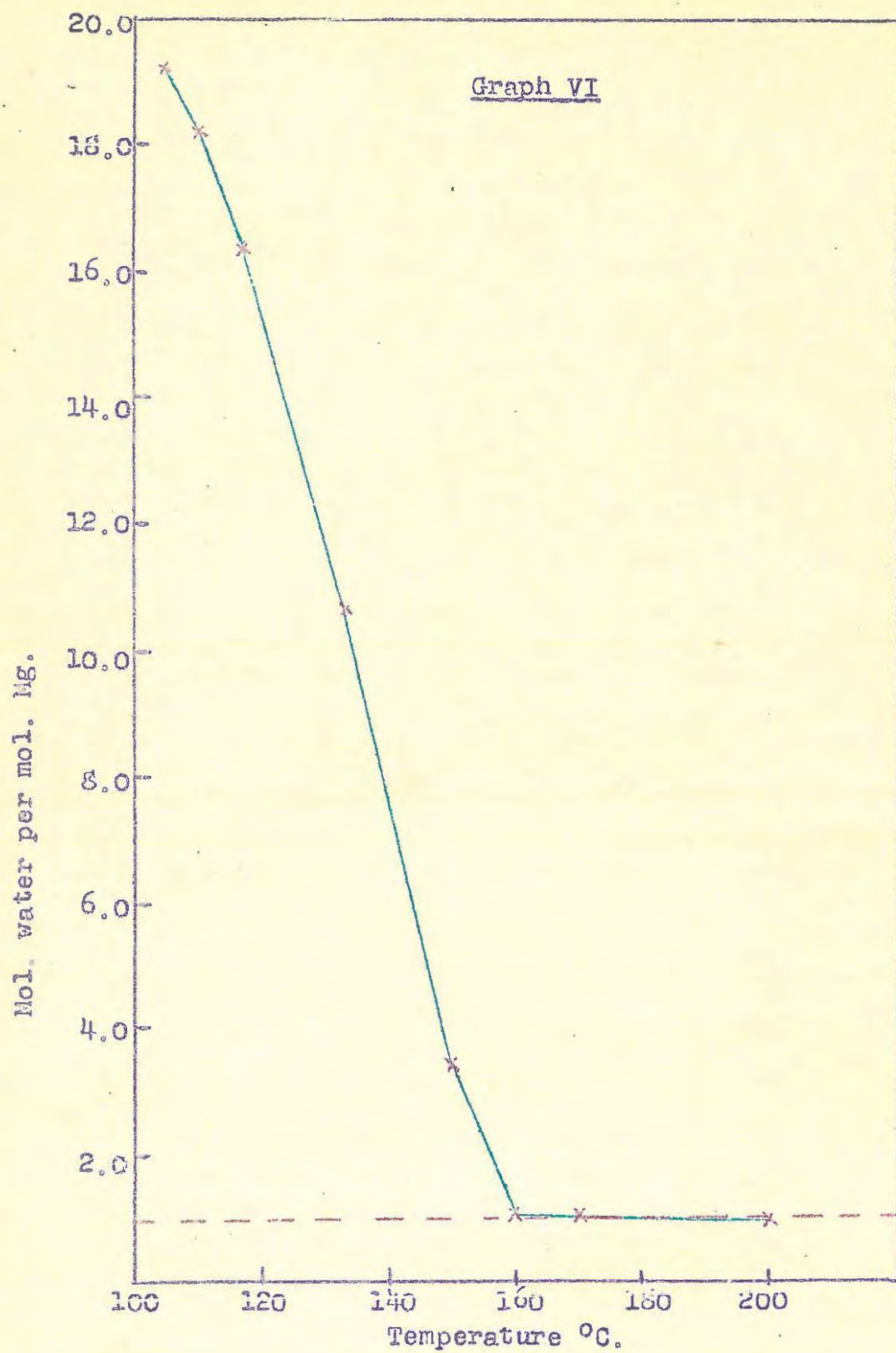


TABLE X.

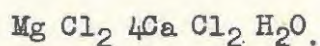
Temperature for 12 hours ° C.	A	B	C	D	E	X Mean	x- (MgCl ₂) (CaCl ₂) = H ₂ O	Mol. H ₂ O per Mol. Mg.
105	0.3580	0.3543	0.361	0.3507	0.3513	0.355	0.1388	19.27
110	0.3504	0.3453	0.3468	0.3413	0.3552	0.3473	0.1311	18.2
117	0.3404	0.3358	0.3344	0.3265	0.3324	0.3339	0.1177	16.35
133	0.3168	0.3042	0.2617	0.2884	0.2929	0.2928	0.0766	10.63
150	0.2602	0.2446	0.2287	0.2349	0.2368	0.2409	0.0247	3.43
160	0.224	0.2232	0.2234	0.2242	0.2239	0.2237	0.0075	1.04
170	0.2236	0.2233	0.2233	0.2239	0.2238	0.2235	0.0073	1.01
200	0.2236	0.2221	0.2222	0.2230	0.2230	0.2228	0.0066	0.92
Theoretical weight of Mg Cl ₂ + Ca Cl ₂ = 0.2162 grams.								

A graph was drawn of temperature versus mols. H₂O / Mol. magnesium (graph VI). It was seen that the residue lost water steadily until there was 1 mol. of water left per mol. magnesium at 160° C. This was not displaced by heating to 170° C and 200° C. The residue had a composition Mg Cl₂ 4Ca Cl₂ H₂O.

The presence of the one H₂O molecule per molecule magnesium was significant. It appeared that the presence of the 4Ca Cl₂ prevented the reaction;



from occurring probably by stabilising the H₂O. This was very strong evidence that a double salt was formed having the formula



Extensive work has been done on the system $\text{Ca Cl}_2 - \text{Mg Cl}_2 - \text{H}_2\text{O}$ at 0°C ., -15°C . and -30°C . by Lightfoot and Prutton (66) and at 110°C . by Assarson (67). ✓

Two double salts namely $2\text{Ca Cl}_2 \cdot \text{Mg Cl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ca Cl}_2 \cdot 2\text{Mg Cl}_2 \cdot 12\text{H}_2\text{O}$ have been described, the former existing only above a temperature of 93°C . No work has been done on the $\text{Ca Cl}_2 - \text{Mg Cl}_2 - \text{H}_2\text{O}$ system at temperatures of 150°C to 160°C and there was a strong possibility that a compound like $\text{Mg Cl}_2 \cdot 4\text{Ca Cl}_2 \cdot \text{H}_2\text{O}$ might be formed, following the trend. ✓

$2\text{Mg Cl}_2 \cdot \text{Ca Cl}_2 \cdot 12\text{H}_2\text{O}$ above 21.95°C .

$\text{Mg Cl}_2 \cdot 2\text{Ca Cl}_2 \cdot 6\text{H}_2\text{O}$ above 93°C .

$\text{Mg Cl}_2 \cdot 4\text{Ca Cl}_2 \cdot \text{H}_2\text{O}$ above 150°C .

SUMMARY.

A critical account was given of a rapid argentometric method for determining the total exchangeable cations in ammonium acetate leachates. The ammonium acetate leaching process has been tested on six different soil types. Fifty-six South African soil samples, representing twenty-two soil ~~types~~^{groups}, have been analysed for individual exchangeable cations, pH and total exchangeable cations. The values for total exchangeable cations in the soils examined were found to vary over the range 1.07 to 92.27 m.e./100 gms. soil.

The hydrolysis of magnesium chloride has been studied in the presence of calcium chloride and evidence has been found of the formation of a calcium-magnesium chloride double salt, above 150° C.

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