BASE EXCHANGE IN SOILS.

A study of the reproducibility of base exchange values for some South African soils, as indicated by leaching with normal ammonium acetate solution.

by

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BASE-EXCHANGE EQUILIBRIA IN SOILS.

Next to the lime requirement of a soil, no other characteristic is so widely used yet so little understood as its base-exchange capacity. Its importance in soil problems is well recognised and a large amount of work has been done on the subject.

The concept of base-exchange equilibria which is most generally accepted today, is that expressed in the following terms by Magistad, Fireman and Mabry (1):

> "It is believed that these reactions follow chemical laws and that definite equilibriums exist between the proportion of each cation on the exchange complex and the concentration of these cations in the soil solution."

Theoretical and experimental studies of base-exchange equilibria involving these concepts have been described by Gapon (2), Kerr (3), Magistad et al (1), Marshall & Gupta (4), Vanselow (5) and others.

Base-exchange equilibria, as ordinarily defined, are not identical with Donnan equilibria. When a system e.g. a soil, containing colloidal clay, two cationic species, and one or more anionic species is filtered, the filtrate may be a phase in Donnan equilibrium with the suspension residue phase. The two phases at the moment of filtration constitute an intact thermodynamic system and we may say, in a rigorous thermodynamic sense, that each of the ionic

/species

species in the filtrate phase is in equilibrium with the ionic species in the suspension-residue phase.

If the suspension-residue phase is now washed, the ions remaining may be said to be on the colloid, but the washed material and the original filtrate must now be regarded as separate systems. They are no longer phases of an intact thermodynamic system and cannot be said to be in equilibrium. The relationship between the ions left on the colloid after washing, and those left in the original filtrate, is frequently spoken of as a base-exchange equilibrium, though it seems clear that it cannot represent a true equilibrium.

On the other hand, the number of cations of each species left in the suspension residue before it is washed may be arbitrarily divided into those which are on the colloid and those which are not. The relationship between those which are on the colloid and those which are in the filtrate or suspension phase, is also usually considered as a base-exchange equilibrium. Inasmuch as no completely defined reaction has actually occurred, and since many of the ions cannot be described as being either on the clay or not on the clay, since they may be present as continuous ion swarms surrounding the particles, it would seem that this concept of base-exchange equilibrium is not entirely clear.

When a solution of sodium chloride is mixed with, a suspension of a potassium clay, there will occur a re-distribution of the K^+ and Na^+ concentrations as functions of the distance from the particles. No real "base-exchange" can, however, be regarded as having taken place until filtration has occurred and there has been separation of the suspension liquid from the clay residue. After separation it can be said that base exchange has occurred and that it is the result of the equilibration of the two phase system. Equations of the mass-action type which have been derived by various workers purporting to give the relation between the ions on the colloid and those not on the colloid must, therefore, be regarded as being arbitrary in nature rather than expressions of definite chemical laws.

In addition to the theoretical importance of studies of base-exchange equilibria, their agricultural importance may be emphasized. The application of the principles involved should however be carefully considered. When potassium and calcium are added to a soil in the form of fertilizers or soil amendments, they tend to replace preferentially sodium and magnesium and also to replace hydrogen more readily than do sodium or magnesium. The availability of these ions is probably not greatly affected, particularly in view of the concept of contact exchange feeding of plants as developed by Jenny and Overstreet (6). On the other hand, these effects may become very important when moderate leaching by rain or careful irrigation removes the excess electrolyte in the soil solution without markedly affecting the exchange complex, as is the case in the moderately arid regions of our country. Again, in more humid regions or where excessive irrigation with fresh mountain water under good drainage conditions is practised, the equilibria may be progressively shifted so that the marked tendency of hydrogen-ion to replace other cations may become the factor of predominating importance.

Relation of Crystal Structure to Base Exchange.

The colloidal fraction of the soil contains a high percentage of the total exchangeable bases of the whole soil, but a considerable part of the magnesium of the colloidal fraction is not replaceable in the ordinary sense of the term, and the same is true in some cases, at least, for calcium, potassium and sodium. It was shown by Hendricks and Fry (7) and by Kelley, Dore, and Brown (8) that soil colloids are composed, in considerable part at least, of crystalline material, and that the base-exchange capacity of soil colloids can be increased merely by reducing the natural size of the individual particles that compose this colloidal fraction. It has long been known that the natural zeolites have pronounced base-exchange properties, In addition Lemberg (9) showed more than half a century ago that analcite can be converted into leucite, and vice versa, through a base exchange process; Sullivan (10) and others have shown that a wide variety of the primary minerals may undergo base exchange to a limited extent upon treatment with salt solutions. Despite these and other investigations, however, it is generally held that both the constituents of soils and of pure minerals may be subdivided into two fairly sharply defined classes; namely, those whose bases are replaceable and those whose bases are non-replaceable.

Kelley and Jenny (11) found that the base-exchange capacities of several minerals falling within each of

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these classes tend to approach each other upon grinding to a sufficient degree of fineness. For example, the exchange capacity of both orthoclase and muscovite can be raised to a comparatively high level (from 76 to 91·5 or more m.e. per 100 gms) merely by grinding the sample to extreme fineness. What is still more surprising, the same is true of kaolinite and pyrophyllite. On the other hand, substances like quartz, colloidal silica, precipitated alumina, ferric hydroxide, bauxite and talc, have only low base-exchange power as determined by the ammonium acetate method, even though finely ground.

According to modern concepts of crystal structure, (Bragg, Goldschmidt, Pauling) each silicon ion in the silicates is surrounded by four closely packed oxygen ions arranged in the form of a tetrahedran. The relative sizes of oxygen and silicon ions (Si=0.8 Å, O=2.7 Å) make possible a very close packing of four oxygen ions around each silicon ion. In quartz each oxygen ion is a part of adjacent tetrahedra, which are so arranged that the negative charges of the oxygen ions are just balanced by the positive charges of the silicon ions. Consequently, quartz is electrically neutral, except on the surface, and contains no bases in the ordinary sense. In other silicates, such as the amphiboles, some of the oxygen ions lie between two silicon ions and some are attached to silicon ions on one side only. Such minerals always contain enough positive ions to balance the remaining charges of the oxygen ions. In certain of the

/alumina-silicates, such as the feldspars and zeolites, the aluminium ions (1.1Å) are also present in tetrahedra, being surrounded by four closely packed oxygen ions. Since the aluminium ion bears only three positive charges, these minerals must contain additional cations (bases) sufficient to balance the excess negative charge of the aluminium tetrahedra. Potassium performs this function in orthoclase, biotite and muscovite; sodium plays a similar role in albite, analcite and natrolite; and calcium in anorthite and scolecite. From the foregoing it follows that the base-exchange power of crystalline minerals may be explained on the basis, first, of accessibility and, second, of the strength of the attractive force by which the bases are held to the lattice. More precisely, it may be said, that only those metallic cations which perform the function of balancing the excess negative charges of the tetrahedral groups are reversibly replaceable by ammonium. With the platy minerals of the mica group~~s~~, these metallic cations occur on the surface of the cleavage planes; in the zeolites and feldspors they occur on the surface of internal cavities. These cavities are large enough in the zeolites to permit access to the ions of a solution, whereas with the feldspars the structure is more compact; the bases are similarly situated in the lattice of both types of minerals.

Mattson and Csiky (12) in a paper on cation exchange-maximum in alumina-silicates made the following interesting observations; that in the presence of aluminium and ferric

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hydroxides and also in the presence of magnesium, the cation exchange capacity of silica gel is substantially increased and that less of the stronger base aluminium hydroxide than of the weaker base ferric hydroxide is required to attain a maximum exchange; however, beyond this maximum, that is, in higher proportions of the bases, the stronger base suppresses the exchange power of the silicic acid more than the weaker base. It therefore appears that silicic acid is activated when in partial combination with a base, but that its activity or exchange capacity is again suppressed when the combination with the nondisplaceable cations of the base is more complete. The maximum in the cation exchange-capacity of alumine-silicates has been found to be at a molar ratio of about 9 mols SiO_2 to 1 mol Al_2O_3, as compared with the corresponding ratio (4.2:1) of ferric silicates.

The Determination of Exchangeable Bases.

In the study of base exchange values for a given soil, it is usual to determine the individual exchangeable bases - calcium, magnesium, sodium, potassium, as these figures give a fairly good index as to a soil's fertility. The exchangeable hydrogen is also of importance and this value, together with the total exchangeable bases, each being expressed in mgm. equivalents per 100 gms. soil, gives the base exchange capacity of the soil. The exchangeable hydrogen can thus be found by difference and the percentage base saturation can be calculated from any two of the above quantities. Although this generalization was arrived at theoretically, it has been substantiated experimentally by Parker (13) and others.

As base exchange is a reversible reaction, complete replacement can only be effected if the replaced ions are removed from the sphere of action. Equilibrium between the soil and the displacing solution is very rapidly established, even in the cold. It should be noted that both the clay and humic fractions of a soil contribute to its exchange capacity. Weight for weight, the organic exchange complex possesses an exchange capacity which may be several times that of the inorganic fraction.

The exchangeable bases are removed from the base exchange complex either by electrodialysis, which will be discussed later, or by leaching the soil with a suitable salt solution or with a dilute acid.

Prianishnikov (14) appears to have been the first to determine the exchangeable bases in soils by a leaching process and he used ammonium acetate. His work, however, was overlooked until Schallenberger (15) published a paper on the use of this reagent.

Kelley and Brown (16) leached soils with solutions of ammonium chloride and hydrochloric acid of different concentrations and showed that nearly the same quantities of calcium, magnesium, potassium, and sodium, were replaced from the same soil by $^{N}/_{25}$ HCl and by N. ammonium chloride solutions. Dilute hydrochloric acid was also used in one of the original methods of Gedroiz (17) but its use is not always permissible since in some soils significant amounts of the exchange complex itself may be destroyed. Neither can it be used conveniently for soils containing large quantities of calcium carbonate.

To reduce the attack on the exchange complex, Williams (18) introduced the use of a weakly dissociated acid instead of hydrochloric acid and he leached soils with 0.5 N acetic acid to replace the exchangeable ions. However, many soils have been encountered in which very incomplete replacement of the exchangeable ions has been obtained with this reagent, even when considerably larger volumes of leachate have been collected. Its use can only be recommended for sandy soils low in adsorbed metal ions.

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A quite remarkable fact which was noticed amongst the work of these early investigators was the close agreement between the quantities of the exchangeable bases extracted by electrodialysis and by leaching the soil with N ammonium chloride, N ammonium acetate and $^N/_2$ acetic acid solutions. This showed that the same constituents were probably removed from the exchange complex by these different methods. The determination of the exchangeable cations in soils of the humid regions, devoid of salts and calcium carbonate is straightforward. In soils containing calcium carbonate, however, the determination of exchangeable calcium becomes a very difficult problem. Ammonium chloride dissolves appreciable amounts of calcium carbonate so that the Calcium in the leachate will represent the exchangeable Calcium as well as some calcium derived from the carbonate dissolved. In Gedroiz's method for soils containing calcium carbonate, the amount of carbonate in the soil is determined before and after extraction and the amount of calcium found is corrected by an amount equivalent to the carbonate dissolved. It is assumed that the latter consisted entirely of calcium carbonate. Such a method, based on difference determinations, is not capable of great accuracy in the presence of much calcium carbonate, since the errors of all the determinations fall upon the value for exchange-

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-able calcium.

In Hissink's (19) method for the determination of the exchangeable cations in calcareous soils, magnesium sodium and potassium are determined in the ammonium chloride extract in the usual manner. Another portion of the soil is leached with normal sodium chloride, in which calcium carbonate is much less soluble, and two separate litres of leachate are collected. The whole of the exchangeable calcium is replaced, and contained in the first litre, together with calcium derived from the solution of calcium carbonate. The calcium in the second litre is derived from the solution of calcium carbonate only, and it is assumed to be equal in amount to that dissolved during the preparation of the first litre of leachate. The difference between the amounts of calcium contained in the first and second litres thus represents the amount of exchangeable calcium.

Tiurin (20) pointed out that the carbon dioxide dissolved in the sodium chloride solution combines with the calcium carbonate in the soil forming calcium bicarbonate. He leached 10 gms. of soil with successive portions of 500 ml of N sodium chloride solution, and determined the carbonate and bicarbonate in each portion of the leachate by titration with $^N/_{50}$ hydrochloric acid, using methyl orange as indicator. Calcium and magnesium were also determined in each portion, and when

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the sum of the calcium and magnesium no longer exceeded the carbonate and bicarbonate content of the leachate, the replacement of the calcium and magnesium was considered to be complete.

For the determination of calcium and magnesium in soils containing carbonates, alcoholic potassium chloride and aqueous and alcoholic barium chloride have been suggested at different times, since calcium carbonate is less soluble in these reagents than in sodium chloride. However, the values obtained are no better than those given by the sodium chloride method and, in the case of barium chloride, analytical difficulties, in the complete separation of barium from calcium, are introduced.

In Williams' method, carbonates and total calcium are determined in the same portion of soil, the former by liberation in vacuo of carbon dioxide by acetic acid, and the latter by continued leaching of the soil with more acetic acid. The difference between the total amount of calcium found and the amount equivalent to the carbonates present corresponds to the exchangeable calcium. It is assumed that no magnesium carbonate is present. The method is suitable for soils with small amounts of carbonates, but in highly calcareous soils the proportion of carbonate calcium to exchangeable calcium is such that the experimental errors of the determination would reduce the accuracy of the results. Moreover, as previously

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mentioned, extraction with acetic acid does not always remove the whole of the exchangeable cations in heavy clay soils.

Kelley (21) considers the accurate determination of exchangeable calcium and magnesium in alkali soils to be impossible by any known method, on account of the presence of carbonates and silicate of calcium and magnesium in such soils. He determines the sum of exchangeable potassium and sodium by usual methods, and the total exchangeable metal ions, by an ammonia absorption method and regards the difference in these two values as exchangeable calcium and magnesium. No attempt is made to separate calcium from magnesium. Bray and Willhite (22) describe the following method of determining the total exchangeable bases : 10 gms of air-dry soil are leached with 500 ml of neutral N. ammonium acetate solution. The filtrate is evaporated to dryness in a 600 ml Pyrex beaker on a steam-bath. The residue is gently heated on a silica plate over a Bunsen burner for a few minutes, and then at a full red heat for 20 minutes. After cooling, an excess of standard acid is added, the solution is warmed and the bottom of the beaker is rubbed with a glass rod tipped with rubber. The back titration is made with standard alkali, using methyl red as indicator. This method depends on the conversion of the acetates of the metallic ions to carbonates by ignition. It is still a standard method for the rapid determination of total exchangeable bases and more will be said of it in this connection further on.

Another method due to Parker (13) is described as follows : 5 or 10 gms of soil are placed in a Gooch crucible and leached with 250 ml of neutral N. barium chloride solution. The leachings are titrated with $^{N}/10$ Barium hydroxide solution to determine the amount of hydrogen replaced by barium, phenolphthalein being used as indicator. The soil is then leached with N. ammonium chloride solution until the leachings give no test for barium, and barium is then determined in the ammonium chloride leachings as barium sulphate. Expressed in mgm. equivalents, the amount of barium absorbed minus the hydrogen replaced gives the exchangeable base content of the original soil. As no reference to this method has been found in any of the later publications on this subject, it apparently has fallen into disuse.

A new method of extracting the exchangeable bases was tried by Di Gléria (23), namely by boiling with ammonium chloride. He showed that boiling ammonium chloride caused a stoichiometrical decomposition of precipitated carbonates, and he proposed the use of this treatment to eliminate soil carbonates in base-exchange studies and suggested that the ammonia found in 200 ml of the distillates from boiling ammonium chloride suspensions be used to compute the proportion of carbonates. Di Gléria concluded that absorbed bases cause no appreciable

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liberation of ammonia from the boiling ammonium chloride solution. His proposal for the determination of soil carbonates was therefore based on the premise that the ammonia evolved is due solely to the reaction indicated by the equation :

$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + (NH_4)_2 CO_3$.

Because of the possible adaption of this principle to certain absorption and base-exchange investigations, Shaw and MacIntire (24) studied the solvent action of boiling ammonium chloride upon unusual carbonate and absorbed residues from different calcic and magnesic additions to certain soils, especially to several of known lysimetric history. They found that ammonia-liberations from soil suspensions in boiling neutral ammonium chloride were caused, not only by carbonates, but also by absorbed bases, which Di Gléria had concluded were not affected by the ammonium chloride treatment. The ammonia-liberations were found to approximate closely the joint values for the carbonates decomposed and for the absorbed bases replaced. Puri and Uppal (25) reviewed a number of methods of finding base-exchange capacity of soils and showed that different methods refer to different points on the titration curves of soils and, as such, are arbitrary and empirical. They conclude by saying that the only satisfactory method of defining the base-exchange properties of soils is through their titration curves, the determination of which is just as easy as is the finding of base-exchange capacity by any of the better known methods.

Tedrow and Gillam (26) published a paper on the base-exchange capacity of the organic and inorganic fractions of several soils.. For the different horizons a variation of from 17 - 86% of the total base-exchange capacity could be attributed to the organic fraction of the soil. In surface soils, the organic content contributes roughly 50% on the average, to the total exchange capacity. They also found the coefficient of correlation between the organic exchange capacity and the percentage organic matter was +.90.

Cantino (27) proposed a semi-micromethod for exchange capacity which is a modification of the method of Kelley and Chapman (28). One-gram aliquots of soil, rather than 25-50 gms are used. The prolonged leaching process which involved the use of ammonium acetate is replaced with a series of short digestion periods, using a soil-ammonium acetate mixture, followed by centrifuging the soil suspension. After removal of the excess ammonium acetate with methyl alcohol, the total ammonia fixed by the soil is liberated by a semimicro Kjeldahl distillation, and the ammonia is determined quantitatively with Nessler's reagent. Comparisons with results obtained by a standard macromethod show quite a reasonable degree of accuracy was obtained as well as a saving of time.

/Electrodialysis

Electrodialysis has been used to remove the exchangeable cations from soils and this method would appear to offer many advantages, since the ions are obtained free from the large amounts of neutral salt or acid used in their replacement by other methods. However, errors arising due to the presence of soluble salts and also the difficulty in securing complete removal of the magnesium ion in many soils, make this method unsuited for quantitative work. Shirley (29) worked on this subject and he apparently disagrees with previous workers as regards the incomplete removal of magnesium, but it must be remembered that he unfortunately only worked on one type of soil, in which the magnesium was probably easily replaceable.

Ammonium Acetate Leaching.

The various procedures adopted for determining exchange capacity and exchangeable cations, in general, lead to very similar values for the quantities of cations exchanged and usually rank the exchangeable cations in similar orders of importance. However, as with determinations of most other "available" constituents, the determination of exchange capacity and of cations exchanged between a soil and a salt solution is not very exact in the quantitative sense. The probable cause is the slowness in the attainment of equilibrium between the coarser soil grains and mineral particles and the liquid with which they are in contact together with the indefinite nature of that equilibrium. This arises from the possibility of interactions between the colloidal constituents in the humus-silica-sesquioride-base-acid-salt solution system. Fortunately, rough indications are generally sufficient for practical purposes, and the author has therefore attached a greater importance to convenience in the analytical operations than to absolute accuracy and has attempted to establish the degree of reproducibility of the results yielded by this method of leaching.

Shirley (29) used the following solutions for leaching: 0·5N acetic acid, N.Ammonium chloride, N. Ammonium acetate, 0·5N Ammonium carbonate, and 0·1N oxalic acid in N.ammonium acetate. He found that ammonium acetate gave the most

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reliable and consistent results for exchangeable bases as well as being most suitable for rapid analysis by means of Bray & Willhites method (22). He also found that N. ammonium acetate possesses a negligible decomposition effect on the soil particles.

Golden, Gammon and Thomas (30) determined the exchangeable bases and total exchange capacity on 10 widely different soils using various reagents for extraction purposes : N. Ammonium Acetate, N. ammonium formate, N. ammonium chloride, N. Barium acetate, N. barium formate, N. barium, N. Manganous acetate, N. Manganous chloride, N.potassium acetate potassium chloride. Boiling N.ammonium chloride, N/2 acetic acid, N/20 hydrochloric acid and N/5 cupric acetate were also used. They found that solutions of the ammonium salts of organic acids displaced at ordinary temperatures more cations than any of the other salt solutions. The Barium salts were absorbed in large quantities by the exchange complex but when absorbed did not displace equivalent amounts of other cations. The potassium ion was highly absorbed by the exchange complex. The manganous and cupric acetate solutions gave good and consistent values for the total exchange capacity and were found to be rapid in use. The chloride anion regardless of the cation by which it was accompanied, led to low displacement and absorption values. The acetate anion gave the highest and most consistent

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results, both for exchangeable bases and the total exchange capacity. It seemed as though ammonium acetate solution was the best for displacement while potassium or barium acetate solutions were superior for estimating the total exchange capacity.

In addition to the findings of these workers, a number of the theoretical and practical points in favour of the use of ammonium acetate should be mentioned, all of which go to prove that this reagent can hardly be bettered for the purpose in view. It is a neutral salt and its solutions have pronounced buffer properties around pH7, as is well known from the fact that the dissociation constants of both acid and base are small and practically equal in magnitude - about $1{\cdot}8 \times 10^{-5}$ at 25°C. Theoretically this is a very important point because it means that any hydrogen displaced by the exchange reaction, with the salt from the unsaturated absorption complex in the case of acid soils, will be but slightly ionized and hence comparatively inactive in giving rise to complicating reactions. Because the H^+ concentration of the solution is not increased to any considerable extent by the accumulated product of the exchange reaction, replacement of NH_4^+ from the solution for H^+ in the absorption complex of the soil can proceed to a maximum.

Ammonium is never naturally a major soil base, but can function as such under laboratory conditions, and it

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is easily

determined. The acetates of all soil bases are readily soluble. Moreover, the salt has the outstanding analytical advantage of being almost completely volatile at a comparatively low temperature. Every trace can be removed either by gentle ignition or by treatment with suitable reagents. A solution of the highest purity can easily be prepared from inexpensive chemicals of reagent grade. Ammonium acetate in solution has, to some degree, an effect upon the surface tension of water which is similar to that shown by the alkali metal salts of the fatty acids. It has wetting and penetrative powers which are superior to those of solutions of, say, barium chloride. This aids in the removal of exchanged cations by leaching.

Leaching seems to be the logical method of procedure, for it subjects the soil to the continuous action of fresh reagent; an efficient leaching process should result in the complete removal of exchangeable bases and in equilibration in a minimum of time and by the use of a minimum volume of solution. At a sufficiently high concentration the author has not found any troublesome tendency for aqueous ammonium acetate at pH7 to disperse clay soils; the leaching process is not noticeably slower than is the case when using a dilute acid or other salt solution. About the only defects in its application to base-exchange determinations on soils are (i) the difficulty in titrating an excess of acid or base in a large volume of the strongly saline solution, and (ii) its

/solvent

solvent effect upon calcareous material, which is greater than that of, say, barium chloride.

It was with these considerations in mind that the decision was made to limit the investigation to the determination of the reproducibility of the results obtained by the use of a normal solution of ammonium acetate alone for leaching samples of characteristic South African soils.

EXPERIMENTAL WORK.

Soil Types used in Investigation.

C. R. van der Merwe (31) compiled a soil map and thesis titled "Soil Groups and Sub-groups of South Africa" in which he classified our soils on modern pedalogical lines. The author attempted to obtain samples from all characteristic soil regions in the Union, as indicated by van der Merwe's map, and in this way to supplement van der Merwe's data on base exchange, as this was rather limited. Unfortunately this was not altogether practicable, as answers to requests for soil samples from some sources have not even by this time been received. The investigation has, therefore, had to be restricted to those regions from which samples could be obtained in sufficient time. They are as follows :-

1) Desert Soil taken near Venterstad in the Cape. Red brown sandy loam.
2) Solonetzic soil sample taken near Queenstown. Brown sandy loam, fairly dense, rather porous homogeneous mass which breaks up into clods, lumps and finer material on slight pressure.
3) Gley-like Podsolic soil of the High Veld Prairie type taken near Bethal. Brownish black clay.
4) Podsolic soil of the Eastern Province Semi-coastal belt type taken near East London - Bluish-grey sandy loam, crumbly.
5) Lateritic Yellow Earths - sample taken near Cedara. Light brown clay-much humus.

6) Brown to Reddish Brown Ferruginous Lateritic Soil type taken near Estcourt. Brown clay, breaking into clods, very hard.

7) Aeolian Sandy Soil type taken near Glen (O.F.S.). Reddish brown loamy sand, crumbly.

8) Grey Sandy Soil taken near Humansdorp (Witte Els Bosch) - crumbly grey sandy loam.

9) Gravelly Sandy Clay Loam on clay taken near Stellenbosch. Yellow porous clay.

10) Reddish Brown Sandy Loam on Lime and Sandy Loams taken near Port Alfred. Greyish brown fine sandy loam.

11) Sandy loam on Lime and Clays - taken near Uitenhage. Brownish clay, much humus, with granular structure when dry.

Preparation of samples.

The soil samples were taken so as to fulfil the requirement of being so far as possible uniform samples of soil types rather than representative of a definite piece of land. The samples were spread out on trays, the bigger lumps and clods being broken up without grinding. They were air-dried for three days. The soil was then sifted through a sieve with holes 2 mm. in diameter. The coarser material was again crushed and sieved until only primary particles and organic residues remained on the sieve. These were discarded. The 2 mm. samples of air-dried fine soil were kept in clean stoppered

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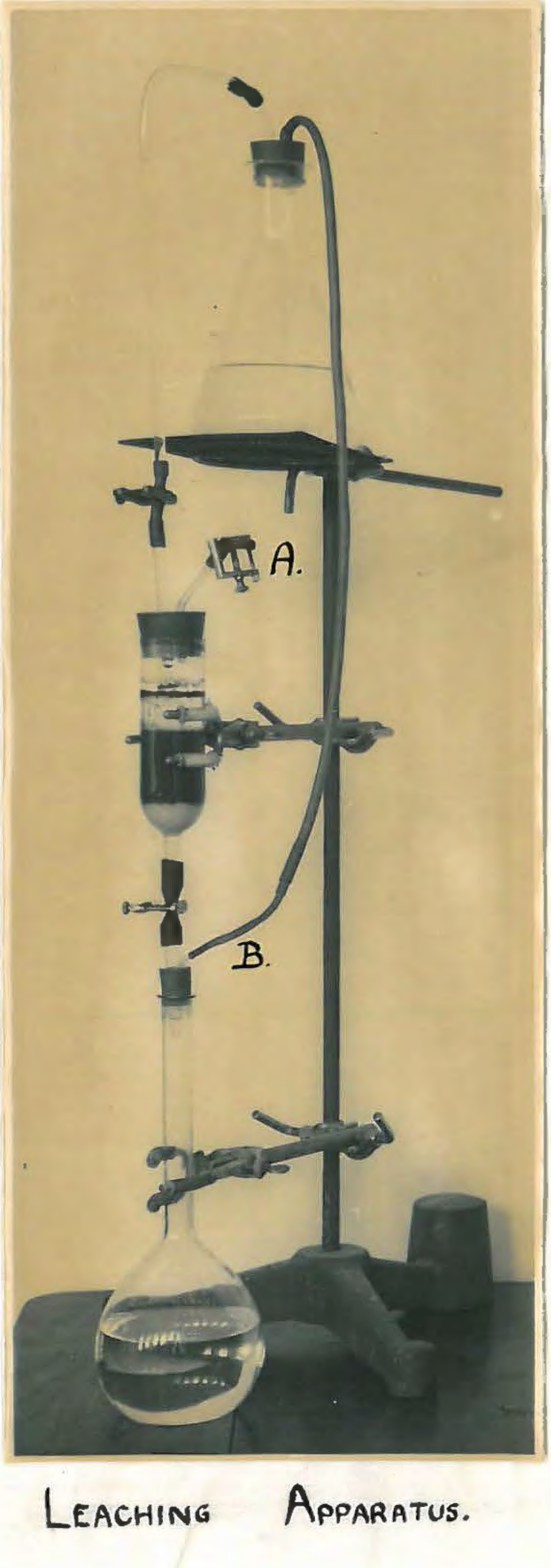

LEACHING APPARATUS.

bottles.

Ammonium Acetate solution.

The normal ammonium acetate solution was made up according to the method of Schollenberger and Dreibelbis (31): Bulk solutions of ammonia and acetic acid of approximately 2N strength were made up, their exact strengths determined by titration and equivalent amounts of each solution mixed to give exactly N ammonium acetate solution. The pH was adjusted to exactly 7·00, a glass electrode being used for the pH determinations.

Leaching Apparatus.

The dimensions of the filter tube of conventional form are 40 mm. diameter, 150 mm. height of body and stem 50 mm. long. The tube easily holds 100 gms. of an average mineral soil, air-dried and sifted to pass 2 mm. The apparatus as shown in accompanying plate consists of a 1-litre Erlenmeyer flask with the reservoir of ammonium acetate, the filter tube and a 1000 ml. standard flask for collecting the leachate. All connections are made by glass and rubber tubing, bent as shown, to form a closed system. Both leaching solution and leachate are thereby protected thus minimising the possibility of change in pH arising from loss of ammonia or absorption of carbon dioxide. The author used a standard flask to collect the leachate, as suitable aliquots, for carrying out the various determinations, could easily be taken from this solution. It also ensured that reproducible conditions would exist

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throughout since exactly 1000 ml. of solution were allowed to pass through the soil in the filter tube during each leaching.

Leaching.

A small pledget of cotton wool is stuffed loosely into the stem of the leaching tube to form a flat pad which serves as a filter in preventing the accidental passage of soil grains into the leachate, and which has no tendency to cause the filter tube to crack. Some water is allowed to run through and then some ammonium acetate solution, to make sure that the percolation rate will not be slowed by the cotton wool being too tightly compacted. Draw the excess solution through and rearrange the pad, if necessary. Now pour the sample (the author used 100 gm. portions for greater accuracy since the values of total exchangeable bases were small) into the filter tube together with about 75 ml. of ammonium acetate solution, sufficient to cover the whole sample. To prevent shrinkage on wetting and the caking of a clay soil, it is best to close the screw clamp C at the bottom of the filter tube stem (which regulates the rate of flow) and first to pour the ammonium acetate solution into the tube, the soil being then added; in this manner one finds no difficulty in regulating the rate of flow which will remain constant for a considerable period of time so that the leaching will require very little

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further attention. Assemble the apparatus as shown in the plate. Open the clamp at A and separate the air return tube at B. Blow gently through the rubber tube to start the siphon. As soon as the solution is well over the surface of the soil in the filter tube, close A and reconnect B. The time for leaching should be not less than 4 hours, but no longer than overnight, if the nature of the soil permits. Here again, the author adopted a standard time of four hours except in the case of the Stellenbosch soil sample which would not leach satisfactorily in less than 14 hours.

Method of Analysis.

Collect exactly 1000 ml. of leachate (solution A).

Calcium

Take a 200 ml. aliquot from solution A and evaporate to dryness in a 400 ml pyrex beaker on a waterbath. This is conveniently done overnight. When dry, heat on a silica plate with a Bunsen burner, slowly at first, and gradually increase the flame to its maximum, heating with full flame for about fifteen minutes so that all organic matter is oxidised. The residue should be completely white after this treatment.

Dissolve the residue in 5 ml. 6N hydrochloric acid and add distilled water to bring the volume to approximately 100 ml. Heat to boiling on the hotplate and add 5-10 ml.

/of a solution

of a solution containing 10% each of oxalic and acetic a acids, and with sufficient bromcresol green indicator to produce a distinctly yellow tint. Now add dropwise a solution of ammonium hydroxide (6N) 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 or Schleicher and Schüll No. 589[2] paper, washing the ppt. with hot very dilute ammonia solution, and adding the first few washings to the filtrate containing magnesium. If little or no calcium oxalate was precipitated at once, digest the mixture for several hours, with occasional additon of a drop of ammonia if necessary, to separate the small amount of calcium (according to Chapman (33)).

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 a titration flask. Titrate this solution at 55-60°C with $N/_{50}$ standard potassium permanganate to a faint rose tint that does not fade after stirring thoroughly for a few seconds. Do a blank determination on 200 ml. of the N. ammonium acetate leaching solution. One millilitre N. permanganate corresponds to 1 mgm. equivalent of Calcium, i.e. to 0.02004 gms. in the aliquot taken.

/Magnesium.

Magnesium.

To the cooled filtrate and first washings from the calcium oxalate precipitate combined, add 0.5 - 1.0 gms. hydrated diammonium hydrogen phosphate in solution, followed by strong ammonia solution dropwise and with constant and vigorous stirring. Rub the inner walls of the beaker and strike them with the stirring rod to encourage the crystallization and adherence to the glass of the precipitated $Mg(NH_4)PO_4.6H_2O$.

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, or for not less than four hours. Filter on a Whatman No. 42 or S&S.599[3] filter paper and wash well with cold water containing $1/_{10}$th of its volume of strong ammonia solution; wash finally with alcohol to expedite the drying of the filter paper. The paper with 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 to a flask by piercing the bottom of the filter and washing with hot water. Add a drop or two of a methyl red-methylene blue mixed indicator and an excess of standard decinormal hydrochloric acid. Titrate back with standard decinormal 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 0.01216 gms) of magnesium in the aliquot taken.

(The mixed indicator is prepared by dissolving 0.125 gms methyl red and 0.083 gms. methylene blue in 100 ml. absolute alcohol. This indicator is green in alkali and violet blue in acid, the end-point corresponding to a steel-grey colour.)

POTASSIUM.

Reagents :

Sodium Cobaltinitrite : Prepare an aqueous solution, containing 1.0 gms. 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 1 litre. Before use, remove any trace of free iodine with a drop or two of

/thiosulphate

thiosulphate.

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 $N/_{50}$ potassium permanganate.

Starch (0.1%) Freshly prepared for each set of determinations.

Asbestos. Place a suitable quantity of gooch asbestos in a large porcelain basin. Add a few permanganate crystals and enough 20% sulphuric acid to cover the whole mass. Digest on a boiling 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 till 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/50) Dissolve 3.25 gms. $Na_2S_2O_3.5H_2O$ (A.R. grade) in water and make to 5 litres. Add 1 ml. chloroform which keeps the solution stable. Standardise and check the normality every fortnight.

Potassium Permanganate (N/50) Dilute to a normal solution of potassium permanganate to N/50. Standardise and check at regular intervals.

Analytical Procedure.

Evaporate a suitable aliquot (200 ml.) of solution A to dryness on the waterbath. When completely dry ignite on a silica plate with full Bunsen flame to remove

/all

all the organic matter. When the residue is completely white, add 1 ml. of 6N. hydrochloric acid, and rinse down the sides of the containing vessel with distilled water from a wash-bottle. This is to convert the salts to chlorides since these are very soluble in water. Again evaporate to complete dryness. This residue is now taken up in 10 ml. water and heated to incipient boiling on a hotplate. 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 150 ml. beaker. Evaporate the filtrate to 10 ml. and add 1 ml. N. nitric acid and mix well. Bring the contents of the beaker to ± 20°C, add 5 ml. sodium ~~cobaltinitrite reagent also at 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 nitric 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 solution,allowing the washings to drip into the beaker. (Leave the glass-rod in the beaker.) Immediately bring the contents of the beaker to the boil on a hotplate so as to dissolve the precipitate as quickly as possible, preventing any cobalt hydrate from forming. Dilute the resultant green solution

/to

to 50 ml. with water and cool.

Add a slight excess of N/50 Potassium permanganate (±15 ml. for 2.5 mg. K_2O) from a burette and slowly,10 ml. 50% sulphuric acid. (Be careful to avoid excessive frothing). Leave for about twenty minutes, heat to 40^oC, add 5 ml. 10% potassium iodide solution and immediately titrate the liberated iodine with N/50 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. (This method was developed by Steyn (34)).

Potassium = (.1818 x ml.$KMnO_4$xNormality of $KMnO_4$)M.e.

Sodium.(Ref. Barber & Kolthoff (35) & Kolthoff & Lingane(36))

Reagents

1) A. Uranyl acetate ($2H_2O$)...10 gms.
   Acetic acid, 30%....... 6 gms.
   Water to make..........65 gms.
   B. Zinc acetate ($2H_2O$).....30 gms.
   Acetic acid, 30%....... 3 gms.
   Water to make..........65 gms.

After the salts in 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

chemicals which go to make up the reagent. When 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 - Another aliquot (200 ml.) is taken from solution A and evaporated to dryness. After ignition, and addition of 1 ml. 6N hydrochloric acid, it is again evaporated to complete dryness, taken up in water and filtered, in exactly the same way as was described for the potassium determination. This filtrate, containing the chloride, is now evaporated down to 1 ml., cooled down to 20°C, 10 ml. of the reagent zinc uranyl acetate solution added and the whole well mixed. The solution is allowed to stand for at least thirty minutes and is then filtered through a gooch crucible. The precipitate is transferred by means of a wash-bottle containing the 95% alcohol saturated with the triple salt. The precipitate is washed 5 times with this alcohol (2 ml. portions) and finally with ether in which the precipitate is completely insoluble. Air is now drawn through the crucible to remove the ether. A vacuum-type dessicator is now used as a suction flask and the precipitate in the gooch crucible is dissolved in 5% sulphuric acid, the washings being collected in the original beaker that was used for precipitation, giving about 50 ml. of solution.

This solution was reduced at room temperature in a

Jones reductor 12 mm. in diameter, containing a 14 cm. column of amalgamated zinc. To the reduced solution (after aeration to convert any uranium^3 to uranium^4) add 5 ml. ferric chloride solution (2%), 5 ml. phosphoric acid and 5 drops of barium diphenylanine indicator and titrate with standard decinormal potassium dichromate from a microburette.

1 ml. dichromate = 0.01665 m.e. sodium.

In determining the sodium and potassium by a volumetric process, the author found that a considerable amount of time and labour was saved. All previous workers in this field have adopted the gravimetric method of analysis.

It is desirable to do blank determinations on 200 ml. of the N. ammonium acetate leaching solution for each of the above four cations, Calcium, Magnesium, Sodium and Potassium.

Considerable time was saved by allowing the longer evaporations to continue on the waterbath overnight.

The results for the total analysis of each soil are given in the following tables. Values are expressed as milli-equivalents per 100 gms. of soil. Each soil was leached in triplicate and each leachate was analysed separately.

TABLE 1.

Leachate No.	Soil type	Soil pH	Ca	Aver	Mg..	Aver.	Na	Aver.	K	Aver.	Sum total bases	Aver.
V 1.	Venterstad	6.15	4.13	4.12	2.55	2.56	0.01	0.02	0.53	0.53	7.22	7.23
V 2.			4.01		2.55		0.03		0.51		7.10	
V 3.			4.21		2.59		0.03		0.55		7.38	
Q 1	Queenstown	6.40	3.28	3.39	1.43	1.45	0.04	0.04	0.43	0.46	5.18	5.35
Q 2.			3.46		1.48		0.05		0.47		5.46	
Q 3			3.43		1.45		0.03		0.49		5.40	
B 1.	Bethal	5.25	2.34	2.34	1.27	1.26	0.07	0.07	0.43	0.41	4.11	4.08
B 2.			2.35		1.25		0.09		0.40		4.09	
B 3.			2.33		1.25		0.06		0.40		4.04	
E.L.1	East London	5.66	4.28	4.30	1.21	1.21	0.14	0.14	0.43	0.37	6.06	6.02
E.L.2			4.33		1.16		0.15		0.32		5.96	
E.L.3			4.29		1.25		0.14		0.37		6.05	
C 1.	Cedara	5.84	6.57	6.57	7.47	7.49	0.08	0.08	0.11	0.13	14.23	14.27
C 2.			6.49		7.44		0.08		0.11		14.12	
C 3			6.66		7.55		0.08		0.17		14.46	
E 1.	Estcourt	5.68	6.48	6.33	7.24	7.27	0.04	0.05	0.20	0.21	13.96	13.86
E 2.			6.27		7.24		0.06		0.21		13.78	
E 3.			6.23		7.34		0.04		0.22		13.83	
G 1	Glen	6.62	2.92	2.96	1.34	1.33	0.01	0.02	0.28	0.35	4.55	4.65
G 2.			3.02		1.35		0.00		0.42		4.79	
G 3.			2.93		1.31		0.03		0.35		4.62	
W 1	Witte Els Bosch	5.55	1.40	1.40	1.29	1.34	0.10	0.10	0.23	0.24	3.02	3.08
W 2.			1.40		1.40		0.10		0.23		3.13	
W 3.			1.40		1.34		0.11		0.25		3.10	

Leachate No.	Soil type	Soil pH	Ca	Aver.	Mg.	Aver.	Na	Aver.	K	Aver.	Sum total bases	Aver.
S 1			3.67		0.69		0.13		0.24		4.73	
S 2.	Stellenbosch	5.35	3.51	3.61	0.67	0.69	0.11	0.11	0.22	0.22	4.51	4.63
S 3.			3.64		0.70		0.10		0.21		4.65	
P 1.			1.59		0.61		0.02		0.29		2.51	
P 2.	Port Alfred	5.75	1.62	1.60	0.54	0.58	0.02	0.02	0.27	0.27	2.45	2.47
P 3.			1.60		0.60		0.02		0.24		2.46	
U 1			39.59		5.29		0.30		1.57		46.75	
U 2.	Uitenhage	6.90	39.21	40.55	5.40	5.37	0.30	0.30	1.55	1.59	46.46	47.81
U 3.			42.86		5.43		0.30		1.64		50.23	

The pH determinations were done in the usual manner: 20 gms. of the air-dry soil were shaken with 100 ml. of aerated distilled water for one hour and the pH determination made using a glass electrode.

If values for the total exchangeable bases for a soil are all that are necessary for any particular purpose, these are usually determined by a separate and more rapid procedure than that necessary for the total analysis. The figures for the individual exchangeable bases are, therefore, not always determined.

Bray and Willhites method (22) is the most widely used rapid method and this method is the one which has been applied to a number of the soils under examination by the author. The results are given in Table II (200 ml. aliquots from solution A were used for this method.) Since these results were not very satisfactory, the author attempted to find other ways of obtaining more satisfactory values: after evaporation of a suitable aliquot (50 ml.) from solution A and ignition to oxidise all organic matter, one ml. 6N hydrochloric acid is added (or sufficient to convert all of the remaining salts to chloride). Rinse down the sides of the containing vessel (Pyrex beaker) and evaporate completely to dryness on a hotplate, any excess hydrochloric acid being thereby driven off. The residue of chlorides is then taken up in about 40 ml. of water and titrated with standard decinormal silver nitrate, using a microburette with potassium chromate as indicator. This

/gives

gives the number of milli-equivalents of chloride present and therefore also the number of milli-equivalents of total bases present. The results of a few determinations by this method are also given in Table II. All values are expressed as m.e. bases/100 g. of soil.

TABLE II

Leachate No.	Soil type	Sum total bases.	Bray & Willhites' method.	Chloride method.
V 2	Venterstad	7.10	6.79	-
Q 1	Queenstown	5.18	-	5.12
Q 2		5.46	4.95	5.24
Q 3		5.40	5.21	-
B 3	Bethal	4.04	3.58	-
EL 1	East London	6.06	5.77	5.96
EL 2		5.96	5.86	-
EL 3		6.05	5.24	5.94
C 1	Cedara	14.23	13.59	-
C 2		14.12	-	12.84
C 3		14.46	13.96	-
E 2	Estcourt	13.78	-	12.62
E 3		13.83	-	12.88
G 1	Glen	4.55	4.51	4.66
G 2		4.79	4.76	4.80
G 3		4.62	4.56	-
W 2	Witte Els Bosch	3.13	-	3.18
W 3		3.10	-	3.06
S 1	Stellenbosch	4.73	4.31	4.50
S 2		4.51	-	4.58
S 3		4.65	4.04	-
P 1	Port Alfred	2.51	-	2.64
P 2		2.45	-	2.66
P 3		2.46	-	2.66

TABLE II contd.

Leachate No.	Soil type	Sum total bases	Bray & Willhites' method.	Chloride method.
U 1	Uitenhage	46.75	-	46.4
U 2		46.46	-	47.1
U 3		50.23	-	49.7

Unfortunately determinations could not be made on all leachates as some of these had been completely used up for the total analysis, this being indicated by the blank spaces.

From the values above it can be seen that those obtained by Bray and Willhites' method are, in general, very low and quite inconsistent. The author attributes this to variations, during the day, of the gas pressure in the burners with consequent variation of the temperature during the ignition and which in some cases was therefore probably not high enough, resulting in incomplete conversion of the whole of the acetates to carbonates.

The values obtained by the Chloride method, however, were higher and more consistent. Except for the Cedara and Estcourt soils, the results agreed fairly well with those obtained from the total analysis.

In considering this method from a theoretical point of view, the author concluded that a possible cause of error might be loss of hydrochloric acid from hydrated magnesium chloride at temperatures above 105°C. Since the hotplate, even with the control switch on "low",

/attained

attained a temperature well in excess of 105°C, low results from this cause might well arise. However, on examination of the results the only values which were conspicuously low, were those obtained for the Cedara and Estcourt soil samples, and it was only in these two cases that the values for magnesium were seen to exceed those for calcium. It appeared that this might be the factor responsible for the discrepancy rather than the high value for the total exchangeable bases, especially since it was noted that good agreement was obtained for the Uitenhage sample, where the total exchangeable bases were very much higher. It was, therefore, considered advisable to investigate the effect of the calcium/magnesium ratio on the final result.

Solutions of calcium and magnesium chloride of known strengths were prepared and mixed in varying proportions. To each of these mixed solutions in 150 ml. Pyrex beakers, 1 ml. 6N hydrochloric acid was added and the solution evaporated completely to dryness on the hotplate. The residue in each case was taken up in ± 40 ml. distilled water, 1 ml. 5% potassium chromate added and the chloride titrated against standard decinormal silver nitrate using a microburette. A clean white porcelain plate was placed under the beaker during the titration. The results which were obtained are given in the following table.

/Separate

(Separate aliquots of the Calcium Chloride and the magnesium chloride were also evaporated on the hotplate in the presence of excess hydrochloric acid and while the calcium chloride gave theoretical values, the magnesium chloride after evaporation gave results which were about 40% too low, showing that considerable proportions of hydrochloric acid might be lost.)

TABLE III.

Ratio Ca: Mg	Value obtained in ml.AgNO3	Average	Theoretical Value	% Error
1 : 4	7.15 7.16 7.17	7.16	9.28	23
1 : 2	4.52 4.52 4.39	4.48	5.58	20
0.62 : 1	2.02 2.02 2.00 2.10	2.04	2.43	16
0.72 : 1	2.38 2.32 2.40	2.37	2.59	8.5
0.97 : 1	2.24 2.40 2.12	2.25	2.40	6.3
0.97 : 1	2.28 2.16 2.30 2.20 2.18 2.22 2.30 2.22	2.23	2.39	6.9
1.43 : 1	3.46 3.50 3.45	3.47	3.67	5.5
1.9 : 1	3.49 3.49 3.50 3.48 3.50 3.49 3.48 3.49	3.49	3.54	1.4
2 : 1	5.52 5.52 5.51 5.52	5.52	5.61	1.6
3.6 : 1	2.74 2.74 2.74 2.72 2.73 2.74	2.74	2.77	1.1

TABLE 111 (Contd.)

Ratio Ca: Mg.	Value obtained in ml.Ag NO3	Average	Theoretical value	% Error.
3.9 : 1	2.94 2.92 2.93 2.95 2.93 2.92 2.92 2.94	2.93	2.96	1
3.9 : 1	5.85 5.83 5.84	5.84	5.85	0.2
4 : 1	9.28 9.26 9.27	9.27	9.34	0.8
4 : 1	4.66 4.65 4.66 4.64 4.62 4.64 4.65 4.64 4.63 4.65	4.64	4.67	0.6
4.2 : 1	4.75 4.74 4.75 4.74 4.73 4.73	4.74	4.75	0.2
5.8 : 1	4.09 4.08 4.09 4.05 4.08 4.05 4.04 4.08	4.07	4.11	1

TABLE III (contd.)

Ratio Ca : Mg.	Value obtained in ml.Ag NO3	Average	Theoretical value	% Error
6 : 1	6.53 6.54 6.50 6.48 6.48	6.51	6.54	0.5
6.4 : 1	6.67 6.70 6.66 6.65	6.67	6.67	0
7.7 : 1	5.21 5.20 5.22	5.21	5.25	0.8
9.6 : 1	6.38 6.36 6.37 6.36	6.37	6.36	0.2

From the above table it seems quite evident that as long as the proportion of calcium to magnesium is 4 : 1 or greater, there is no appreciable loss of hydrochloric acid from the magnesium chloride during the evaporation. It would appear as though the magnesium and calcium chlorides might form a double salt less subject to hydrolysis than magnesium chloride alone, c.f. Mellor (37).

Reproducibility of the Results.

The results just reported gave rise to feelings of optimism as to the possibilities of the method for the rapid determination of total exchangeable bases in soils. The modified method was therefore tested during an investigation of the reproducibility of the ammonium

/acetate

leaching process on the sample taken in the East London district.

Twelve 100 gm. portions of the soil were leached for four hours and 1000 ml. of leachate were collected. A total analysis was then made on each individual leachate. In addition, 200 ml. aliquots were used to determine the total bases by Bray and Willhites' method and 50 ml. aliquots for the same determination, by the modified chloride method. The results are given in Table IV, the values being expressed as m.e./100 gms. soil.

TABLE IV

Leachate No.	Calcium	Magnesium.	Sodium	Potassium.	Sum total bases	Bray & Willhites method	Chloride method
EL 4	4.37	1.26	0.08	0.47	6.18	5.86	6.06
EL 5	4.34	1.23	0.13	0.42	6.12	6.00	6.10
EL 6	4.39	1.18	0.09	0.45	6.11	5.93	6.12
EL 7	4.29	1.14	0.13	0.40	5.96	5.96	5.92
EL 8	4.31	1.20	0.13	0.37	6.01	5.96	6.08
EL 9	4.36	1.20	0.09	0.44	6.09	6.03	6.04
EL 10	4.32	1.22	0.10	0.34	5.98	5.99	5.98
EL 11	4.33	1.22	0.09	0.30	5.94	5.67	6.00
EL 12	4.31	1.17	0.10	0.42	6.00	5.72	6.00
EL 13	4.29	1.20	0.09	0.44	6.02	5.69	5.96
EL 14	4.27	1.26	0.09	0.42	6.04	5.86	6.02
EL 15	4.31	1.23	0.11	0.37	6.02	5.82	5.96
Average.					6.04	5.87	6.02

The results in Table IV show quite conclusively that the chloride method is much more reliable than Bray and Willhites' method and it was therefore used in determining the reproducibility of the leaching process with each of

/the other

the other soil samples.

Before proceeding with the other soils, the author decided to make quite certain that the time of leaching had no appreciable effect on the amounts of bases replaced from the soil, since previous workers make no definite statement in this connection.

Six 100 gm. samples of East London soil were leached for twelve hours, and another six for eighteen hours, with the following results for the total bases, as determined by the chloride method :

12 hours	18 hours
6.00 m.e.	6.10
6.02 m.e.	6.08
5.98 m.e.	6.02
6.04 m.e.	6.04
6.06 m.e.	6.02
6.02 m.e.	6.00
Average : 6.02 m.e.	Average : 6.04 m.e.

From these values it seems reasonable to conclude that an extension of the time of leaching, from four hours to eighteen hours, makes no appreciable difference in the amounts of bases replaced from the soil.

The results obtained in determining the reproducibility of the leaching process will now be given in the form of a separate table for each soil. In every case twelve 100 gm. portions were leached for four hours (except in the case of the Stellenbosch soil which took eighteen hours) and 50 ml. aliquots were taken from each leachate for the determination of total bases by the chloride method. For

/the

the soils in which the ratio of Ca : Mg was less than 4 : 1, sufficient of a standard solution of calcium chloride was added just before the final evaporation, so as to raise this ratio to the desired value. This ensured that accurate values would be obtained. (All values are expressed as m.e./100 gms. soil).

Venterstad Soil

Total Bases.	Deviations from Mean.	Deviations^2
7.26	0.06	0.0036
6.86	0.34	0.1156
7.34	0.14	0.0196
7.28	0.08	0.0064
7.30	0.10	0.0100
7.48	0.28	0.0784
7.00	0.20	0.0400
6.86	0.34	0.1156
7.24	0.04	0.0016
7.20	0.00	0.0000
7.28	0.08	0.0064
7.26	0.06	0.0036
Mean=7.20	$\text{Sum of Deviation}^2 =$	0.4018

$$\text{Error} = \sqrt{\frac{\text{Sum of Deviations}^2}{(n-1)}}$$

$$= \sqrt{\frac{0.4018}{11}}$$

$$= 0.19$$

$$\%\ \text{Error} = \frac{.19 \times 100}{7.20} = 2.64$$

Value for Venterstad Soil : 7.20 ± 0.19 m.e./100 g. soil.

Queenstown Soil

Total bases	Deviations from Mean	$Deviations^2$
5.60	0.27	.0729
5.28	0.05	.0025
5.38	0.05	.0025
5.00	0.33	.1089
4.88	0.45	.2025
5.38	0.05	.0025
5.28	0.05	.0025
5.88	0.55	.3025
5.28	0.05	.0025
5.40	0.07	.0049
5.32	0.01	.0001
5.30	0.03	.0009
Mean=5.33	Sum of $Dev.^2$ =	.7052

Error = 0.25

% Error = 4.7

Value for Queenstown Soil; 5.33 ± 0.25 m.e./100 g. soil.

Bethal Soil

Total bases	Deviation from Mean.	Dev.^2
3.70	0.34	.1156
4.06	0.02	.0004
4.26	0.22	.0484
4.20	0.16	.0256
3.70	0.34	.1156
4.06	0.02	.0004
4.20	0.16	.0256
4.14	0.10	.0100
3.96	0.08	.0064
4.04	0.00	.0000
4.12	0.08	.0064
4.06	0.02	.0004
Mean=4.04	Sum of Dev.^2 =	.3548

Error = 0.18

% Error = 4.46

Value for Bethal Soil : 4.04 ± 0.18 m.e./100 g. soil

East London Soil.

Total bases.	Deviation from Mean.	Dev.^{2}
6.06	0.04	.0016
6.10	0.08	.0064
6.12	0.10	.0100
5.92	0.10	.0100
6.08	0.06	.0036
6.04	0.02	.0004
5.98	0.04	.0016
6.00	0.02	.0004
6.00	0.02	.0004
5.96	0.06	.0036
6.02	0.00	.0000
5.96	0.06	.0036
Mean=6.02	Sum of Dev.^{2} =	.0416

Error = 0.019

% Error = 0.32

Value for East London Soil : 6.02 ± .02 m.e./100 g. soil

Cedara Soil

Total bases	Dev. from Mean	Dev.^{2}
14.16	0.12	.0144
14.56	0.28	.0784
14.56	0.28	.0784
14.20	0.08	.0064
13.76	0.52	.2704
14.32	0.04	.0016
14.56	0.28	.0784
14.36	0.08	.0064
13.96	0.32	.1024
14.40	0.12	.0144
14.20	0.08	.0064
14.28	0.00	.0000
Mean= 14.28	Sum of Deviation^2 =	.6576

Error = 0.24

% Error = 1.68

<u>Value for Cedara Soil : 14.28 ± 0.24 m.e./100 g. soil</u>

Estcourt Soil

Total bases.	Deviation from Mean	Dev.^{2}
13.56	0.21	.0441
14.16	0.39	.1521
14.00	0.23	.0529
13.56	0.21	.0441
13.60	0.17	.0289
13.76	0.01	.0001
13.76	0.01	.0001
13.68	0.09	.0081
13.88	0.11	.0121
13.56	0.21	.0441
13.76	0.01	.0001
14.36	0.41	.1681
Mean=13.77	Sum of Dev.^{2} =	.5548

Error = 0.22

% Error = 1.60

Value for Estcourt Soil : 13.77 ± 0.22 m.e./100 g. soil

Glen Soil.

Total bases	Dev. from Mean	Deviation^2
4.62	0.01	.0001
4.66	0.03	.0009
4.72	0.09	.0081
4.58	0.05	.0025
4.58	0.05	.0025
4.68	0.05	.0025
4.64	0.01	.0001
4.60	0.03	.0009
4.58	0.05	.0025
4.60	0.03	.0009
4.64	0.01	.0001
4.66	0.03	.0009
Mean-4.63	Sum of Dev.^{2} =	,0220

Error = 0.014

% Error = 0.30

Value for Glen Soil : 4.63 ± 0.01 m.e. /100 g. soil

Witte Els Bosch.

Total Bases.	Deviation from Mean.	Deviation^2
3.12	0.08	.0064
3.10	0.06	.0036
2.72	0.32	.1024
3.04	0.00	.0000
3.08	0.04	.0016
3.16	0.12	.0144
2.98	0.06	.0036
3.08	0.04	.0016
3.14	0.10	.0100
3.08	0.04	.0016
3.00	0.04	.0016
2.98	0.06	.0036
Mean= 3.04	Sum of Dev.^2 =	.1504

Error = 0.12

% Error = 3.95

Value for Witte Els Bosch Soil : 3.04 ± 0.12 m.e./100 g.soil

Stellenbosch Soil

Total Bases	Deviation from Mean	Deviation^2
4.60	0.00	.0000
4.66	0.06	.0036
4.60	0.00	.0000
4.50	0.10	.0100
4.70	0.10	.0100
4.78	0.18	.0324
4.58	0.02	.0004
4.60	0.00	.0000
4.40	0.20	.0400
4.50	0.10	.0100
4.68	0.08	.0064
4.60	0.00	.0000
Mean=4.60	Sum of Dev.^2 =	.1128

Error = 0.10

% Error = 2.17

Value for Stellenbosch Soil : 4.60 ± 0.10 m.e./100 g.soil

Port Alfred Soil.

Total Bases.	Deviation from Mean	Dev.^{2}
2.56	0.06	.0036
2.52	0.02	.0004
2.48	0.02	.0004
2.44	0.06	.0036
2.52	0.02	.0004
2.56	0.06	.0036
2.42	0.08	.0064
2.56	0.06	.0036
2.54	0.04	.0016
2.46	0.04	.0016
2.40	0.10	.0100
2.58	0.08	.0064
Mean=2.50	Sum of Dev.^{2} =	.0416

Errpr = 0.02

% Error = 0.76

Value for Port Alfred Soil : 2.50 ± 0.02 m.e./100 g.soil

The Uitenhage soil was not analysed any further, as it was decided that the sample was probably taken from cultivated land instead of being virgin soil, since such a high value for the total replaceable bases was quite uncharacteristic of that type of soil. The very high calcium content and the very highly coloured leachate seemed to indicate possible manuring of the soil, especially as the magnesium content had not risen appreciably.

When this work had been finished, it was decided to devote more time to the study of the chloride method for the rapid determination of the total bases.

As the hydrolysis of magnesium chloride is only appreciable above 106°C, it was considered worth while to complete the evaporation at a lower temperature than that of the hotplate. The evaporation was therefore done on a waterbath and although this took much longer, the results were even more promising than those obtained in the earlier experiments on the Ca:Mg ratio. The results obtained by evaporating on a waterbath, are given in Table V.

TABLE V.

Ratio Ca:Mg.	Titration value in ml. AgNo$_3$ Soln.	Average	Theoretical value	% Error
0.97: 1	2.39 2.40 2.39 2.38 2.40 2.39 2.40 2.38	2.39	2.39	0
1.9 : 1	3.55 3.55 3.54 3.54 3.55 3.53 3.55 3.55	3.545	3.54	0.1
3.9 : 1	3.01 3.01 3.01 3.01 3.00 3.00 2.99 3.01	3.005	3.00	0.2
5.8 : 1	4.19 4.20 4.17 4.19 4.17 4.19 4.18 4.18	4.18	4.18	0

Aliquots of the individual solutions of calcium and of magnesium chloride were also evaporated on the waterbath and neither showed any loss of hydrochloric acid after evaporation.

As these results appeared to be so promising, the method was applied to two of the soil samples. The following table gives the total exchangeable bases in m.e./100 g. soil as determined by titration with silver nitrate after evaporation to dryness, ignition and then evaporation with hydrochloric acid on a waterbath.

Glen Soil	Queenstown Soil
4.72	5.14
4.68	5.22
4.60	5.16
4.62	5.52
4.62	5.32
4.64	5.36
4.66	5.16
4.60	5.38
4.58	5.48
4.66	5.34
4.68	5.52
4.64	5.28
4.64 ± 0.04	5.32 ± 0.14

SUMMARY.

A very reliable method for the total analysis of the ammonium acetate leachate has been outlined. This is both simple and straightforward and is more rapid than any which have been seen in the literature. It is particularly applicable where a worker must perform a large number of routine analyses in the minimum of time.

Shirley (29) and other workers have shown that 1000 ml. of leaching solution is generally necessary to extract all the exchangeable bases. The present investigation has shown that the time of leaching makes no appreciable difference to the amounts of bases replaced, as long as this exceeds four hours.

Two alternative methods have been introduced for the rapid determination of the total exchangeable bases in a soil and they are considered to be more reliable than that of Bray and Willhite. It is suggested that the two new methods might yield a still greater degree of accuracy if larger aliquots were to be used for each determination.

It is further pointed out that the values obtained by the chloride methods are more likely to represent correct values than the sum totals of the bases as determined individually, since these are arrived at by summing the results of four different estimations, each of which is liable to experimental error, whereas in the

/chloride

chloride methods there is only one perfectly straightforward determination.

The values for the total exchangeable bases in the soils examined were found to vary over the range 2.50 to 14.28 m.e. per 100 g. soil, with a variance of up to ± 0.25 m.e. per 100 g., corresponding to a percentage error of up to ±4.7%. These figures are based on the analysis of 12 separate leachings of each soil with normal ammonium acetate solution of pH 7.00. This rather wide variance can be attributed to the fact that the exchangeable bases in some soils are more easily replaceable than in other soils.

It is regretted that the shortage of time and the non-availability of a complete range of samples of all typical South African soils has prevented the attainment of an original objective, namely, a statistical evaluation of the base exchange figures for all South African soil types.

It would also have been of great interest to have been able to establish exactly the composition of the double salt of calcium and magnesium, whose existence has been postulated to explain the effect of the Ca/Mg ratio on the results yielded by the first chloride method.

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