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The Measurement of the Degree of Saturation of Soils with Bases

By R. H. Walker, B. J. Firkins and P. E. Brown

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AND MECHANIC ARTS

C. F. CURTISS, Director

AGRONOMY SECTION
SOILS

AMES, IOWA
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SUMMARY AND CONCLUSIONS

1. To determine the degree of saturation of a soil, data must be secured to show the amount of replaceable bases, replaceable hydrogen and base exchange capacity.

2. Experiments have been conducted to determine the accuracy of various methods for these determinations.

3. A study was first made of the electrodialysis method for replaceable bases, using both the Mattson and the Bradfield cells.

4. When 100 grams of soil were electrodialyzed in the Mattson cell for 45 hours, the results seemed satisfactory when compared with the data secured with other methods.

5. When a smaller amount of soil (10 grams) was electrodialyzed in either the Mattson or the Bradfield cell for a shorter time, the end point was not definite and the results could not be considered accurate. Furthermore, there was a continued extraction of basic materials from the soil after more bases had been removed by electrodialysis than were known to be present in a replaceable form in the soil. Hence, it appears that the error in this method may be greater than that caused by solubility effects in the leaching methods.

6. The Hissink (T — S) method for determining the replaceable hydrogen in the soil was compared with the method developed by Parker.

7. In a number of Iowa soils differing widely in characteristics and in soils which had been treated with various amounts of limestone of different degrees of fineness, the Hissink method gave practically the same amounts of replaceable hydrogen.

8. There seemed to be no correlation between the replaceable hydrogen in the soil, when measured by the Hissink method, and the hydrogen ion concentration. With the Webster silty clay loam which had a pH of 7.48, the Hissink method showed more replaceable hydrogen than was found in the Tama silt loam which had a pH of 4.79.

9. The amount of replaceable hydrogen found by the Hissink method was greater in all the soils tested than the total base exchange capacity of the soils. According to Kelley, when this method is used, not only does the barium hydroxide added to the soil react with the exchangeable hydrogen but other side reactions occur. The results with the method are certainly rather unsatisfactory.

10. According to the accepted theories of base exchange, the Parker method for determining replaceable hydrogen is
sound in principle and the data secured in this work show that it will give accurate and reliable results.

11. The Parker method for determining the base exchange capacity of soils was also found to give excellent results. The principle of this method has been well established and the method has been used, with certain modifications in technic, by other investigators.

12. After the replaceable hydrogen and base exchange capacity are determined by the Parker method, the amount of replaceable bases and the degree of saturation with bases may be calculated.

13. This method has been tested on a number of Iowa soils and on soils treated with various amounts of lime of different degrees of fineness. In all cases satisfactory results have been secured.

14. In general it is evident that of all the methods tested, that proposed by Parker seems to give the best picture of the actual condition of the base exchange complex in soils.

15. Certain modifications in the technic of this method have been suggested for future work.
The Measurement of the Degree of Saturation of Soils with Bases

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Since the inception of the base exchange concept and its appearance in soils literature, many investigations have centered around the development of methods which would give a true indication of the relationship of the bases to the absorption complex in the soil. Among the early investigators, the names of Gedroiz, Hissink and Kelley are outstanding. These men contributed much to the theory of base exchange, and the methods which they developed have served as a basis for practically all the methods suggested by later workers.

Recently much attention has been directed to the study of base exchange phenomena, and it has been found that the original methods do not give entirely satisfactory results. The recognition of this fact has led to the development of numerous modifications of the earlier methods.

It is generally accepted that when the degree of saturation of a soil with bases is to be determined, data must be secured showing the amount of replaceable basic ions, the replaceable hydrogen ions and the total absorptive capacity of the soil for bases. Most methods involve the direct determination of two of these quantities and the calculation of the third by difference. For example, in one method, the amount of replaceable bases and the total absorptive capacity of the soil are determined by analysis. Then, by subtracting the former from the latter, the amount of replaceable hydrogen is calculated. Similarly, either the amount of exchangeable bases or the total exchange capacity of the soil may be determined indirectly.

In order to measure the replaceable bases in the soil, some investigators have used dilute acids; others have employed solutions of neutral salts; and still others have made the determination by electrodialysis.

Probably greater difficulty has been experienced in developing a method for measuring the unsaturation of the soil, or the exchangeable hydrogen as it has been called in the more recent work, than in devising a method for measuring the bases. Some methods suggested have involved the measurement of the amount of a base, such as barium hydroxide, which a soil will absorb, and in others the hydrogen ions have been replaced in the soil by the basic ion of a neutral salt solution and titrated in the leachate to pH 7.0.

The methods devised for the measurement of the total absorptive capacity of the soil have been rather uniform. They
generally require saturation of the soil with a single ion, after which the amount of that ion held in the soil is determined. If an ammonium salt is used, the determination is made by distillation, but if a salt of barium or of some other base is used, the basic ion must be replaced and determined quantitatively by a standard chemical method.

Many experimental data have shown that certain methods for studying the degree of saturation of soils with bases are not reliable and do not give a true picture of the actual condition in the soil. Other methods, however, have given some evidence of value. It is obvious, therefore, that considerable difficulty may be encountered in the selection of a satisfactory method for such work.

EXPERIMENTAL

There has been no attempt in these investigations to make a comprehensive study of all the methods in use, but it seemed desirable to devote some attention to the selection of a suitable and reasonably accurate method for measuring the degree of saturation of soils with bases as a necessary preliminary to a proposed study of the base exchange reactions in some Iowa soils.

The electrodialysis method for determining the replaceable base content of soils was first studied as it had been used previously in this laboratory by Humfeld (7) and Alben (1) and had appeared promising. For replaceable hydrogen the Hissink (T—S) method was used. The degree of saturation (V), which was defined by Hissink as the ratio of the quantity of absorbed bases actually present in the soil (S) to the quantity (T) which the soil is capable of binding, was then calculated.

These methods did not prove entirely satisfactory; others were studied and comparisons made. The method proposed by Parker (15), in which the exchangeable hydrogen and the total exchange capacity of the soil are determined directly and the exchangeable bases indirectly, was the subject of special study and was finally adopted. The results of the investigations of these methods are presented in the following pages.

THE ELECTRODIALYSIS METHOD

Mattson (14) was the first to apply the principle of electrodialysis to the determination of replaceable bases in soils. He found that the bases were very readily replaced and that the order of replacement was practically the same as when solutions of a neutral salt were used. There was close agreement between the results obtained with this method and those secured with ammonium chloride solutions or dilute hydrochloric acid.
At about the same time, Bradfield (2, 3) developed another type of a cell for electrodialysis of soils. He also secured a close agreement between the results obtained by electrodialysis and by the use of a neutral salt solution.

Later Wilson (19) compared the electrodialysis method with the ammonium chloride replacement method. He used the two-compartment cell developed by Bradfield. The amounts of calcium replaced by the two methods were much the same, but the amounts of magnesium and potassium obtained from certain soils were somewhat variable. Wilson concluded that the electrodialysis method, when conducted with a relatively small current flow, gave results which more nearly represented the amount and proportion of cations which are available as nutrients for growing plants than did the normal ammonium chloride solution method.

Chapman and Kelley (5) also noted fairly close agreement between the amounts of exchangeable bases found in humid soils by the neutral salt extraction and the electrodialysis methods.

EXPERIMENTS WITH THE MATTSON CELL

In the studies reported here an attempt was made to determine the replaceable bases directly by electrodialysis. The method of electrodialysis followed was essentially the same as that developed by Humfeld and Alben (8, 9). One hundred grams of soil were placed in the center compartment of the Mattson cell and electrodialyzed for 45 hours. The dialysate solutions were withdrawn and titrated to neutrality at the end of 3, 9, 21, 33 and 45 hours, using methyl red as the indicator. The results were then calculated and expressed as milligram equivalents of ions per 100 grams of soil. The data secured in some preliminary determinations using two cells and three Iowa soils are shown in table I.

TABLE I. THE REPLACEABLE BASES IN SOME IOWA SOILS USING THE ELECTRODIALYSIS METHOD

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Cell No. 1 M.E.</th>
<th>Cell No. 2 M.E.</th>
<th>Average M.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grundy silt loam</td>
<td>16.86</td>
<td>17.12</td>
<td>17.00</td>
</tr>
<tr>
<td>Grundy silt loam</td>
<td>17.11</td>
<td>17.25</td>
<td>17.18</td>
</tr>
<tr>
<td>Shelby loam</td>
<td>14.06</td>
<td>13.51</td>
<td>13.78</td>
</tr>
<tr>
<td>Tama silt loam</td>
<td>12.83</td>
<td>12.57</td>
<td>12.71</td>
</tr>
</tbody>
</table>

It is evident from the data given in table I that quite satisfactory agreement between the results of duplicate analyses may be secured by this method. It cannot be asserted, however, that the true amount of replaceable bases in the soils is shown, but the work of Mattson, Bradfield, Wilson, and Chapman and Kelley would seem to warrant the assumption.
It seemed from these results that this method might be considered reliable for base exchange determinations. It is extremely time-consuming, however, requiring two days to make duplicate determinations. For analyses of a large number of soils a quicker method would certainly be more desirable if equally reliable results could be obtained. In an effort to devise such a method, the Mattson cell was altered by removing the center piece of rubber between the two sheets of parchment paper. Ten grams of soil, instead of the usual 100 grams, were then placed between the two parchment membranes. Thus it was possible to distribute the soil in a thinner layer, and a more rapid extraction of the absorbed bases was permitted.

![Graph showing the rate of electrodialysis of 10 grams of Tama silt loam.]

**Fig 1.** The rate of electrodialysis of 10 grams of Tama silt loam when conducted in the Mattson cell.

The rate of extraction of bases from a sample of the Tama silt loam is shown in fig. 1. The extraction was extremely rapid during the first 1/2 hour and then gradually decreased, becoming practically constant after 21/2 hours. Assuming that the replaceable bases were completely removed from the soil when the rate of extraction was at a minimum constant value (at 21/2 hours), it might be concluded that this soil contained 18.4 M. E. of bases per 100 grams of soil. This figure is almost 50 percent greater, however, than those given in table I for the same soil, and it is certainly too high, perhaps due to the large amount of current. The following experiment was planned to test this point.

Samples of the Tama silt loam were electrodialyzed in two Mattson cells, using 10 grams of soil for each test. The current was kept at 150 volts and the amperage was practically constant at 0.35 ampere, after the second change of solution.
The experiment was repeated later, using the same soil, in order to check the method. The results of these determinations are shown in fig. 2. At the end of two hours, the amount of bases extracted by this method was about the same as was shown in table I for the same soil. The curves indicate, however, that all the bases were not extracted at the end of two hours. After three hours of electrodialysis, the amount of bases extracted was about the same in all four determinations, the average being 13.94 M. E. This is one M. E. higher than the amount obtained when 100 grams of the same soil were electrodialyzed for 45 hours.

The results obtained by the electrodialysis of 10 grams of the Tama silt loam in the Mattson cell, with a current of only 110 volts, are shown in fig. 3.

It is evident from an examination of the curves in fig. 3 that with a current of 110 volts, twice as much time was required to remove practically the same amount of bases from the Tama silt loam as with a current of 150 volts.

The results obtained in the electrodialysis of 10 grams of the Grundy silt loam with a current of 150 volts in the Mattson cell are shown in fig. 4. From these curves it is difficult to determine the time at which the replaceable bases were completely removed from the soil. After six hours of electrodialysis, when base replacement is as-

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Fig. 2. Electrodialysis of Tama silt loam in the Mattson cell at 150 volts.

Fig. 3. Electrodialysis of Tama silt loam in the Mattson cell at 110 volts.

Fig. 4. Electrodialysis of Grundy silt loam in the Mattson cell at 150 volts.
sumed to be complete, the amount of replaceable bases averaged 18.93 M. E. per 100 grams of soil for the four determinations. This is approximately two M. E. greater than the figure recorded in table I for the same soil after electrodialysis of 100 grams of soil for 45 hours. If it is considered that the end point was reached in three hours, the results are still slightly higher than when the larger amount of soil was used.

The results of these experiments with the Mattson cell show that the amount of bases removed from soils depends upon the size of the sample used, the voltage of the current and the length of time electrodialysis is continued.

EXPERIMENTS WITH THE BRADFIELD CELL

At the same time that the experiments on electrodialysis with the Mattson cell were being carried out, similar tests were made with the Bradfield cell. Essentially the same apparatus and technic were employed as those used by Bradfield (2) and Wilson (19).

The results obtained by the electrodialysis of the Tama silt loam under a current of 150 volts, are shown in fig. 5. After three hours of electrodialysis, at which time base replacement may be considered complete, 13.05 M. E. of bases were extracted from this soil as an average of four determinations. In curve III significantly lower results are shown than in the case of the other three curves, and it seems probable that all the bases had not been extracted in the determinations in which those results were secured. The average of the results shown in the other three curves is 13.43 M. E., or only 0.51 M. E. less than the average results secured when 10 grams of the same soil were electrodialyzed in the Mattson cell under the same voltage, and 0.71 M. E. greater than the results obtained by electrodialyzing 100 grams of the soil in the same cell for 45 hours.

The results secured by electrodialyzing 10 grams of the Tama silt loam in the Bradfield cell with a current of 110 volts are shown in fig. 6. It is evident that the rate of extraction at this voltage was less than that secured at 150 volts, and more time was required to extract an equivalent amount of bases. At
the end of six hours, 13.90 M. E. of bases had been extracted. This was 0.47 M. E. more than was extracted in three hours at 150 volts and only 0.04 M. E. less than the amount extracted when 10 grams of the same soil were electrodialyzed in the Mattson cell at 150 volts.

The results of the electrodialysis of the Grundy silt loam in the Bradfield cells at 150 volts are shown in the curves in fig. 7. It seems that more time was required to extract the bases from this soil than from the Tama silt loam under the same conditions, assuming base replacement to be complete after six hours of electrodialysis. The results of this test were quite inconsistent, however, and duplicate analyses did not agree satisfactorily. The results shown in curve I are much higher than those obtained by electrodialysis of the same soil in the Mattson cell when either 10 or 100 grams of soil were used. The results in curve IV are considerably lower while those in curves II and III were similar to those obtained in the other determinations.

In all these experiments, as is apparent in the curves, it was very difficult to determine the exact point at which the absorbed or replaceable bases had been completely removed from the soil. While the dialysate solutions were titrated to the neutral point of methyl red and the final results were calculated on that basis, the curves seem to indicate that the extraction
was not complete at that point. It also seems that the extraction, even tho the rate was slow, was practically continuous, and the longer the soil was electrodialyzed, the greater was the amount of basic ions removed.

From all the results secured it seems that the difficulty of fixing the end point for the extraction of bases is one of the chief objections to the electrodialysis method. The wide variations in the results, undoubtedly due almost entirely to this difficulty, certainly make this method quite unsuitable for determining the replaceable bases in soils.

MEASURING THE EXCHANGEABLE HYDROGEN IN SOILS

Hissink (6) first developed a method for measuring the exchangeable hydrogen in soils. He also determined the amount of exchangeable bases and calculated the degree of saturation of the soil, without determining the total exchange capacity.

According to Hissink, if the amount of exchangeable bases (S) is subtracted from the total exchange capacity (T), the
difference \((T - S)\) represents the amount of exchangeable hydrogen. He suggested that it be measured by conductometric titration against a base, preferably barium hydroxide. Plotting cubic centimeters of base against conductivity, he secured two straight lines, one the base line and the other the acid line. The point of intersection of these two lines was assumed to represent the quantity of base required to replace the exchangeable hydrogen of the soil.

Hissink also found that the conductivity at all points on the base line was proportional to the amount of base in solution. Instead of measuring the conductivity, therefore, he simply titrated the quantity of base which still remained in solution. Curves were then plotted and \((T - S)\) determined in the same manner as in the conductometric method.

![Graph](image)

**Fig. 8.** Exchangeable hydrogen, \((T - S)\), for Grundy silt loam according to the Hissink method.

**EXPERIMENTS WITH THE HISSINK METHOD**

The method of Hissink was studied in this work, using the following procedure:
Ten-gram quantities of soil were placed in each of sixteen 50 cc. Erlenmeyer flasks. To two of these, 10 cc. of one-tenth normal barium hydroxide were added. Twenty cc. of the hydroxide were added to two flasks and amounts increasing by 10 cc. were added to the other flasks in duplicate, the last two flasks receiving 80 cc. Sufficient water was added to each flask to bring the total volume of solution up to 80 cc. The flasks were stoppered and shaken occasionally for three days. Then they were allowed to stand overnight. Twenty-five cc. of the supernatant solution were carefully pipetted into another flask and titrated to neutrality against N/10 HCl, using phenolphthalein as the indicator. From these figures the milligram equivalents of barium remaining in the solution were calculated per 100 grams of soil and plotted against the cubic centimeters of barium hydroxide added.

The curves for exchangeable hydrogen, or (T − S) in the Grundy silt loam, the Tama silt loam and the Shelby loam are shown in figs. 8, 9 and 10. The point where the straight line intersects the base line in each graph represents the amount of exchangeable hydrogen in milligram equivalents, per 100 grams of soil. From the data thus obtained and those for exchangeable bases given in table I, the total base exchange capacity and degree of saturation of these soils have been calculated. The results are presented in table II.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Exchangeable bases (S)</th>
<th>Exchangeable hydrogen (T − S)</th>
<th>Exchange capacity (T)</th>
<th>Degree of saturation (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grundy silt loam</td>
<td>16.99</td>
<td>44.50</td>
<td>61.49</td>
<td>27.64</td>
</tr>
<tr>
<td>Tama silt loam</td>
<td>12.71</td>
<td>38.00</td>
<td>50.71</td>
<td>25.06</td>
</tr>
<tr>
<td>Shelby loam</td>
<td>13.78</td>
<td>34.00</td>
<td>47.78</td>
<td>28.84</td>
</tr>
</tbody>
</table>

These data show that the soils tested varied somewhat in content of exchangeable hydrogen. From a consideration of the pH, the colloidal content and the general physical and chemical properties of these soils, however, greater differences in exchangeable hydrogen were expected. It seemed also that the amount of exchangeable hydrogen in these soils, according to this method, was too great when compared with the amount of replaceable bases. Furthermore, it did not appear reasonable that the Grundy silt loam should have almost three times as many milligram equivalents of hydrogen as the total amount of calcium, magnesium, potassium and other replaceable bases in the exchange complex. In this connection it may be noted that Kelley (10) found that normal soils of neutral or alkaline re-
action do not have any important amount of hydrogen as a constituent of the exchange complex. In a later paper, Kelley and Brown (13) concluded that most of the soils studied, altho distinctly acid, did not contain a large absolute amount of replaceable hydrogen ions.

Parker (15) determined the degree of saturation of a sample of Grundy silt loam, the origin of which he did not give, and found it 75.5 percent saturated with bases. The Grundy silt loam tested in this work showed a saturation of 27.64 percent. It should not be inferred that samples of the same soil type would necessarily have the same degree of saturation, but they certainly would not differ as widely in degree of saturation as in the case of the two figures given. Furthermore, the amount or replaceable bases in the two soils may be compared. The soil Parker used contained 22.84 M. E. of bases and the Grundy silt loam used in this work contained approximately 17 M. E. of replaceable bases (table I). With these amounts of

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Fig. 9. Exchangeable hydrogen, (T - S), for Tama silt loam according to the Hissink method.
replaceable bases the two soils would need to show an extremely large difference in base exchange capacity if as large differences in degree of saturation as recorded really occurred. They probably did not differ so widely. It seems much more probable that the differences are due to the methods used in determining the exchangeable hydrogen. It is believed that the Hissink method for determining exchangeable hydrogen gives values which are much too high and which do not represent the true condition of unsaturation in the soil.

To study further the value of this method for measuring the exchangeable hydrogen in soils, analyses were made on samples of four soils which differ widely in reaction. A determination was also made of the colloid content of these soils by the hydrometer method of Bouyoucos (4). It seemed probable that these soils would show greater differences in the amount of exchangeable hydrogen than the Grundy, Shelby and Tama soils, because of the wider range in hydrogen ion concentration.

![Graph](image)

Fig. 10. Exchangeable hydrogen, \((T - S)\), for Shelby loam according to the Hissink method.
TABLE III. THE pH, EXCHANGEABLE HYDROGEN AND COLLOID CONTENT OF SOME IOWA SOILS

<table>
<thead>
<tr>
<th>Soil type</th>
<th>pH</th>
<th>Exchangeable hydrogen (T-S) M. E.</th>
<th>Colloid content Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marshall silt loam</td>
<td>5.78</td>
<td>38.00</td>
<td>35.1</td>
</tr>
<tr>
<td>Waukesha silt loam</td>
<td>5.90</td>
<td>49.00</td>
<td>33.0</td>
</tr>
<tr>
<td>Webster silty clay loam</td>
<td>7.48</td>
<td>40.50</td>
<td>46.0</td>
</tr>
<tr>
<td>Clarion loam</td>
<td>6.98</td>
<td>25.00</td>
<td>19.0</td>
</tr>
</tbody>
</table>

The results secured in this test are given in table III. While these data do show greater differences in the amount of exchangeable hydrogen present than was apparent in the earlier tests (table I), some inconsistencies occur in the results. The Webster silty clay loam which was distinctly basic showed a larger amount of exchangeable hydrogen than the Marshall silt loam which was acid in reaction. It was found also that the difference between the amounts of exchangeable hydrogen in the Marshall silt loam and in the Waukesha silt loam, which were about the same in reaction, was greater than the difference between the amounts in the Marshall silt loam and in the Webster silty clay loam which were widely different in reaction. Furthermore, it was shown that the amount of exchangeable hydrogen in the Clarion loam, which was neutral in reaction, was considerably less than that in the Webster silty clay loam which was basic in reaction.

These data would indicate that the amount of exchangeable hydrogen was not at all related to the reaction or pH of these soils. Apparently it was more closely associated with the colloid content. Undoubtedly the colloid content of a soil does influence greatly its absorptive capacity for bases and hence will affect the amount of replaceable basic and hydrogen ions in the soil. It is reasonable to assume, however, that the amount of replaceable hydrogen would have a direct relation to the hydrogen ion concentration of the soil. Schollenberger and Dreibelbis (18) found that the pH of soils in the field plots varied somewhat regularly with the exchangeable hydrogen in the soils. It seems, therefore, that the method used in this work did not give a very accurate measure of exchangeable hydrogen.

To test the method further, it was used to determine the amount of exchangeable hydrogen in samples of the Tama silt loam taken from field plots which had received various amounts of lime of different degrees of fineness. The lime was applied to these soils in the spring of 1927, just prior to the seeding of the small grain and legume crops. The soil samples were taken in June, 1929. Composites of nine samples of surface soil from each plot were used for the analyses. The data for
TABLE IV. THE EFFECT OF VARIOUS AMOUNTS OF LIME OF DIFFERENT
DEGREES OF FINENESS ON THE EXCHANGEABLE HYDROGEN CONTENT
BY THE HISSINK METHOD AND THE HYDROGEN ION CONCENTRATION
OF THE TAMÀ SILT LOAM

<table>
<thead>
<tr>
<th>Plot no.</th>
<th>Kind of lime</th>
<th>Amount of lime lbs. per A.</th>
<th>Hydrogen ion concentration pH</th>
<th>Exchangeable hydrogen M. E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td></td>
<td>5.25</td>
<td>39.5</td>
</tr>
<tr>
<td>2</td>
<td>40-mesh</td>
<td>1,750</td>
<td>5.56</td>
<td>38.2</td>
</tr>
<tr>
<td>3</td>
<td>40-mesh</td>
<td>3,500</td>
<td>5.63</td>
<td>38.2</td>
</tr>
<tr>
<td>4</td>
<td>40-mesh</td>
<td>7,000</td>
<td>5.98</td>
<td>36.5</td>
</tr>
<tr>
<td>5</td>
<td>40-mesh</td>
<td>14,000</td>
<td>6.35</td>
<td>34.5</td>
</tr>
<tr>
<td>6</td>
<td>Quarry-run</td>
<td>1,750</td>
<td>5.55</td>
<td>38.5</td>
</tr>
<tr>
<td>7</td>
<td>Quarry-run</td>
<td>3,500</td>
<td>5.52</td>
<td>38.0</td>
</tr>
<tr>
<td>8</td>
<td>Quarry-run</td>
<td>7,000</td>
<td>5.86</td>
<td>34.5</td>
</tr>
<tr>
<td>9</td>
<td>Quarry-run</td>
<td>14,000</td>
<td>6.94</td>
<td>33.5</td>
</tr>
</tbody>
</table>

Exchangeable hydrogen (T - S) and the hydrogen ion concentration are shown in Table IV. These data show that in all but one case, the amount of exchangeable hydrogen in the soils from the various plots was decreased slightly with each increase in the amount of lime applied. The inverse ratio between the lime applied and the exchangeable hydrogen, however, was not the same in all cases. For instance, in the soils receiving the 40-mesh limestone, 3,500 pounds per acre, representing one-half the lime requirement as determined by the Iowa test, decreased the amount of exchangeable hydrogen 1.3 M. E. Seven thousand pounds of lime supplying the full lime requirement, decreased it 3.0 M. E. and 14,000 pounds, or twice the lime requirement, decreased it 5.0 M. E. In the soils treated with quarry-run limestone, 3,500 pounds decreased the amount of exchangeable hydrogen 1.5 M. E.; 7,000 pounds decreased it 5.0 M. E., and 14,000 pounds decreased it 6.0 M. E. Owing to the natural variations in soils, it might be expected that the results secured from samples of soils from different plots would vary as they did in this case. Data obtained in other work not reported here, however, emphasize the fact that these variations in results are not due entirely to soil differences but to inaccuracies in the method used.

These data, like those in Tables II and III, show that the soil treatments have only small effects on the soil. With the methods used it is apparent that there are chances for erroneous conclusions, especially when the data are shown on curves. Unless the data for (T - S) are of such a nature that, beyond the hydrolysis phase of the curve, a straight line may be drawn thru every point on the graph, there may be some variation in the exact position of the line. Hence, the conclusions regarding the amount of exchangeable hydrogen in a soil may vary considerably depending upon the location of the line drawn on the graph.
It seems from these data that this method did not give a true measure of the amount of exchangeable hydrogen in soils, and attention was directed to the method developed by Parker (15).

EXPERIMENTS WITH THE PARKER METHOD

The Parker barium acetate-ammonium chloride method was suggested about the time that the conclusion was reached that the methods discussed above were not entirely satisfactory. According to this method, the exchangeable hydrogen is determined in the leachings after passing 250 cc. of neutral normal barium acetate thru 10 grams of soil in a gooch crucible. After the exchange capacity of the soil is saturated with barium, the barium ions are completely replaced with ammonium ions by leaching the soil with 250 cc. of normal ammonium chloride solution. The excess ammonium chloride is removed by leaching with ethyl alcohol and the absorbed ammonia is determined by distillation. Thus the total exchange capacity of the soil is determined. From the data showing the amount of exchangeable hydrogen and the total exchange capacity, the degree of saturation with bases is calculated.

Parker and his co-workers have used the method extensively, and they consider it relatively simple and rapid. It was tested by using it for the analysis of the same soils which had been analyzed by electrodialysis and by the Hissink method for \((T - S)\) or exchangeable hydrogen. The data obtained in tests on six Iowa soils are recorded in table V.

TABLE V. THE EXCHANGEABLE HYDROGEN CONTENT AND TOTAL EXCHANGE CAPACITY OF SOME IOWA SOILS DETERMINED BY THE BARIUM ACETATE-AMMONIUM CHLORIDE METHOD OF PARKER AND THE CALCULATED AMOUNT OF EXCHANGEABLE BASES AND THE DEGREE OF SATURATION

<table>
<thead>
<tr>
<th>Soil type</th>
<th>pH</th>
<th>Exchangeable hydrogen M. E.</th>
<th>Exchangeable hydrogen M. E.</th>
<th>Exchangeable bases M. E.</th>
<th>Degree of saturation percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grundy silt loam</td>
<td>5.09</td>
<td>9.12</td>
<td>25.92</td>
<td>16.80</td>
<td>64.81</td>
</tr>
<tr>
<td>Tama silt loam</td>
<td>4.79</td>
<td>8.07</td>
<td>21.00</td>
<td>12.93</td>
<td>61.57</td>
</tr>
<tr>
<td>Shelby loam</td>
<td>5.51</td>
<td>6.08</td>
<td>19.70</td>
<td>13.62</td>
<td>69.14</td>
</tr>
<tr>
<td>Marshall silt loam</td>
<td>5.78</td>
<td>5.70</td>
<td>22.75</td>
<td>17.05</td>
<td>74.94</td>
</tr>
<tr>
<td>Waukesha silt loam</td>
<td>5.90</td>
<td>7.70</td>
<td>29.00</td>
<td>21.21</td>
<td>73.14</td>
</tr>
<tr>
<td>Webster silty clay loam</td>
<td>7.48</td>
<td>0.66</td>
<td>34.80</td>
<td>34.80</td>
<td>100.00</td>
</tr>
</tbody>
</table>

In these tests the amount of exchangeable hydrogen in the soils was found to be much less than was indicated with the Hissink method. The amount of exchangeable bases was greater in every case than the amount of exchangeable hydrogen and hence the degree of saturation with bases was over 50 percent in all the soils and 100 percent for the Webster silty clay loam. These results seem much more reasonable since the soils tested
are all productive and should contain a greater amount of basic ions than of hydrogen ions in the exchange complex. In very poor soils with a high hydrogen ion concentration, a degree of saturation as low as that secured with the Hissink method might be expected.

While an absolute correlation between the hydrogen ion concentration and the content of exchangeable hydrogen did not occur, there was a very close relationship. The Webster silty clay loam, which had a pH above 7.0, contained no exchangeable hydrogen. The Marshall silt loam, the Shelby loam and the Grundy silt loam showed an increasing hydrogen ion concentration in the order named and an increasing exchangeable hydrogen ion content in the same order. With the Tama silt loam and the Waukesha silt loam there was not as close an agreement between these two factors. Even with these soils, however, the greatest hydrogen ion concentration corresponded with the largest amount of exchangeable hydrogen.

It seems much more reasonable to expect such a relationship between the hydrogen ion concentration and the content of exchangeable hydrogen than that secured when the exchangeable hydrogen was determined by the Hissink method. Certainly the Webster silty clay loam which had a pH of 7.48, should not show as much as 40 M. E. of exchangeable hydrogen which was the amount found by the Hissink method. In fact the Parker method did not give as high a figure as this for the total exchange capacity of the soil. This was true not only for the Webster silty clay loam but for all the other soils tested. Furthermore with the Parker method, the amount of exchangeable hydrogen was so small in all the soils tested that the degree of saturation was greater than 50 percent, and the Webster silty clay loam, which was basic, was completely saturated with basic ions.

To test the Parker method further, it was employed for an analysis of samples of Tama silt loam, taken from plots treated with various amounts of limestone of varying degrees of fineness. These were the same soils which were analyzed by the Hissink method (see table IV). The results are shown in table VI.

These data show that the amount of exchangeable hydrogen in these soils was decreased from 7.88 M. E. in the untreated soil to 4.95 M. E. where 3½ tons of 40-mesh limestone were applied and to 1.44 M. E. where 7 tons were applied. When 7 tons of quarry-run limestone were employed the amount of exchangeable hydrogen in the soils was reduced to 4.2 M. E. The amount of exchangeable bases in these soils was increased proportionately. The degree of saturation was increased from 63.85 percent to 76.43 percent by the addition of 3½ tons of
TABLE VI. THE EFFECT OF DIFFERENT AMOUNTS OF LIMESTONE OF VARYING DEGREES OF FINENESS ON THE HYDROGEN ION CONCENTRATION AND THE EXCHANGEABLE HYDROGEN CONTENT DETERMINED BY THE PARKER METHOD AND ON THE CALCULATED AMOUNT OF EXCHANGEABLE BASES AND THE DEGREE OF SATURATION OF THE TAMA SILT LOAM

<table>
<thead>
<tr>
<th>Plot no.</th>
<th>Kind of lime</th>
<th>Amount of lime lbs. per A.</th>
<th>pH</th>
<th>Exchangeable hydrogen M.E.</th>
<th>Exchange capacity M.E.</th>
<th>Exchangeable bases M.E.</th>
<th>Degree of saturation percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>None</td>
<td>5.25</td>
<td>7.88</td>
<td>21.80</td>
<td>13.92</td>
<td>63.85</td>
</tr>
<tr>
<td>2</td>
<td>40-mesh</td>
<td>1,750</td>
<td>5.56</td>
<td>7.11</td>
<td>21.15</td>
<td>14.04</td>
<td>66.38</td>
</tr>
<tr>
<td>3</td>
<td>40-mesh</td>
<td>3,500</td>
<td>5.63</td>
<td>6.66</td>
<td>20.90</td>
<td>14.24</td>
<td>64.13</td>
</tr>
<tr>
<td>4</td>
<td>40-mesh</td>
<td>7,000</td>
<td>5.98</td>
<td>4.95</td>
<td>21.00</td>
<td>16.05</td>
<td>76.43</td>
</tr>
<tr>
<td>5</td>
<td>40-mesh</td>
<td>14,000</td>
<td>6.93</td>
<td>1.44</td>
<td>20.70</td>
<td>19.26</td>
<td>93.04</td>
</tr>
<tr>
<td>6</td>
<td>quarry-run</td>
<td>1,750</td>
<td>5.55</td>
<td>6.74</td>
<td>21.37</td>
<td>14.63</td>
<td>68.40</td>
</tr>
<tr>
<td>7</td>
<td>quarry-run</td>
<td>3,500</td>
<td>5.52</td>
<td>5.55</td>
<td>20.95</td>
<td>15.40</td>
<td>73.50</td>
</tr>
<tr>
<td>8</td>
<td>quarry-run</td>
<td>7,000</td>
<td>5.86</td>
<td>4.20</td>
<td>20.25</td>
<td>16.05</td>
<td>79.26</td>
</tr>
<tr>
<td>9</td>
<td>quarry-run</td>
<td>14,000</td>
<td>6.94</td>
<td>1.44</td>
<td>21.50</td>
<td>20.96</td>
<td>93.30</td>
</tr>
</tbody>
</table>

40-mesh limestone and to 93.04 percent by 7 tons of the same material. With the quarry-run limestone, 3½ tons increased the degree of saturation to 79.26 percent and 7 tons increased it to 93.3 percent.

It is apparent from these data that the differences shown by this method, in the amounts of exchangeable hydrogen, induced by additions of various amounts of limestone of different degrees of fineness to this soil type, were so great that they may serve as a measure of the effects of lime on the soil. Likewise the changes in the degree of saturation of this soil, as influenced by applications of lime, were also sufficiently definite to serve as an indication of the effects of lime.

Parker secured very close agreement of duplicates in the analyses made with this method. The same has been true in this work. If the barium acetate and ammonium chloride solutions are prepared so that they are exactly pH 7 in reaction, and all the ordinary precautions for analytical work are observed, it is possible to secure duplicate results that agree satisfactorily. The two operations in which errors are most likely to occur are the adjustment of the reaction of the barium acetate solution and the titration of the exchangeable hydrogen to the point of neutrality. Small errors here are magnified when the degree of saturation is calculated. By using the quinhydrone electrometric method, however, errors in this determination may be reduced to a minimum.

Recently, Schollenberger and Dreibelbis (17) have determined the replaceable hydrogen in soils by a method based on the same principles. They first leached the soil with ammonium acetate, of pH 7.07 and then titrated the leachings to the same reaction with 0.2 N ammonium hydroxide, using the quinhydrone electrometric titration method. They secured excellent
results, judging from the agreement of duplicate determinations made at different times. Their method has not yet been studied.

In general it appears that the Parker method is the most satisfactory of all those tested, for estimating the amount of exchangeable hydrogen in soils. It is the simplest and the easiest to operate and by its use many soils may be analyzed in a comparatively short time. But what is more important it seems to give a better quantitative picture of the actual condition of the base exchange complex in the soil.

It is possible that the technic of the method may be improved by following the suggestion made by Schollenberger and Dreibelbis, whose work referred to above was published after the completion of the studies reported here.

MEASURING THE BASE EXCHANGE CAPACITY OF SOILS

The Parker method (15) was also followed in the determination of the base exchange capacity of soils. It is essentially the same in principle as that developed by Kelley and Brown (12) and it has been employed with slight modifications by a number of investigators. The method involves leaching the soil with neutral, normal ammonium chloride, after all the bases in the original soil have been replaced by barium, through treatment with barium acetate. As it is carried out, 10 grams of soil in a gooch crucible are leached with 250 cc. of normal barium acetate and then with the same amount of neutral, normal ammonium chloride solution. The occluded ammonium salts are then removed from the soil by washing with alcohol until the leachings are free from chlorides and the soil is transferred to an 800 cc. Kjeldahl flask. Five grams of heavy magnesium oxide and about 200 cc. of distilled water are added and the ammonia is distilled into N/10 acid. The excess acid is titrated against N/10 alkali using methyl red as the indicator. The amount of ammonia found is considered to be equivalent to the base exchange capacity of the soil. The results are expressed in terms of milligram equivalents per 100 grams of soil.

The method was employed to determine the base exchange capacity of three Iowa soils, the Grundy silt loam, the Shelby loam and the Tama silt loam six months after they had been treated in pots in the greenhouse with various amount of chemically pure calcium carbonate. The results appear in table VII. The duplicate determinations agreed very closely in all but one case, as is evident from an examination of the data. The base exchange capacity of all the soils was increased quite regularly by the increasing additions of calcium carbonate, but no large differences were noted in the effects of the various applications.
TABLE VII. DUPLICATE DETERMINATIONS OF THE BASE EXCHANGE CAPACITY OF SOME IOWA SOILS, SIX MONTHS AFTER TREATMENT WITH VARIOUS AMOUNTS OF CHEMICALLY PURE CALCIUM CARBONATE IN THE GREENHOUSE

<table>
<thead>
<tr>
<th>Soil treatment. Amounts of calcium carbonate per acre</th>
<th>Grundy silt loam M. E.</th>
<th>Shelby loam M. E.</th>
<th>Tama silt loam M. E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check</td>
<td>23.00</td>
<td>18.75</td>
<td>20.00</td>
</tr>
<tr>
<td>1 ton</td>
<td>24.60</td>
<td>18.80</td>
<td>20.60</td>
</tr>
<tr>
<td>2 tons</td>
<td>24.70</td>
<td>18.50</td>
<td>20.50</td>
</tr>
<tr>
<td>3 tons</td>
<td>25.00</td>
<td>19.10</td>
<td>20.80</td>
</tr>
<tr>
<td>4 tons</td>
<td>25.60</td>
<td>19.75</td>
<td>20.85</td>
</tr>
<tr>
<td>5 tons</td>
<td>25.50</td>
<td>20.00</td>
<td>20.60</td>
</tr>
<tr>
<td>6 tons</td>
<td>25.50</td>
<td>20.50</td>
<td>21.60</td>
</tr>
</tbody>
</table>

**PROPOSED MODIFICATION OF THE METHOD**

Since the completion of this work, Chapman and Kelley (5) have reported that it is possible to replace all the exchangeable hydrogen of the absorption complex with the ammonium ion of a neutral, normal ammonium acetate solution without previous treatment with a barium salt. Schollenberger and Dreibelbis (17) have also used ammonium acetate in a similar way.

It seems possible, therefore, that the method of Parker may be shortened considerably, without decreasing its accuracy, by replacing the absorbed bases and hydrogen in the original soil by an ammonium acetate solution. The leachate thus obtained may be used as at present for determining the amount of replaceable bases and hydrogen. The occluded ammonium salts may then be washed from the soil with alcohol and the soil will be ready for the ammonium determination. This modification will be compared with the original method of Parker in the near future.

There are two other possibilities of improving the technic of the determination which will be tested later. In the first place, the hydrogen may be replaced in a closed system to prevent a loss by contact with the air, as has been proposed by Schollenberger (16); further, the determination of absorbed ammonia in the soil may be made by the aeration method suggested by Kelley (11) rather than by distillation.
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