An Intensive Study of an Acid Soil.

A comparison of the different methods for estimating the "lime requirement" and the degree of saturation of Soils.

Thesis submitted by:-

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Introduction

Owing to its extreme importance in practical Agriculture no problem in Soil Chemistry has received more attention than that of Soil Acidity or "Sourness". The knowledge that it may be remedied by the application of lime has been known from the earliest times, but the problem of determining the exact amount necessary to bring a "sour" soil into a state of fertility is an extremely difficult one, being affected as it is by the type of soil, the plant, the buffering action of the soil and the climate. Various methods have been suggested for the determination of this "lime requirement" but it is doubtful if any one method will suffice for all plants, on all types of soil, under all climatic conditions.

The problem has been attacked in two ways:-

(1) By measuring the concentration of H' ions or pH i.e. the intensity factor of the acidity and the effect of lime thereon - and

(11) By measuring the potential acidity or "lime requirement"

As regards the second method workers in different countries have suggested various methods and it was with the object of comparing these methods, as well as determining the effect of lime on other factors including the crop yield, that this investigation was begun. For this purpose a small piece of "acid" land at Boghall, the experimental farm of the Edinburgh and East of Scotland College of Agriculture was obtained. The field which was roughly half an acre in size had not been cultivated for some time and was covered with weeds, mostly as might be expected from the acid nature of the soil, spurry and sheep's sorrel with some hemp nettle and redshank. The soil was of two types (Soil Survey of Boghall Farm by Dr. Ogg, formerly Soil Advisory Officer) mostly a brownish chocolate coloured loam with a fairly high percentage of sand with patches of a darker loamy mineral soil containing a considerable amount of organic matter.

The land was not very well drained and the lower layers of soil showed the yellowish iron oxide staining characteristic of water-logging. Previous to this investigation the land had been cleaned and sewn with barley, but the crop was almost a complete failure only a few patches surviving after the first few weeks. A small part of the surviving plants ripened, while the rest failed to do so, remaining green and stunted throughout the season, the grain remaining almost wholly undeveloped. In 1929 a series of 10 plots, i.e. 5 in duplicate each 5 yards by 4 yards were laid down and lime applied in accordance with the amounts determined in accordance with the Tovborg-Jensen method which will be discussed later. A month after liming barley was sewn at the rate of 1 lb. per plot i.e. about four bushels per acre. The plots were sampled before liming and at intervals of one year for two years afterwards, the work carried out being briefly as follows:-

(1) Description of soil - mechanical analysis - organic matter

(2) Liming of plots, Tovborg-Jensen method - effect of liming

on pH - change of pH during growing season - change in drying soil.

(3) Acidity as measured by Kappen's method, i.e. hydrolytic acidity and as measured by Daikahura's method i.e. exchange acidity.

(4) Lime requirement as determined by Hutchison-McLennan method.

(5) Exchangeable bases - increase of exchangeable Calcium and effect on Aluminium due to liming - aluminium and toxicity to plants.

(6) Comparison of various methods proposed for determination of the saturation value of soils (Hissink, Gehring and Wehrmann, Kelly, Bobko & Askinasi, Page & Williams, Crowther & Basu).

(7) Effect on yield of crops.

(8) Summary and conclusions.

Mechanical Analyses and percentage Organic Matter

Before beginning any detailed description of the methods employed for the measurement of acidity, a short account of the soil of the plots is given, more particularly as regards the silt, clay and organic matter content, as these are the chief factors concerned in the problem of absorption of Calcium and other exchangeable bases, saturation values, &c.

Table 1 Gives the mechanical analyses of the various soils which were carried out according to the "Revised Official Method for the Mechanical Analyses of Soils" (58).

Table 1

Plot	Coarse Sand		Fine Sand		Silt		Clay		Loss on
	Dried at 105°C.	Ignited	Dried at 105°C.	Ignited	Dried at 105°C.	Ignited	Dried at 105°C	Ignited	Ignition
1	24.7	23.9	23.9	23.6	16.8	15.8	22.5	18.5	10.7
2	19.6	19.2	23.8	23.5	14.8	14.0	22.0	17.8	13.4
3	23.2	22.7	22.8	22.5	16.0	15.0	22.2	16.8	14.3
4	22.6	22.2	22.9	22.6	15.0	14.3	22.0	17.3	14.1
5	13.8	13.6	21.1	20.6	17.3	15.8	25.0	18.8	20.1
6	11.9	11.2	20.0	20.9	18.0	15.8	26.5	20.8	21.4
7	17.4	16.8	21.1	20.9	16.0	14.0	22.8	17.4	18.6
8	20.8	20.4	19.8	19.6	16.2	14.8	23.0	18.5	15.5
9	20.0	19.6	20.8	20.6	17.8	15.5	22.8	18.8	15.4
10	22.7	22.2	23.3	23.0	15.0	14.3	22.3	18.0	12.3

As can be seen the amounts of Fine Sand, Silt and Clay vary but little throughout the plots, but the amount of Coarse Sand shows considerable variation ranging from 24.7% in Plot 1 to 11.9% in Plot 6. This is accounted for almost emtirely by the variation in organic matter or more correctly "Loss of Ignition" which it will be noted varies from 10.7% in Plot 1 to 21.4% in Plot 6.

Organic Matter. Though loss on ignition is sometimes taken as a measure of the organic matter this is not strictly correct as the loss on ignition at least in mineral soils includes, along with the organic matter, the water of constitution of the Clay.

The problem of determining quantitatively the organic matter in soils has not yet been satisfactorily solved though various methods have been proposed and are in use.

The methods adopted may be classified into two groups

(1) The extraction of the organic matter or "humus" by some alkali and its subsequent precipitation by acid as for example the determination of the α fraction according to Waksman (71).

The amount extracted by this method appears to depend on the temperature and strength of the alkali used and on the time of extraction and in a critical review of the methods employed Waksman & Stevens (72) state that not more than 30 - 50% of the soil organic matter is extracted by such means.

(1b) The oxidation of the humified portion of the organic matter by some oxidising agent e.g. H_2O_2 as in the method of Robinson & Jones (59)

(2) The second method is the determination of the total carbon content of the soil. The percentage carbon obtained is then multiplied by the factor 1·724 to give the total organic matter present. This factor is based upon the work of Van Bemmelen, Wollny and others who found the amount of carbon present in organic matter to be 58%. The carbon may be estimated by (1) the dry combustion method, the most satisfactory, or (2) a wet combustion method e.g. by chromic acid or by permanganate. This latter method has been found to give considerably lower results than the former (57)

A modification of the total carbon method which has been suggested and which has been used in the present work is that of Robinson, McLean & Williams (60). In this method the carbon is oxidised by concentrated H_2SO_4 as in the ordinary Kjeldahl method, the SO_2

liberated being trapped by means of standard iodine solution. The amount of carbon found by this means multiplied by 2 may be taken as a rough measure of the organic matter present. The factor 2 is based (1) on the fact that the amount of carbon obtained is found to be consistently lower than that obtained by the dry combustion method and (II) on the assumption that the factor 1·724 previously mentioned is also too low. This factor has also been criticised by Read & Ridgell(60) who hawe suggested that the amount of carbon present in organic matter should be taken as 50 - 52% instead of as formerly 58% and by Lunt (48) who suggests 53 - 55%. The method given above would abviously not be suitable for soils which contained considerable amounts of reducing substances other than carbon but with this exception it appears to give approximate results and is moreover suitable for routine use. At the present time when the nature, composition and structure of the organic matter in soils is almost entirely unknown, it is doubtful whether strict adherence to any one method for its determination can be justified.

Table 2 gives/(1) the amount of carbon calculated from the amount of SO_2 evolved,(2) amount carbon actually present i.e. C x 1·116 (Robinson's factor) (3) percentage organic matter calculated from 1 and (4) the loss on Ignition :-

Table 2.

Plot	Carbon(1) by SO_2	% Carbon i.e.(1) x 1·116	% Organic Matter i.e.(1) x 2	Loss on Ignition
1	5.03	5.61	10.1	10.7
2	6.77	7.55	13.5	13.4
3	7.52	8.20	15.0	14.3
4	7.65	8.54	15.3	14.1
5	9.88	11.03	19.8	20.1
6	10.60	11.82	21.2	21.4
7	10.52	11.74	21.0	18.6
8	7.88	8.79	15.8	15.8
9	7.63	8.51	15.3	15.4
10	6.31	7.04	12.6	12.3

As can be seen the values for Organic Matter and Loss on Ignition agree extremely well.

Nitrogen and Carbon - Nitrogen Ratio

As it has been suggested that on the basis of the theory that the carbon : nitrogen ratio in soils is usually 10 the organic matter could be obtained by multiplying the percentage of nitrogen present by 20, the amount of nitrogen was determined after the estimation of the carbon. The results are given in Table 3, which gives percentage of Nitrogen present, Organic Matter obtained by multiplying % Nitrogen by 20 and by multiplying % Carbon by 2, i.e. from Table 2 and also the C: N ratio.

Table 3 - overleaf :-

Table 3

Plot	% Nitrogen	Organic Matter		C/N
		N x 20	C x 2	
1	.43	8.6	10.1	13.1
2	.50	10.0	13.5	16.0
3	.56	11.2	15.0	15.5
4	.49	9.8	15.3	17.4
5	.65	13.0	19.8	17.2
6	.73	14.6	21.2	17.4
7	.79	15.8	21.0	15.9
8	.49	9.8	15.8	14.3
9	.65	13.0	15.3	13.5
10	.54	10.8	12.6	13.0

There is little or no agreement between the organic matter as estimated by the nitrogen content and by the carbon content and also the carbon : nitrogen ratio varies considerably from the ratio 10 : 1. In an investigation into the carbon : nitrogen ratio of soils Leighty & Shorey(45) found that the ratio varied between 3 and 35 and it is considered doubtful whether the organic matter content can be correctly estimated from the nitrogen content of the soil. In the above samples the carbon : nitrogen ratio increases as the % organic matter increases, possibly due to the fact that the organic matter in the higher samples is not so well decomposed as in the lower.

Measurement of Acidity and Lime Requirement

The methods adopted are as mentioned in the introduction grouped into two classes:-

(1) Measurement of intensity or pH

(2) Measurement of the potential acidity or "lime requirement"

(1) May be measured either(a)colorimetrically by means of indicators in a water extract of the soil as in Gillespie's drop ratio method (26) or (b)electrometrically by means of the hydrogen electrode or Biilmann's quinhydrome electrode method (5). This last has been used throughout this investigation in accordance with the procedure recommended by Biilmann and Tovborg-Jensen (6) but using a saturated K Cl calomel electrode instead of the Veibel electrode (69).

Attempts have been made to correlate the pH value with the "lime requirement" but such attempts can naturally only be made on soils of a similar type. Saint (63) found little agreement though Ogg and Dow(52) working on Scottish soils found a certain agreement but with numerous exceptions.

Table 4 gives the pH values of the plots along with the pH values when measured in a normal solution of K Cl as suggested by the International Society of Soil Science:-

Table 4.

Plot	pH(Water)	pH(N.KCl)
1	4.81	4.06
2	4.77	3.98
3	4.68	3.91
4	4.70	3.98
5	4.44	3.68
6	4.49	3.65
7	4.49	3.70
8	4.68	3.87
9	4.75	4.06
10	5.08	4.27

It will be seen that the degree of acidity is extremely high and would be classified with the exception of 1, 9, and 10 under the group "intensely acid" if one adopts the suggestion of Hardy (29) who has proposed that soils might be classified into exchange reaction groups 3 - 3.9, 4 - 4.9 &c. according to their reaction in N KCl.

(2) Measurement of Potential Acidity or "Lime Requirement"

The methods which have been proposed for this estimation may be classified into two groups:-

A. (a) The determination of the amount of base required to raise the pH of the soil to a certain value e.g. methods of Tovborg-Jensen (67) or Hardy & Lewis (30).

(b) The amount of base left unneutralised after treating a definite amount of soil with a definite amount of base for a certain period of time, e.g. Hutchison-McLennan Method (35).

B. The second class is that in which the amount of base required to neutralise the acidity released on treating the soil with a solution of a hydrolysable salt, e.g. sodium acetate or calcium acetate(Kappen's method) or that released on treating the soil with a solution of a neutral salt, e.g. KCl as in Daikahura's method is estimated. From field experiments a factor connecting the amount of base required in the laboratory and the amount of lime which should be applied in the field has been obtained.

Methods in Class 2A (a)

The method adopted in this work is that given by Tovborg-Jensen (67) and also Christensen-Jensen (12) though it has been suggested, in part at least, by others (19) It consists in adding to 10 gms of soil varying amounts of $Ca(OH)_2$ solution, the total volume being made up to 100 c.c. in each case. The suspension of soil and $Ca(OH)_2$ is left to stand for 24 hours with occasional shaking. At the end of this period any excess $Ca(OH)_2$ is precipitated as $CaCo_3$ by passing a stream of CO_2 through the suspension which is then followed by a stream of air which decomposes any bicarbonate which may have been formed. At this precipitation, if there has been any excess $Ca(OH)_2$, the pH should be in the region of 8.4. By plotting pH values against c.c.'s $Ca(OH)_2$ added, a titration curve is obtained from which the amount of lime necessary to bring the soil to any pH can be determined. The authors then recommend that plots should be laid down and limed, as follows:- No lime, $^1/_3$, $^2/_3$, $^3/_3$, $^4/_3$ of estimated lime requirement which is taken as the amount of lime required to bring the soil to a pH of 7. After a certain period, the pH of the plots is again taken and from the results one can obtain a second curve showing pH of plot against lime added and by consideration of the two curves, the laboratory and the field, a factor connecting the amount of lime added in the laboratory and the amount of lime which should be added in the field to give the same pH can be obtained. Unfortunately it was found that certain variations occurred in each plot, chiefly in the organic matter and it was decided to examine the results of the addition of lime in each plot separately.

Certain points in this method should be noted:-

(1) The choice of the pH value 7 The figure 7 was presumably chosen as being the reaction of a fertile soil and because neutral solutions have that pH, but the choice of this figure is arbitrary and has no special significance. In countries such as Scotland many fertile soils have a pH value below 7 as shown by Ogg and Dow (52) who found that the pH of the greater proportion of soils examined (71%) lay between 5 and 6.5. The figure chosen can, of course, be changed to suit the necessary conditions, such as the crop grown &c., assuming of course that a definite relationship between the lime added in the laboratory and that added in the field can be obtained. Other investigators, e.g. Kutschinsky (44) have suggested a pH of 8.5 as suitable, but this would appear to be unnecessarily high.

(2) The precipitation of the excess $Ca(OH)_2$ by means of a stream of Co_2 would only be necessary in cases where an excess of base remained. In practically all the plots it was found that even with the maximum amount of $Ca(OH)_2$ i.e. 100 c.c.s

$^{N}/_{30}$ $Ca(OH)_2$ the pH barely reached the figure 8. As the pH according to Jensen should reach about 8.4 after the excess $Ca(OH)_2$ had been precipitated, it was unnecessary to carry out this part of the procedure.

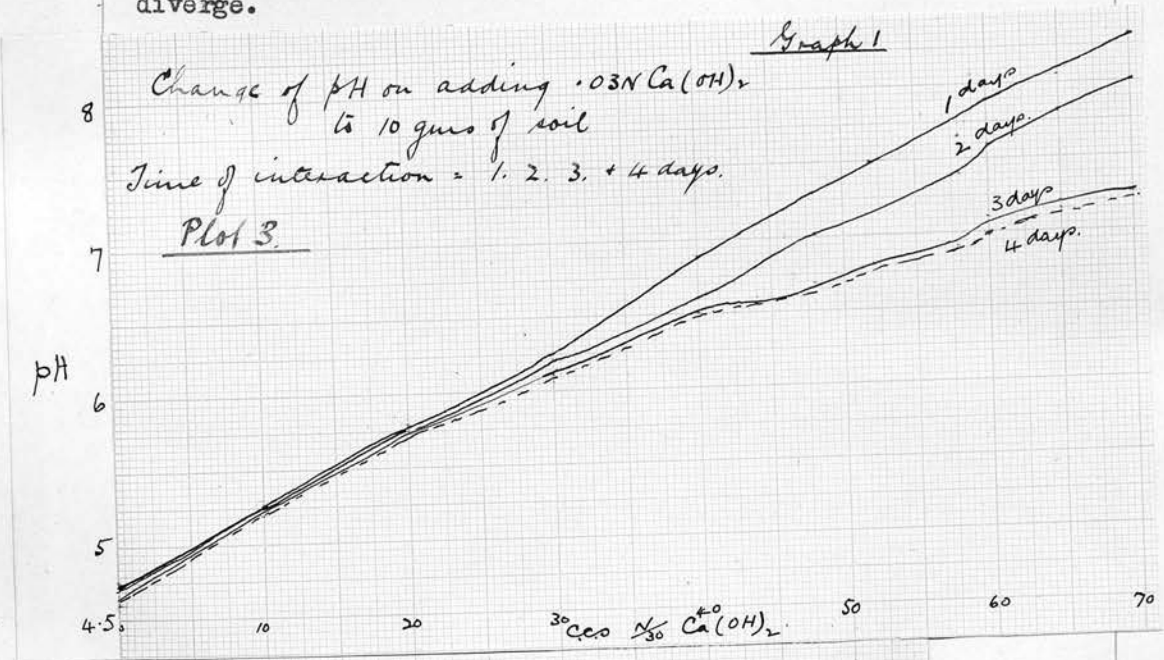
Time required for suspension of soil and $Ca(OH)_2$ to reach equilibrium.

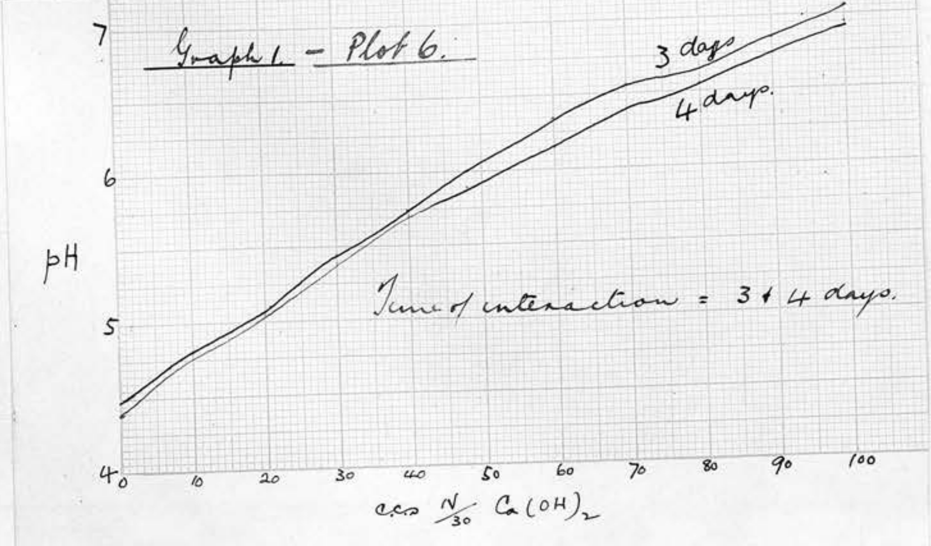
It was found by Jensen(67) that equilibrium in the suspension could be reached in a period of 24 hours at most 48 hours, while Crowther(14) reports somewhat similar results. These findings were not borne out in the course of the present work, as it was found that it was advisable to leave the suspension for a period of at least 4 days before measuring the pH. Table 5 shows the results obtained from the soils from plots 3 & 6 on allowing the suspension to stand for periods of from 1 - 4 days:-

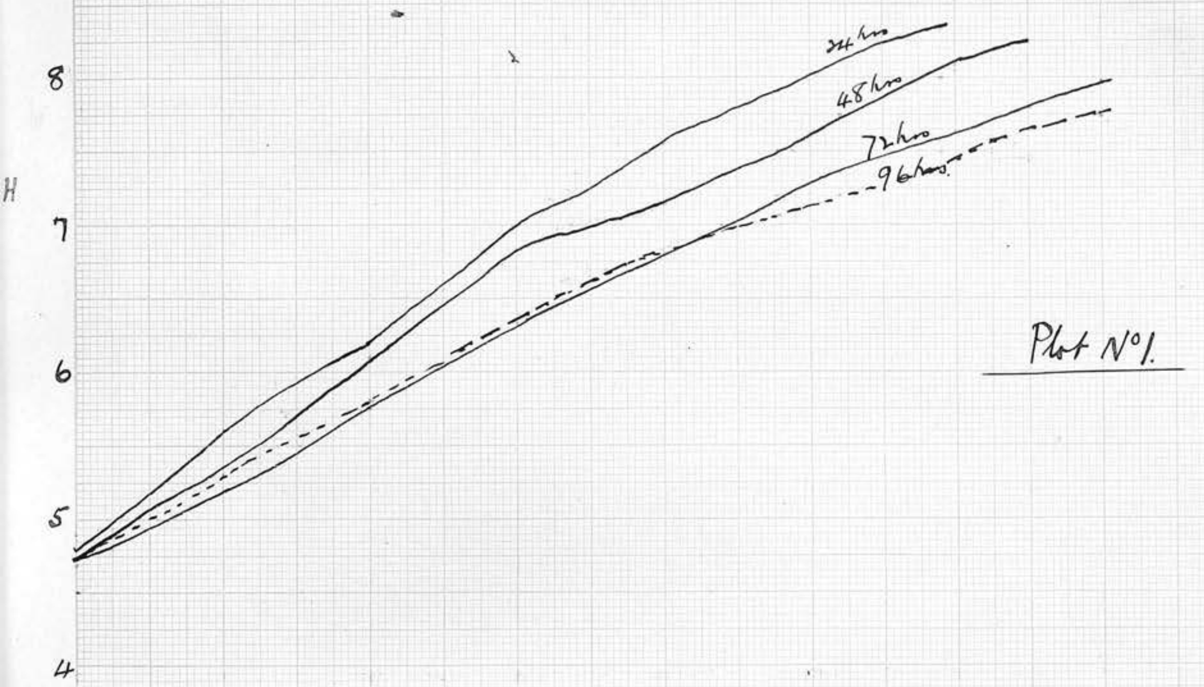
Table 5

pH Plot 3					Plot 6		
c.cs. $Ca(OH)_2$ added	Hrs. 24	Hrs. 48	Hrs. 72	Hrs. 96	c.cs. $Ca(OH)_2$ added	Hrs 72	Hrs. 96
0	4.66	4.61	4.73	4.75	0	4.39	4.40
10	5.33	5.26	5.24	5.27	20	5.05	5.07
20	5.83	5.77	5.71	5.71	40	5.75	5.68
30	6.25	6.20	6.11	6.11	60	6.33	6.13
40	6.90	6.57	6.47	6.48	80	6.65	6.56
52	7.51	7.23	6.80	6.81	90	6.83	6.74
60	7.90	7.60	7.10	6.98	100	7.04	6.95
70	8.29	7.95	7.25	7.25			

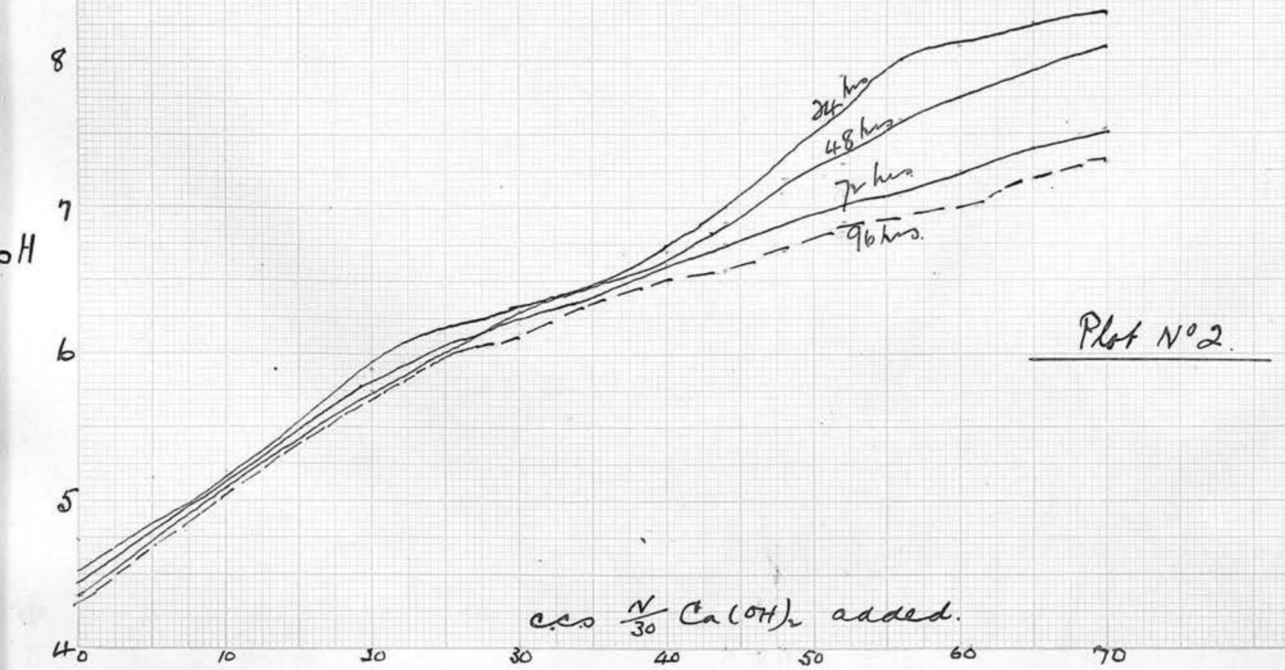
It will be seen that in plot 3 equilibrium appears to have been reached after 4 days, but with the more acid soil from plot 6, the values obtained on the 4th day are still slightly lower than those on the 3rd day. Similar results were obtained in all the plots showing that a period of 48 hours is at least in this case too short a time. It would appear that as long as the final reaction of the suspension is decidedly acid equilibrium is reached fairly quickly, but as it grows more alkaline longer periods are necessary. This can be seen when the graphs, which are typical of the results obtained for each plot, are plotted for the ~~above two~~ plots; 1, 2, 3, & 6. the effect of adding (in plot 3) 30 c.cs $Ca(OH)_2$ to 10 gms. is approximately the same for the four periods, but on adding further amounts the graphs begin slowly to diverge.







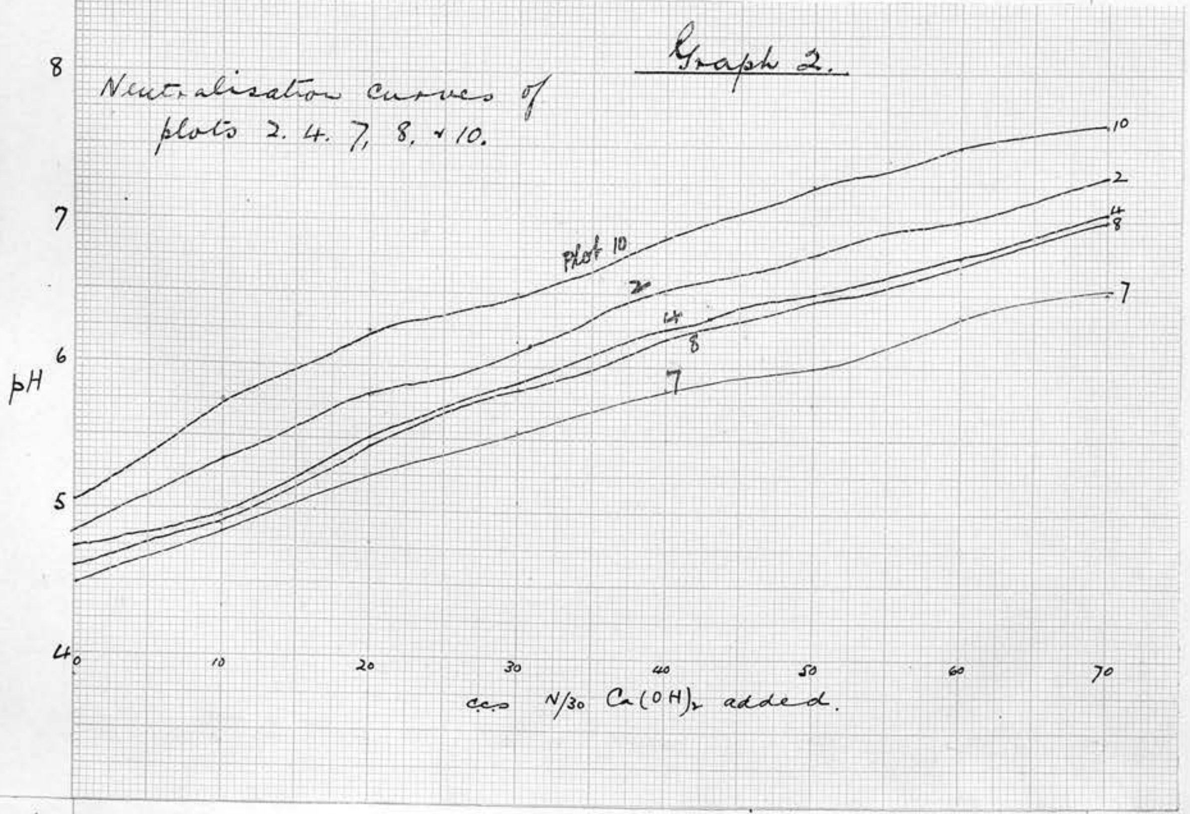
Change of pH on adding $\frac{N}{30}$ $Ca(OH)_2$ to 10 gms of soil
Time of interaction 1. 2. 3. 4. days.



It would appear that 96 hours or even 120 hours would be necessary for the most acid soils to attain equilibrium but the time could be shortened to 48 hours for the less acid soils. A method has been proposed by Hardy & Lewis (30) which apparently shortens the time required. In this a certain amount of 0.2N neutral $CaCl_2$ is added to the soil to which is then added successive amounts of $Ca(OH)_2$ solution, the pH being determined after 3 minutes shaking for each addition. If the pH remains constant after 3 minutes shaking, the time required for each determination would be greatly lessened, but from experiments carried out by Dr. Smith of this college, it appears doubtful if this is the case.

Type of curve obtained and effect of varying amounts of "Humus" on the "buffering power" of the Soil.

The curves obtained, typical examples of which are shown in Graph 2, were smooth and continuous with no definite break at the end point as in the neutralisation curve of a simple acid.



Graph 2.

Neutralisation curves of plots 2. 4. 7, 8, + 10.

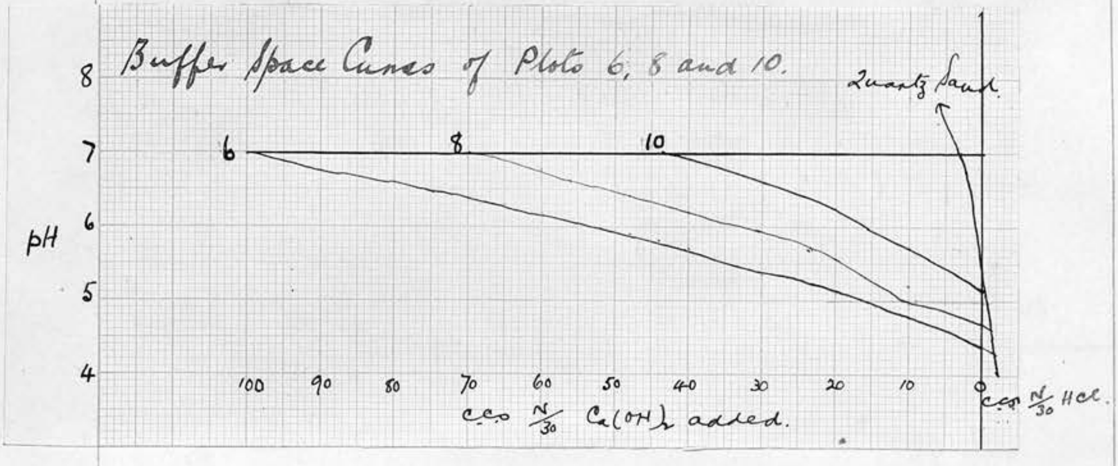
The extent of the buffering action may be gauged roughly by means of the slope of the curve, but owing to the curvature a definite range of pH must be selected or the method suggested by Tovborg-Jensen may be used(67). Briefly, this method consists in treating a substance with no "buffering" action, e.g. a quartz sand with $Ca(OH)_2$ in a similar manner to that already described for soils and comparing the curves obtained. If the soil has no buffering power, which is very unlikely, the two curves will coincide and the greater the buffering power of the soil the greater will be the space between the two curves. The space between is then a measure of the buffer power. If the soil is alkaline, then both it and the sand can be treated with dilute acid. The space between those curves will then be a measure of the buffering action of the soil to acid. In the soils examined, the action against a base is, of course, measured and depends chiefly on the amount of clay and organic matter present. Table 6 shows the initial pH, the percentage of clay and organic matter and the number of c.cs. , N/30, $Ca(OH)_2$ required to bring 10 gms. of soil to a pH of 7 in each of the soils.

Table 6

Plot	Initial pH	% Clay	% Organic Matter	c.cs.$Ca(OH)_2$ to give pH7	Ratio Plot 6 100
1	4.8	22.5	10.1	45	44
2	4.7	22.0	13.5	60	59
3	4.6	22.2	15.0	60	59
4	4.7	22.0	13.5	68	67
5	4.4	25.0	19.8	100	98
6	4.5	26.5	21.2	102	100
7	4.5	22.8	21.0	97.5	96
8	4.7	23.0	15.8	72	71
9	4.7	22.8	15.3	62.5	61
10	5.1	22.3	12.6	44	43

It will be seen that though there is not much difference in the initial pH value, nor in the % Clay, the varying amounts of organic matter cause a large difference in the amount of $Ca(OH)_2$ required. This is also shewn if one adopts the "buffer space" method of Jensen's previously mentioned.

Graph 3 shews the curves obtained for plots 6, 8 and 10 along with the curve obtained for a quartz sand.



As the soils have not all the same initial pH, the buffer space has been measured for each plot between the pH values 5 - 7. The curves for plots 1 - 5, 7 and 9 are given in the appendix. (p86) Table 7 shews the values obtained:-

Table 7

Plot	Buffer Space	Ratio Plot 6 100
1	461	44
2	523	50
3	523	50
4	666	64
5	1000	96
6	1043	100
7	968	93
8	671	64
9	606	58

Plot 6 with highest buffer space has been taken as 100 and the ratio of the others calculated. It will be seen that they agree approximately with the number of c.cs. $Ca(OH)_2$ required to reach pH7. Soil 10 has not been included in the list as, owing to the fact that it had an initial pH value above 5, the buffer power would not be comparable with the other soils. The value actually obtained 323 and ratio 31 is too low.

Amount of Lime ($Ca(OH)_2$) applied per Plot.

In April 1929 the following amounts $Ca(OH)_2$ were applied per plot.

Plot	$Ca(OH)_2$applied	Plot	$Ca(OH)_2$applied
1	Nil	6	Nil
2	24 lbs.	7	24 lbs.
3	48 lbs.	8	48 lbs.
4	72 lbs.	9	72 lbs.
5	96 lbs.	10	96 lbs.

Barley was sewn in May, it being considered that barley, being a crop sensitive to acid conditions would be the most suitable for the purpose. In the following year April 1930 the plots were again sampled, the following results being obtained.

Effect of liming on pH of plots 1 and 2 years after application.

Table 8 (see over)

Table 8.

Plot	pH	Lime	pH (1 year)		pH)2 yrs.)
	Unlimed	Applied	Fresh Samples	Air Dried	Air Dry
1	4.81	0	5.26	4.96	4.63
2	4.77	24 lbs.	5.57	5.51	5.15
3	4.65	48 lbs.	5.70	5.69	5.33
4	4.70	72 lbs.	6.05	6.22	5.79
5	4.44	96 lbs.	6.13	6.25	5.99
6	4.49	0	4.78	4.74	4.32
7	4.49	24 lbs.	5.06	4.90	4.76
8	4.68	48 lbs.	5.34	5.42	5.26
9	4.75	72 lbs.	6.28	6.22	5.85
10	5.08	96 lbs.	7.15	7.21	6.80

In the columns for 1 year after liming, it will be noticed that the reaction of the limed plots has been measured on the wet samples(i.e. immediately after sampling)and on the air dry samples as changes in the reaction of drying soils have been noticed by various observers. Rost and Fieger (61) Joseph and Martin (37) Kelley(40), Snyder(66) consider that the acidity is slightly increased on drying. Aarnio(1) has given results in soils dried at intervals of 100° from 100° to 1000°C. and obtained increased acidity at first followed by decreased acidity, but it is doubtful if a soil dried at such high temperatures would possess the characteristic properties of the soil itself.

Baver(4) found that the reaction was not significantly affected by drying, while Biilmann and Jensen (6) came to the same conclusion. From the figures given on Table 8 it will be seen that,except in the case of plot 1, little or no change has occurred on drying. The values given for the plots 2 years after liming show that the acidity has slightly increased during the year 1930 - 31, the decrease in pH being approximately ·2 - ·3 in each case.

Change of pH during the growing season and comparison of field and laboratory results.

Since the above method of determining the lime requirement depends on comparing the pH in the field with that obtained in the laboratory, the question of the time of sampling arises as it is well known that periodic variations in the hydrogen ion concentration occur throughout the year. Baver (4) reports that the acid soils varied as much as ·92 pH during the period May to September, with a continual increase in acidity the pH returning to approximately the same value in the Spring. Lipman Prince and Blair (47) showed variation in pH during May to November in the soils of barley and soy bean plots which had been treated with sulphur - while Burgess (11) showed variations in plots treated with lime. That the change may be considerable is shewn by Kelley (40) who found that an acid soil might vary by as much as one unit of pH during the growing season. Smith and Robertson(x) have also shewn that wide variations may occur.

Table 9 shows the changes which occurred during the growing season of the year 1930. As the Lime was only applied in April 1929 no measurements were taken throughout that year as it is probable that the lime would not be sufficiently absorbed to give satisfactory results.

Table 9 (see over)

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x Private communication - work unpublished

Table 9

Plot	pH at various times				
	10/4/30	12/7/30.	13/8/30.	19/9/30.	9/4/31.
1	4.96	5.27	5.00	5.04	4.63
2	5.51	5.46	5.72	5.72	5.15
3	5.69	6.03	5.60	5.62	5.33
4	6.22	6.28	5.75	6.52	5.79
5	6.25	6.69	6.62	6.52	5.99
6	4.74	4.71	4.53	4.77	4.32
7	4.90	5.05	5.29	5.00	4.76
8	5.42	6.05	6.40	5.59	5.26
9	6.22	6.36	6.60	6.51	5.85
10	7.21	6.95	7.32	7.43	6.80

~~Private communication - work still in press.~~

Though the results do not show any regular variation, it will be seen that considerable changes occur. Generally speaking the plots become less acid during the growing season with the highest pH,ie. least acidity in either July or August. After August the acidity increases until the following Spring. This is at variance with the results reported by Baver above who found an increase in acidity and suggested that this increase may be due to a dehydration of the colloidal silicates of the soil with consequent decrease in buffer power or to an accumulation of soluble salts in the soil during the Summer. This explanation appears to neglect the effect of the growing plant. The equilibrium which exists between the bases in the soil colloids and those in the soil solution would be influenced to a considerable extent by the growing plant and as the tendency would be for the salts to decrease during the growing season the acidity would tend to decrease. As the plant ceased to to grow the salts would again increase, giving an increase in acidity.

Comparison of field and laboratory results.

The changes in reaction which have been pointed out in the preceding paragraph show that in any investigation where the acidity as measured by the pH value is to be used as a basis of comparison, the soils must be sampled at as far as possible comparative times. It would seem that the best times for such sampling would be in the Spring before the reaction of the soil has been changed by the growing plant, and this time has been adopted in the present work.

The field and laboratory results may be compared in two ways (1) by comparison of the reaction of the original plots with the reaction a certain time after liming, or (2) by determining from the titration curves ofthe limed plots the amount of lime still necessary to bring the pH of the soil to a certain figure.

In order to provide a basis on which to compare the results, the weight of soil to a depth of 9 inches on each plot was determined by weighing 600 c.cs. of each soil. This is admittedly not a very accurate method, but it is probably more accurate than the usual method of assuming a certain weight of soil per acre. That the weights may vary considerably is shewn by Table 10. By determining the weights thus, the amount of lime applied per plot can be calculated in terms of c.cs. $Ca(OH)_2$ per 10 gms. soil and from the titration curve the pH which the soil should give. Table 10 gives the weight of soil per plot, the amount of lime applied, the pH obtained by adding this amount in the laboratory and the pH obtained in the field.

Table 10

Plot	Wt. of Soil per plot	Lime applied	pH from titration curve	pH in field	
				1 yr. after liming	2 years after liming.
1	8410 lbs.	0			
2	7800 "	24 lbs.	6.0	5.57	5.15
3	7800 "	48 "	6.75	5.70	5.33
4	7400 "	72 "	7.2	6.05	5.79
5	7000 "	96 "	7.1	6.13	5.99
6	6700 "	0	-		
7	6560 "	24 "	5.5	5.06	4.76
8	8000 "	48 "	6.4	5.34	5.26
9	8100 "	72 "	7.2	6.28	5.85
10	8410 "	96 "	8.2	7.15	6.80

It will be seen that in no case has the pH in the field increased to the figure obtained in the laboratory, the difference, except in the case of the lowest limed plots 2 and 7, is practically 1. showing that the "lime requirement" measured by this method is considerably less than that under field condition and that therefore the amount of lime actually applied must be greater than the laboratory figures indicate.

The above Table does not give much information regarding this deficiency, but a certain amount of knowledge can be gained by the second method suggested. The method adopted was, as follows. Table 10 gives the pH to which the plots should have risen according to the laboratory figures, but in no case did they do so; from the titration curves of the limed plots the amount of lime necessary to give the first pH value was again calculated and in this way the two figures could be compared. An example from Table 11 which gives the results for all the plots illustrates the method used.

In plot 3 the amount of lime applied, i.e. 48 lbs. should have given a pH of 6.75. A year after liming it was found that it still required 24 lbs. to give a pH of 6.75 so that half as much lime as that originally applied should have been added.

Table 11

Plot	$Ca(OH)_2$ applied	pH in Field	Amount of lime necessary after a year to give laboratory pH
1	0 lbs.	-	-
2	24 "	5.57	5 lbs. $Ca(OH)_2$
3	48 "	5.70	24 " "
4	72 "	6.05	37 " "
5	96 "	6.13	43 " "
6	0 "	-	-
7	24 "	5.06	8 " "
8	48 "	5.24	24 " "
9	72 "	6.28	37 " "
10	96 "	7.15	50 " "

The above Table shows that in each case approximately half as much lime again as that originally applied should be added. This, however, is open to two objections (1) dealing with the time of measuring the pH and (2) which deals more particularly with the calculation above. The effect of the plant on the pH has already been discussed, but the pH apart from that would not remain constant. We must assume that after the application of the lime the pH would rise to a certain maximum and then begin to fall. As can be seen from Table 10 the pH 2 years after liming is lower than that in April 1930 and that if the above calculation were made on the 1931 samples, the lime necessary in excess over that obtained in the laboratory would be still greater than that shown in Table 11. As a fairly common practice is to lime about six months before the crop requiring it is sewn it is probable that to measure the effect after a year would be suitable more particularly as in the above case larger quantities than those used in practice have been applied.

Objection 2. In will be noted in Table 11 that the excess amounts of lime are those calculated from the titration curves and that therefore assuming that this amount would act similarly to the first application half as much again should be added to give the same effect in the field. This means that the amount obtained in the laboratory should be practically doubled to give the same effect in the field. The "lime factor" or the factor by which the laboratory amounts must be multiplied to give the same effect in the field is then in this case roughly equal to 2.

Another method of determining the "lime factor" might be made, as follows:- As the pH of the plots one and two years after liming ~~are~~ is known, one may calculate from the titration curves the amount of lime necessary in the laboratory to give this pH and compare this amount with the amount actually applied. Table 12 shows the results obtained by this method.

Table 12 (see over)

Table 12.

Plot	pH one year	pH two years	lbs. per plot necessary to give this pH in Laboratory		Amount applied	lime Factor	
			1 Yr.	2 Yrs.	Lbs.	1 Yr.	2 Yrs.
1							
2	5.57	5.15	14.5 lbs.	7 lbs.	24	1.7	2.8
3	5.70	5.33	18 "	14 "	48	2.6	3.5
4	6.05	5.79	31 "	26 "	72	2.3	2.8
5	6.13	5.99	50 "	45 "	96	1.9	2.1
6	-						
7	5.06	4.76	12 "	8 "	24	2	3.3
8	5.34	5.26	18 "	16 "	48	2.7	3.0
9	6.28	5.85	39 "	26 "	72	1.8	2.7
10	7.15	6.80	50 "	39 "	96	1.9	2.5

The "lime factor" after 1 year is approximately 2, while after two years it has increased to 3. These results illustrate one of the difficulties mentioned above, i.e. time of sampling .

In their work on Danish Soils Christensen & Jensen(12) found a liming factor of approximately 3(no information given as regards time between liming and time of sampling)which agrees with the two years "lime factor". The factor does not seem to be greatly affected by the amount of organic matter present as the factor for the plots 5 - 8, which contain most organic matter, varies from 1.9 - 2.7 for one year and 2.1 - 3.0 for two years shows roughly the same variation as the other plots. As the "lime requirement" by the laboratory method and in the field may be equally affected by the amount of organic matter, then the factor would be roughly the same for all the soils. For a more correct comparison of the liming factors of different soils, the pH would require to be raised to the same value for each as the factor for a soil whose pH is increased from 5 - 6 may be quite different from the same soil when the pH is increased from 5 - 7, but as can be seen from Table 12 this does not seem to cause any decided change.

B. Lime Requirement Methods of Kappen and Daikahura.

Kappen's Method - Hydrolytic Acidity(39) In this method the amount of base required to neutralise the acidity obtained by treating an acid soil with a solution of an hydrolysable salt usually sodium or calcium acetate is determined and from the amount of base required the lime-requirement of the soil may be calculated. Kappen has suggested that soil acidity may be classified into four groups, viz:- (1) Hydrolytic Acidity, (2) Exchange Acidity, (3) Neutral Salt Decomposition and (4) Active Acidity:-

(1) Hydrolytic Acidity is that developed on treating a soil as above. If a soil is only slightly acid, it will only show acidity when treated with a hydrolysable salt, but not when a salt such as sodium or potassium chloride is used. The acidity which develops with sodium or potassium chloride is known as "Exchange Acidity" and is supposed to be due to the replacement of "Aluminium" by the cation of the salt added, with consequent productions of Aluminium Chloride, which on hydrolysis gives rise to acidity. The "Neutral Salt Decomposition" type is that giving higher acidity than the exchange acidity, while the acidity shown by soils which are practically denuded of replaceable bases is called "Active Acidity".

Explanation of various types :- Hydrolytic Acidity. To explain this acidity Kappen has put forward the following conception. Owing to the hydrolysis of sodium acetate to sodium hydroxide and acetic acid, there will be an excess of OH ions in solution owing to the sodium hydroxide being more strongly dissociated than the acetic acid. The soil absorbs the OH ions which take with them the Na ions leaving an excess of acetic acid in solution giving rise to hydrolytic acidity.

The idea of hydroxyl absorption by the soil has been criticised by Page (54) who has pointed out that there is little or no evidence that absorption by the soil of OH ions or other anions occurs. He is also of opinion that soil acidity is of one kind only and has advanced a theory whereby if one assumes that H ions, as well as the bases of the soil can be replaced by the cation of an added salt, the four types of acidity are what might be expected from soils of increasing acidity, i.e. soils which show an increasing proportion of replaceable H ions in the soil complex. Page's conception is much simpler and appears to explain the various phenomena equally well with that of Kappen's, whose classification of soil acidity into 4 types which merge gradually into one another and which on many soils could not be distinguished from each other, is perhaps unnecessarily complex. This, however, need not debar the method from being extremely useful in practical routine work, as it is possibly the simplest of the many methods which have been suggested for the determination of lime requirement.

The procedure adopted by Kappen is as follows (39) 100 gms. air-dry soil are shaken for one hour with 250 c.cs. normal sodium or calcium acetate. The solution is filtered

and 125 c.cs. of the filtrate are titrated with ·1N sodium hydroxide using phenolphthalein as indicator. The number of c.cs. required, usually denoted as Y 1 is a measure of the hydrolytic acidity.
To determine the lime requirement calcium acetate is used and the titre for 125 c.cs. filtrate multiplied by 4.5 gives the number of double centriers of pure $CaCO_3$ required per hectare.

Kgs. soil
1 double centrier = 2 cwts., 1 hectare = 2·4 acres = 3,000,000

A method embodying the same principle was suggested by Jones (36) in America in 1913. Jones used 5.6 gms. soil, 0.5 gms. calcium acetate and 200 c.cs. water and titrated 100 c.cs. against ·1 N NaOH the number of lbs. CaO per acre required being determined by multiplying the alkali titre by 3600. The amount of soil used is perhaps rather small, but its simplicity in use was a decided advantage over the somewhat laborious method of Veitch (70), which was then in common use.

As in all the methods for estimating lime requirement, the ratio between soil and solution is an important factor thus Csiky and Eperjessy(16) found in investigating 42 soils of varying acidity that the amount of alkali required when the ratio of soil to solution was 1 : 2.5 (Kappen's ratio) varied from 2 - 10 times the amount required when the ratio was changed to 1 : 60. Rath(56) also found variations when the ratio was changed.

Hissink (33) has suggested that the time of shaking might be increased to 3 hours and that the amount of soil used should be 25 gms. or alternatively that the weight of soil used should depend on the amount of clay and humus present.

The estimation of these substances, however, would be laborious in a routine method.

Results using Sodium and Calcium Acetate.

As has been stated either of the above salts may be used, the latter being used for the lime requirement. That the two values may vary considerably is shown in Table 13 which gives the results for the plots unlimed, one and two years after liming.

Table 13.

	Unlimed		CaAc	1 Yr. after		CaAc.	2 Yrs after		CaAc.
Plot	CaAc	NaAc	NaAc	Ca Ac	NaAc	NaAc.	CaAc.	NaAc.	NaAc.
1	40.8	30.6	1.3	-	-	-	-	-	-
2	49.7	37.2	1.3	35.8	25.0	1.4	33.1	24.9	1.4
3	57.8	40.2	1.4	30.1	19.8	1.5	25.3	23.0	1.1
4	57.6	38.1	1.5	31.3	13.8	2.1	25.6	15.7	1.6
5	77.0	52.5	1.5	36.8	15.8	2.2	26.2	13.0	2.0
6	78.6	52.2	1.5	-	-	-	-	-	-
7	75.2	52.7	1.4	62.2	43.7	1.4	56.6	44.5	1.3
8	63.2	43.8	1.4	45.1	28.0	1.6	35.8	23.7	1.5
9	53.7	40.0	1.3	25.6	13.3	1.8	22.2	14.9	1.5
10	35.0	36.4	1	12.7	16.0	2.1	9.0	5.1	1.9

The Table shows that the ratio between the two values is approximately 1.5. This may possibly be due to the fact that calcium, being a more powerful replacing base than sodium, displaces more H. ions and thus gives rise to a greater acidity

Comparison of Christensen-Jensen and Kappen's Method.

As mentioned before, the amount of lime necessary according to Kappen to remove the hydrolytic acidity and to bring the soil to a pH of 7 is obtained by multiplying the alkali titre by 4.5. This can be reduced to lbs. $CaCO_3$ per plot. Further, the number of milligram equivalents per 100 gms. soil necessary to give pH 7 is obtained by multiplying the alkali titre by 0.3. Table 14 gives the lbs. $CaCO_3$ necessary to bring each plot to pH 7; the number of milligram equivalents necessary according to each method, and also the pH which is obtained in the laboratory by adding to the soil the amount of lime required by Kappen's method.

Table 14.

Plot	Lbs. $CaCO_3$ per plot to give pH 7		M. eq. per 100 gms.			pH obtained in laboratory by adding Kappen's amt. $CaCO_3$ to soil
	Kappen	Chris.-Jensen	Hyd. Ac.	Kappen	Chris-Jensen	
1	51	63	8.2	12.2	15	6.6
2	58	78	9.5	14.9	20	6.5
3	68	78	11.6	17.3	20	6.8
4	64	84	11.5	17.3	22.6	6.5
5	81	117	15.4	23.1	33.3	6.4
6	79	114	15.7	23.6	34	6.4
7	74	106	15.0	23.6	32.5	6.4
8	75	96	12.6	19.0	24	6.6
9	65	84	10.7	16.1	20.8	6.6
10	44	62	7.0	10.5	14.5	6.6

As can be seen the amount of lime required by Kappen's method is lower than that required by the Jensen method, i.e. the factor 4.5 is in this case too low. The last column gives the pH value obtained by adding to 10 gms. soil the number of c.cs. $Ca(OH)_2$ equivalent to the hydrolytic lime requirement. The values range from 6.4 to 6.8 with an average of 6.5. In a similar comparison by Kutschinsky(44) it was found that the factor 3 gave good results in bringing the soil to pH 7 and suggests other factors to bring the soil to various pH values 4 for 7.5, 5 for pH 8 and 6.5 for 8.5. He considers that 6.5 would be a suitable factor for bringing a soil into a state of saturation corresponding to natural conditions. With the above soils 5 would be a convenient factor though this would not raise the pH value to anything like that suggested by Kutschinsky.

Effect in field.

The effect of the lime in the field has been compared with the lime requirement obtained in the laboratory in the following way. From the hydrolytic acidity of the unlimed plots the amount of lime necessary to remove this acidity can be calculated(i.e. according to factor 4.5).

The same estimation one and two years after is then made and, if the factor is correct, the difference between the acidity of the limed and unlimed plots should be approximately the amount actually added. Table 15 shows the results obtained:-

Table 15.

Plot	Lbs $CaCO_3$ necessary to remove hyd. ac.	Lbs. necessary after		amount apparently added after		Amt. actually added	Factor Yr	Yrs.
		1 Yr.	2 Yrs.	1 Yr.	2 Yrs.		1	2
2	58	42	38	16	20	32	2	1.6
3	68	35	29	33	39	64	2	1.7
4	64	35	28	29	36	96	3.3	2.7
5	81	38	28	43	53	128	3	2.4
7	74	61	56	13	18	32	2.4	1.8
8	75	54	43	21	32	64	3.1	2
9	65	31	26	34	39	96	2.8	2.5
10	44	16	11	28	33	128	4.4	4.0

The results show that the effect in the field is again much less than that in the laboratory; from the factor given in the last two columns the effect is roughly $\frac{1}{2}$ - 1/3. This agrees with the results obtained in the previous method and shows that in very acid soils the factor 4.5 is too low for the complete removal of the hydrolytic acidity. It is probable however, that many soils would be quite fertile even though they still showed a slight hydrolytic acidity.

Exchange Acidity (Kappen(39) and Daikahura(17).

As previously mentioned exchange acidity is the acidity obtained by treating an acid soil with a neutral salt, e.g. Potassium Chloride. This acidity is supposed, at least, in the case of mineral soils, to be almost entirely due to the ~~pressure~~ presence of soluble aluminium salts, which, on hydrolysis give rise to acidity - the acidity observed being practically the same as that which would be obtained from the same amount of aluminium chloride solution. This, of course, does not hold good with humus soils. The method is, as follows:-

100 gms. air-dry soil are shaken with 250 c.cs. N KCl for 1 hour. After filtering 125 c.cs. of the filtrate are treated with 0·1 N NaOH using phenolphthalein as indicator and boiling to remove the CO_2. This titre is denoted as Y1 the exchange acidity. The so-called "total acidity" is then obtained by multiplying this titre by 3.5and the amount of calcium carbonate necessary to remove this acidity is obtained by multiplying again by 1.5. This gives the weight calcium carbonate required in double centriers per hectare. Instead of multiplying by 3.5 to obtain the total acidity, it may be more accurately determined by replacing the first 125 c.cs. removed ~~per~~ for titration by another 125 c.cs. N Kcl shaking 1 hour, filtering

and titrating 125 c.c. This second titre is uaually denoted by Y2 & S the total acidity is given by:-

$$S = 2\left(Y_1 + \frac{A1}{1 - K}\right) \quad \text{where } S = \text{total acidity}$$

$$A_1 = Y_2 - \frac{Y_1}{2}$$

$$K = .85 \text{ a constant}$$

The total acidity is the acidity obtained if one kept replacing 125 c.c. with fresh amounts until no more acidity was observed. A similar method had been previously proposed by Hopkins(34) who used 100 gms soil and 250 c.cs. 5% sodium chloride, the total acidity being obtained by using the factor 4. Later, potassium nitrate was found more reactive and substituted for the sodium chloride.

As in the case of the hydrolytic acidity different results are obtained on varying the ratio soil : solution and also on varying the concentration of the salt used. In the above it would probably be an advantage to reduce the amount of soil used and use 200 c.cs. Potassium Chloride. This would be of considerable practical use since, if successive titrations were to be made, it is easier to remove and add 100 c.cs instead of 125 c.cs. Table 16 shows the results obtained using 80 gms. soil and 200 c.cs. Kcl., 100 gms. soil and 250 c.cs. Kcl, and the "total acidity" using the factor 3.5 and Daikahura's formula.

Table 16 (overleaf)

Table 16.

Plot	80 gms.soil 200 c.cs Kcl.				100 gms. soil 250 c.cs. Kcl			
	Y_1	Y_2	$3.5Y_1$	S	Y_1	Y_2	$3.5Y_1$	S
1	12.6	7.0	44.1	34.0	14.8	8.7	51.8	46.2
2	16.7	9.7	58.5	50.8	17.9	11.1	64.1	64.1
3	17.8	10.4	62.3	55.7	19.7	11.4	68.9	63.4
4	17.4	11.0	60.9	65.5	20.4	11.7	71.3	61.2
5	25.2	15.3	88.1	85.8	25.4	15.3	89.0	85.9
6	23.2	13.9	81.2	77.5	27.0	16.9	94.6	99.1
7	23.7	13.9	82.9	74.8	29.3	18.2	102.6	104.8
8	18.9	10.5	66.1	51.9	23.0	13.9	80.1	77.2
9	15.5	9.7	54.2	51.6	19.1	11.3	66.8	59.4
10	8.3	4.7	29.0	23.4	10.4	6.3	36.4	35.4

It will be seen that there is on the whole a satisfactory agreement between the two methods of estimating the total acidity, i.e. $3.5Y_1$ and S. With regard to the acidities measured for 80 gms and 100 gms., while the acidity for 80 gms. is naturally less than that for 100 gms. it is higher than the ratio 4 : 5 showing it would not be possible to assume that the"total acidities" would be proportional to the amount of soil used even if the ratio soil : solution were kept the same in each case.

Comparison of amounts of lime required by above method with the two previous methods.

Table 17 shows the amount of lime required by the three methods mentioned calculated in lbs. $CaCO_3$ per plot.

Table 17.

Plot	Lbs. $CaCO_3$ necessary to remove Exchange Ac.	 Hydrolytic Ac.	$CaCO_3$ to give pH 7.
1	19.4	51	63
2	25.0	58	78
3	24.7	68	78
4	22.6	64	84
5	30.1	81	117
6	33.3	79	114
7	34.4	74	106
8	30.9	75	96
9	24.1	65	84
10	14.9	44	62

The amounts necessary in the case of the exchange acidity are from $^1/2$ - $^1/3$ - those necessary for the hydrolytic acidity and practically a $\frac{1}{4}$ of the $CaCO_3$ necessary to give a pH 7.

Effect in the Field.

It was not possible to obtain any actual data on the amount necessary to remove the acidity in the field as compared with that required in the laboratory, as the lime applied, except in two cases, was greatly in excess of the quantity required. Table 18 gives the exchange acidity as determined 1 and 2 years after liming.

Table 18 (see over)

Table 18.

Plot	Y_1 1st Year	Y_1 2nd Year	Plot	Y_1 1st Year	Y_1 2nd Year
2	3.4	3.0	7	12.5	10.2
3	.9	.76	8	2.4	1.4
4	1.9	.31	9	.6	.30
5	1.0	.52	10	.4	.25

Only in plots 2, 32 lbs. applied for 25 required and plot 7 32 applied for 34.4 required can exchange acidity be said to exist, i.e. from these two cases more than the laboratory amount would be required, but it would be unwise to draw any inference from so few samples.

While the exchange acidity has disappeared from plots 3, 4, 5, 8, 9, and 10 it is apparent that from the previous data given, that these plots except perhaps 10 are still acid. As a further test the pH to which the soil would be raised by adding in the laboratory the proportionate amounts of calcium hydroxide could be determined from the titration curves. The results are as follows:-

Plot	pH	Plot	pH
1	5.5	6	5.3
2	5.7	7	5.6
3	5.6	8	5.7
4	5.5	9	5.5
5	5.5	10	5.7

These show that the pH would not be raised above 5.7 and as the effect in the field would be less, the pH would be less than this figure, showing that the amount of lime by this method is too small. If the exchange acidity is due entirely to the presence of aluminium compounds in solution then exchange acidity would not be shown above pH 5.5 as above this pH aluminium salts would be precipitated. Goy(27) has suggested that this soil may show slight exchange acidity with phenolphthalein which changes about pH 8.2 - 10 and that methyl red, which changes from 4.6 - 6, should be used. The difference shown by this change in his results is very small and would not greatly affect the amount of lime required In general the above results show that the removal of the exchange acidity is not enough and that greater amounts of lime are required. Gehring(22) in a study of the method considers that while the method may be of use in sandy soils it is not of much use on clay mineral soils or on humus soils.

Hutchison-McLennan Method for Lime Requirement(35)

In this method a definite amount of soil is shaken with a solution of standard Bicarbonate and the amount of Calcium taken up by the soil determined by titration of the Bicarbonate before and after shaking. The method has been subjected to critical analysis by Fisher(19) who showed that soils containing free $CaCO_3$ may give a lime requirement, that variations occurred on changing the ratio of soil and solution and on varying the size of soil particle, and that as the pH of the bicarbonate solution is about 6 the soil could not be said to be neutralised when in equilibrium with an acid solution. Crowther & Martin(15) also pointed out this last defect and that therefore the method underestimates the amount of lime required to give a neutral soil in practice. They recommended that three amounts of soil should be used 10, 15 and 20 gms. with a definite volume of bicarbonate solution and the lime requirement determined by interpolation to some arbitrary concentration. MacIntire(49) has also suggested a method involving the use of calcium bicarbonate whereby the soil after treatment shows no lime requirement as in the case with the above method. The soil is treated with bicarbonate, evaporated to dryness, and the residual carbonate decomposed by phosphoric acid, the CO_2 evolved being estimated. This method, however, is rather cumbrous for routine use.

Despite the defects of the Hutchison-McLennan method, it is widely used in this country, possibly owing to the fact that with many of the types of soils found it has given satisfactory results for the crops usually grown.

The method used was as follows:-

10 gms. soil were shaken with 200 c.cs. ·02N calcium bicarbonate for three hours in an end-over-end shaker, the containing bottle having been previously filled with CO_2 to prevent precipitation of calcium carbonate. The suspension was then filtered and an aliquot portion titrated with acid using methyl red as indicator. The results obtained calculated in lbs. $CaCO_3$ per plot are given in Table 19 along with the amounts given by the previous methods.

Table 19

Plot	Lbs. $CaCO_3$ per plot				pH on adding H. McL amt. in laboratory.
	H. McL.	Hyd. Ac.	Exc. Ac.	to give pH	
1	45	51	19.4	63	6.4
2	50	58	25.0	78	6.4
3	54	68	24.7	78	6.5
4	50	64	22.6	84	6.3
5	68	81	30.1	117	6.2
6	65	79	33.3	114	6.1
7	54	74	34.4	106	6.1
8	51	75	30.9	96	6.1
9	43	65	24.1	84	6.1
10	35	44	14.9	62	6.3

In the four methods given it will be seen that the Hutchison-McLennan results are lower than the hydrolytic acidity and much lower than the amount required to give pH 7, especially in the more acid plots 4 - 8. As the amounts obtained by the Hutchison-McLennan method depend partly on the final concentration and pH value of the bicarbonate solution and as this concentration and pH will be the lower the more acid the soil, the divergence between the amount by this method and those required to give a definite pH, in this case 7, will be the greater as the acidity of the soil increases. In the last column is shown the pH which would be obtained in the laboratory by adding the amounts of lime obtained by the Hutchison McLennan method. They vary from 6.1 - 6.5 showing that the amounts added are too small, at least on the very acid soils under investigation.

<u>Effect in the field.</u>

Table 20 shows the lime requirement for the unlimed plots and for the plots one and two years after liming in lbs. $CaCO_3$ per plot.

Table 20.

Plot	Unlimed	Limed 1st Yr.	 2nd Yr.	Diff. 1st Yr.	 2nd Yr.	Amount $CaCO_3$ added
2	50	30	28	20	22	32
3	54	28	24	26	30	64
4	50	20	15	30	35	96
5	68	21	15	47	53	128
7	54	40	35	14	19	32
8	51	24	22	27	29	64
9	43	16	16	27	27	96
10	35	Nil	Nil	-		

It will be seen that the acidity has decreased slightly during the second year, but only slightly, similar results being found by the hydrolytic acidity measurements. It is rather curious that while the acidity as measured by the pH value has increased slightly during that time, the acidity measured by the above two measurements has slightly decreased. In plots 4, 5, and 9 more lime was added than was required by the Hutchison McLennan method yet a considerable lime requirement still exists measured by the same method. If we compare the differences between the unlimed plots and the limed plots, i.e. the amounts lime presumably added with the amounts actually added we find the ratio between the laboratory : field effect varies between 2 & 3, which is comparable with the results already obtained.

The Exchangeable bases. - The amount of bases (including Aluminium in the unlimed soils and the effect of liming thereon

The replaceable bases in each of the plots are shown in Table 21 The calcium and magnesium were estimated by Hissink's method (32) by leaching with sodium chloride; the sodium and potassium by leaching with ammonium chloride, Prescotts Method(55), and the ammonium by leaching with sodium chloride according to McLean and Robinson's method(51). The exchangeable hydrogen is dealt with in a later section. The method of Gedroiz(20) in which the soil is leached with N Barium Chloride until the leachings give the same colour with methyl red as the original solution, the leachings being then titrated with 0·02 N ~~Hcl~~ NaOH and the exchangeable hydrogen estimated was tried, but the results were so indeterminate that the method had to be abandoned. Other methods have been suggested and these are discussed under the section on Saturation Value. The amounts of exchangeable bases are given in milligram equivalents per 100 gms soil except aluminium, which is given as a percentage.

Table 21.

Plot	% Al_2O_3	Ca	Mg.	K.	Na	NH_4
1	.06	5.2	.87	.11	.95	.09
2	.10	4.2	1.03	.16	.75	.14
3	.099	3.6	1.03	.18	.80	.09
4	.101	3.5	.84	.15	.80	.12
5	.154	3.2	1.0	.18	.91	.12
6	.138	4.2	1.1	.15	1.32	.11
7	.129	3.5	.94	.24	.86	.15
8	.088	4.5	.87	.13	.88	.08
9	.086	5.7	.92	.16	.93	.13
10	.016	8.8	1.41	.10	.72	.15

The amount of bases is small showing the highly unsaturated nature of the soil. As the calcium decreases the aluminium increases with, as shown from the other tables, a corresponding increase in acidity.

The amount of potassium is extremely small and is much lower than the amounts of Magnesium and Sodium. Owing to the difficulty in determining such small amounts, it is doubtful if too much reliance can be placed on the results.

Position of Aluminium.

In recent years the part played by Aluminium in plant life has been th e subject of much experiment and discussion, but it cannot be said that its role in soil reaction or in plant metabolism has been definitely established. The cause of the presence of Aluminium in neutral salt extracts is still a matter of controversy. Suggestions have been made that soluble aluminium salts may be formed during the process of nitrification(3) or by the formation of sulphates due to the oxidation of sulphur as the result of bacterial action(2) but this would presume the presence of water soluble aluminium salts, which has been considered doubtful. Denison(18) found that the aluminium obtained by leaching with a solution of potassium nitrate did not diffuse through a collodion membrane and concluded that the aluminium was present as soluble $Al(OH)_3$ (hydrosol); Knight (43) also found aluminium present in the colloidal form. McGeorge(50) in experiments in Hawaiin soils found soluble crystalloid salts of iron and aluminium in soils with a pH below 5.8 and in soils with a pH above 6 only the hydrosol form was present though these pH limits would appear to be too high for soils containing soluble aluminium salts.

Its presence in neutral salt extract has also been considered due to a secondary reaction of the salt. According to this view the acidity resulting in the displacement of hydrogen ions from the adsorptive soil material then dissolves alumina from the alumino-silicic complex and that the aluminium is not "replaced".

The greater the acidity then, in the case of mineral soils, the greater the amount of aluminium dissolved by the active salt a process which is helped by the fact that the alumino-silicic complex tends, as unsaturation of the soil increases, to decompose into its constituent oxides. Page(54) has suggested that if this is so, then hydrogen ions and aluminium hydroxide may exist together in equilibrium in solution and if the concentration of hydrogen ions increases due to their replacement by some added cation, then the Aluminium may also increase due to a further decomposition of the alumino-silicic complex. When an acid soil is leached with successive quantities say 500 c.cs. of a solution of a neutral salt aluminium is usually found in decreasing quantities in each leaching. Such being the case, it is improbable that the aluminium exists in a cationic exchangeable condition, but rather that its appearance is due to some such method as that suggested by Page or that it is dissolved by the acid formed by displacement of H ions from the soil complex.

The question of aluminium has also gained importance from the fact that it has been considered toxic to plant life and that the poor growth obtained on acid soils is due not only to the acidity, but alsoto the presence of aluminium. A number of investigators(3), (7), (13), (62), have described experiments showing the toxic effect of Aluminium and Hartwell & Pember(31) in experiments on barley and rye came to the conclusion that the beneficial effect of manuring with phosphates and lime may be due as much to the precipitation of the active aluminium as to the reduction of the acidity.

On the other hand Line(46) considers that Aluminium is not toxic to plants. He considers that a substance like aluminium which is so widely distributed and in such close contact with plant absorbent substances can hardly have an injurious effect and that it is doubtful whether Aluminium can exist in a soluble form in a soil of pH above 4.5, while the existence of water soluble aluminium salts in soils less acid than pH4 has not yet been definitely proved. From his experiments he concludes that the toxic effect of aluminium reported by other workers is due to the increased acidity caused by the partial hydrolysis of its salts;to their buffering action which prevents the decrease in acidity which an actively growing plant causes in a culture medium ,and also to the precipitation of phosphate as aluminium phosphate and consequent phosphate starvation.

Stoklasa(65) considers that Aluminium has an important physiological function in plant life and that unless present in fairly high concentration is not toxic to plants. In his experiments he found that while in water or artificial cultures very small quantities of aluminium were injurious to plant life, in soils this was not the case. As a general rule the amount of Aluminium below a certain limit which could be added to the soil without having an injurious effect on the plant depended on the amount of calcium present in the soil and on the carbon present as organic matter and that,in pot growth tests, all the plants tested took up Aluminium in larger or smaller quantities when applied in an assimilable form. He also found that,when sterilised and neutralised peat was added to sand cultures, an amount of aluminium could be added without injury to the plant, which proved fatal when added to the sand without peat. He maintained that there was no experimental foundation for the statement that Aluminium compounds have an injurious effect on plant growth.

In order to determine what connection there might be between the exchangeable calcium, the aluminium present, and crop growth, a number of samples were taken in the field where the barley(mentioned in introduction)had partially failed and also from a field in which clover and barley grew well and from a field in which oats were failing. In each sample the amount of exchangeable calcium, the amount of aluminium in an ammonium chloride extract, and the amount of "so-called"active" aluminium. were determined This is the aluminium dissolved by a dilute solution of acetic acid according to the method of "Burgess(10) The results grouped together for comparison according to crop growth are given in Table 22.

Table 22

Soil	% Exch. Ca	% Active Al_2O_3	Al_2O_3 - NH_4Cl Extract	Crop
179	.056	.15	.044	No Barley
188	.197	.033	.020	Good "
180	.062	.015	.041	No Barley
182	.067	.018	.048	do.
181	.069	.016	.041	Barley poor
184	.08	.10	.060	No Barley
183	.13	.05	.002	Barley fairly good
186	.059	.04	.001	No Barley
185	.17	.017	.001	Barley F. G.
187	.09	-	.01	do.
16	.079	.016	.001	Good Clover
17	.113	.013	.009	" " & Barley
18	.054	.065	.024	Oats Failing

Considering first the exchangeable calcium, there is a direct correlation in each group between the amount of exchangeable calcium and crop growth. In all cases where the Barley has failed the amount of exchangeable calcium is very low though the amount varies over the whole group of samples In different groups the amount of calcium which supported plant growth seems inadequate in the case of another soil, e.g. the barley failed in sample 184 which has .08% Calcium, whereas fairly good barley was obtained from soil 187 which has .09%

Calcium. The same peculiarity may be noticed in soils 16 and 18, both of which have a low Calcium content, but while 16 gave good crops those on 18 were failing.

The cause for this variance seems to be closely connected with the amount of Aluminium present. Where the aluminium is high and calcium low the barley has failed. In soils 180, 181, 182 where these conditions are present the barley has failed altogether or else was very poor. In samples 186 and 185 though the aluminium by ammonium chloride extraction is low and the same in both the low Calcium content of 186 seems to have resulted in the failure of the crop. In samples 16 and 18, the opposite appears to hold good: though in both the Calcium is low the crop in soil 18 where the Aluminium is high is failing. Soil 188 also on which the best barley was obtained has a fairly high aluminium content, but the calcium is also high.

Although the above results are too few to say with any degree of definiteness that Aluminium is toxic to barley they would at least appear to indicate that it has an injurious effect. It would also appear that a higher percentage of Aluminium may be tolerated when the calcium is high than when it is low, i.e. between fairly low limits of calcium content. The chief factor, however, in the failure of the crop is probably the lack of Calcium.

The effect of various cations on the plant has been recently published by Gedroiz(21) He has fully saturated soils with a number of different cations and has noted the effect of growing plants, mostly oats, on the saturated soil, and on the saturated soil treated with Nitrogen and Phosphate & withCalcium Carbonate, Nitrogen and Phosphate. From his observations he came to the conclusion that when calcium carbonate was added to the soil in addition to nitrogen and phosphate, a normal crop similar to that in the original soil was obtained only in the soil which had been saturated with Hydrogen. In the soils saturated with magnesium, manganese, iron and aluminium, a crop was obtained smaller however than in the original soil. The plants perished entirely in the soils saturated with the other bases Ammonium, Sodium, Potassium, Cadmium, Barium, Copper, Cobalt, Nickel, both in the presence and absence of Calcium Carbonate. The bases Magnesium, Manganese, Iron and Aluminium when fully saturating the soil were toxic to plants, but to a less extent than reported previously. Of these bases Magnesium and Aluminium were less injurious than Manganese and Iron. He found that Calcium is essential to the life of the plant and that apparently none of the other elements tested except Strontium could take its place.

The experiments with Aluminium do not seem to be absolutely conclusive. No crop was obtained when the soil was fully saturated with Aluminium, but a certain growth was obtained after Calcium Carbonate had been applied. In the first place the soil saturated with Aluminium would probably contain Aluminium in a soluble form, but when Calcium Carbonate was added the Aluminium would be precipitated and would not be in an assimilable form. The question also remains "What is meant by a substance being toxic to plants?". If one saturates a soil completely with say Aluminium and no crop results, one is perhaps not entitled to say that Aluminium is toxic to plants, but only to assume that Aluminium alone does not support growth. By toxicity in the usual sense, one assumes that a certain amount of the toxic substance usually small, is fatal to a plant even when elements necessary for its growth are present. The result of his experiments appear to be that as regards Calcium and Aluminium the chief condition necessary for plantgrowth is that there should be a sufficiency of exchangeable calcium(he found that the plant could not utilise unexchangeable calcium) and that if this were the case the injurious effects of Aluminium were greatly lessened.

<u>Increase in Calcium and Decrease of Aluminium due to Liming</u>

Table 23 shows the increase in Calcium and the decrease in amount of Aluminium in each of the plots one and two years after liming:-

<u>Table 23</u>

Plot	% Al_2O_3			% Exch. Ca.			Increase in Exch. Ca.
	Unlimed	1 Yr.	2 Yrs.	Unlimed	1 Yr.	2 Yrs.	
2	.10	.0056	Nil	.084	.221	.228	.144
3	.099	Nil	"	.073	.273	.288	.211
4	.101	"	"	.069	.408	.392	.323
5	.154	"	"	.064	.526	.560	.494
7	.129	.068	.02	.070	.162	.207	.137
8	.088	Nil	Nil	.091	.262	.316	.225
9	.086	"	"	.113	.438	.421	.308
10	.016	"	"	.176	.540	.520	.344

It will be seen that after two years no Aluminium except a small quantity in No. 7 was obtained and that the exchangeable calcium has increased considerably with little difference between the amounts for the first and second years showing that most of the absorption had taken place during the first year. The amount of Calcium absorbed in lbs. Calcium per plot and as a percentage of the amount applied is given in Table 24.

Table 24.

Plot	Lbs. Ca absorbed	Lbs. Ca. applied	Percentage absorbed
2	10.7	13	80
3	16	26	60
4	24.5	39	63
5	35	52	67
7	9	63	69
8	18	26	69
9	26.2	39	67
10	30.6	52	60

Showing that the Calcium absorbed is between 60 and 70% of that applied.

Effect of Liming on other bases.

It had been proposed to determine the effect of liming on the amounts of the other exchangeable bases present, but the amounts in the unlimed plots were so small that the effects were barely noticeable. The results are given in Table 25 in m. eq. per 100 gms. soilfor the limed and unlimed soils.

Table 25 (see over)

Table 25

Plot	Ca. Unl.	Ca. L.	Mg. Unl.	Mg. L.	K. Unl.	K. L.	Na Unl.	Na L.	NH_4 Unl.	NH_4 L.	Total Unl.	Total L.
1	5.2	-	.87	-	.11	-	.95	-	.09	-	7.22	-
2	4.2	11.1	1.03	.86	.16	.30	.75	.75	.14	.14	7.28	13.15
3	3.6	13.7	1.03	.24	.18	.12	.80	.98	.09	.17	5.70	15.21
4	3.5	21.4	.84	.08	.12	.15	.80	.90	.12	.17	5.40	22.67
5	3.2	26.3	1.-	.16	.18	.12	.91	.86	.12	.16	4.41	27.60
6	4.2	-	1.1	-	.15	-	1.32	-	.11	-	6.88	-
7	3.5	8.1	9.4	.64	.24	.16	.86	1.08	.15	.16	5.69	10.14
8	4.5	13.1	.87	.52	.13	.16	.88	.93	.08	.09	6.46	14.82
9	5.7	21.9	.92	.64	.16	.15	.93	.80	.13	.10	7.84	23.59
10	8.8	27.0	1.4	.62	.10	.10	.72	.76	.15	.12	11.18	28.60

The amount of Magnesium has decreased, the decrease being greater the larger the increase in the calcium. With regard to the others, there appears to be little or no difference, but this was perhaps to be expected considering the amounts originally present ~~per cent~~. The increase in Calcium has taken place almost entirely at the expense of the exchangeable hydrogen. Various methods have been suggested for the determination of hydrogen and it is proposed to deal with this in the next section.

Exchangeable Hydrogen, Stauration Value and Degree of Saturation of the Soil.

It has been shown by Hissink(32) that the determination of the amount of exchangeable bases in the soil is of little use in characterising that soil unless the total amount of base which the soil can absorb is known, and that it is the relation between these two factors which is important. This relation is called the saturation value(usually denoted by V)and is the ratio of the absorbed bases actually present (S) to the total quantity T which the soil is capable of binding S and T being expressed as equivalents, i.e. $V = \frac{100\ S}{T}$

Methods of determining S

The determination of V as seen above depends on the values of S & T and various methods are in use for their estimation. S may be determined by summing the bases which have been determined separately, as already described. As this is a somewhat tedious process, shorter methods have been proposed, e.g. Kappen's method(38) whereby the soil is shaken with 0·1N Hcl and by titration with Soda, the amount of Hcl absorbed by the soil is calculated. From this a value for S is obtained, but of course gives no information as to the relative amounts of each base present, and is only applicable to carbonate face soils.

In the soils investigated here S is the sum of the bases which were estimated separately.

Methods for determining T

The direct leaching method of Gedroiz, which has been mentioned already gives the hydrogen or T - S and if S were known T can be obtained, but the method is not satisfactory and other methods have been adopted.

(1) A definite amount of soil is treated with increasing amounts of an alkaline base e.g. Barium Hydroxide and the amount remaining in solution after a certain period estimated. This gives the amount of H ions present or T - S and hence T if S be known. Hissink's method(32) is typical of this class.

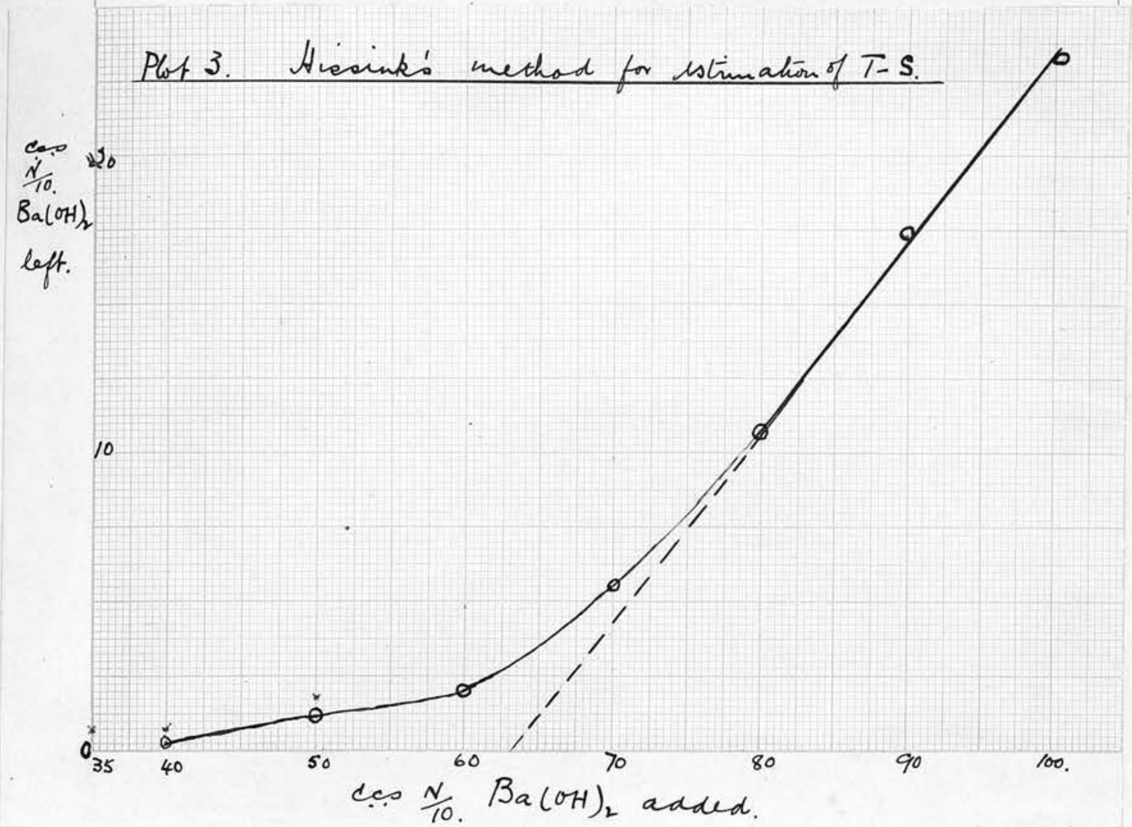
(11) The soil is leached with some neutral salt

solution till all the bases have been replaced by the cation of the leaching solution. This is in turn leached out and the amount estimated. The replacing cations are preferably those which are not already present in the soil or only in small quantity and which may be easily estimated . Such are Ammonium, [Kelley's method(41)] and Barium, [Bobko and Askinasi's method (8) (9).] The method of Ghering and Wehrmann (23) (24) in which the Hydrogen is replaced by Calcium, the Calcium being then estimated by leaching out with Sodium Chloride, and the method of Page and Williams(53), in which the Hydrogen is replaced by the Calcium of $CaCO_3$, the Calcium absorbed being then estimated are also examples of the class in which the Hydrogen i.e. T - S is estimated.

The methods used in this work were those of Hissink's, Bobko and Askinasi, Kelley, Gehring and Wehrmann and Page and Williams.

Hissink's Method.

Varying amounts of .1 N Barium Hydroxide were added to 10 gms of soil. The suspensions were allowed to stand for three days and on the fourth the amount of Barium Hydroxide left unabsorbed was estimated by titrating an aliquot portion of the supernatant liquid with standard alkali. The quantities Barium Hydroxide added are plotted against those remaining in solution. The straight part of the curve is then drawn and produced until it cuts the X-axis; the point of intersection expressed in m. eqs. gives T - S. As an example the graph obtained from plot 3 is shown. The graphs of the other plots are given in the appendix. [pp87-91]


Plot 3. Hissink's method for estimation of T-S.

The above method has been criticised on various grounds.

(1) As in all equilibrium reactions various results are obtained according to the amount of soil used. Hissink considers that enough soil to give 2 gms. of Clay should be taken. As the above soils contained 20% Clay 10 gms. were taken.

(11) Kutschinsky(44) considers that the method is artificial in that the soil is treated with a strongly alkaline solution (pH(11) which does not correspond to natural conditions and that neutralisation of the complex may lead to purely physical absorption of barium oxide ; further, the fact that many soils do not readily yield clear solutions makes titration difficult. He found that results for T were much too high and V therefore too low.

Gericke(25) also found T by this method much higher than that given by other methods.

Kelley(42) has pointed out that the barium hydroxide is absorbed by Silica, Alumina, and Iron Oxides thus giving too high a value for the absorption.

Certain difficulties are also met with in the practical use of the method. Theoretically after the first few points have been plotted, the remainder should be in a straight line. This is not always the case as can be seen from the various graphs. Also the straight line may depend on the number of points plotted, i.e. if say 7 points are plotted the last 3 may be in a straight line, but if 9 are plotted, the last 3 though giving a straight line may not be in the same line as the first, e.g. in plots 4 & 5 entirely different results could be obtained according to the points chosen. In each the last two points have been chosen to indicate the straight part of the graph.

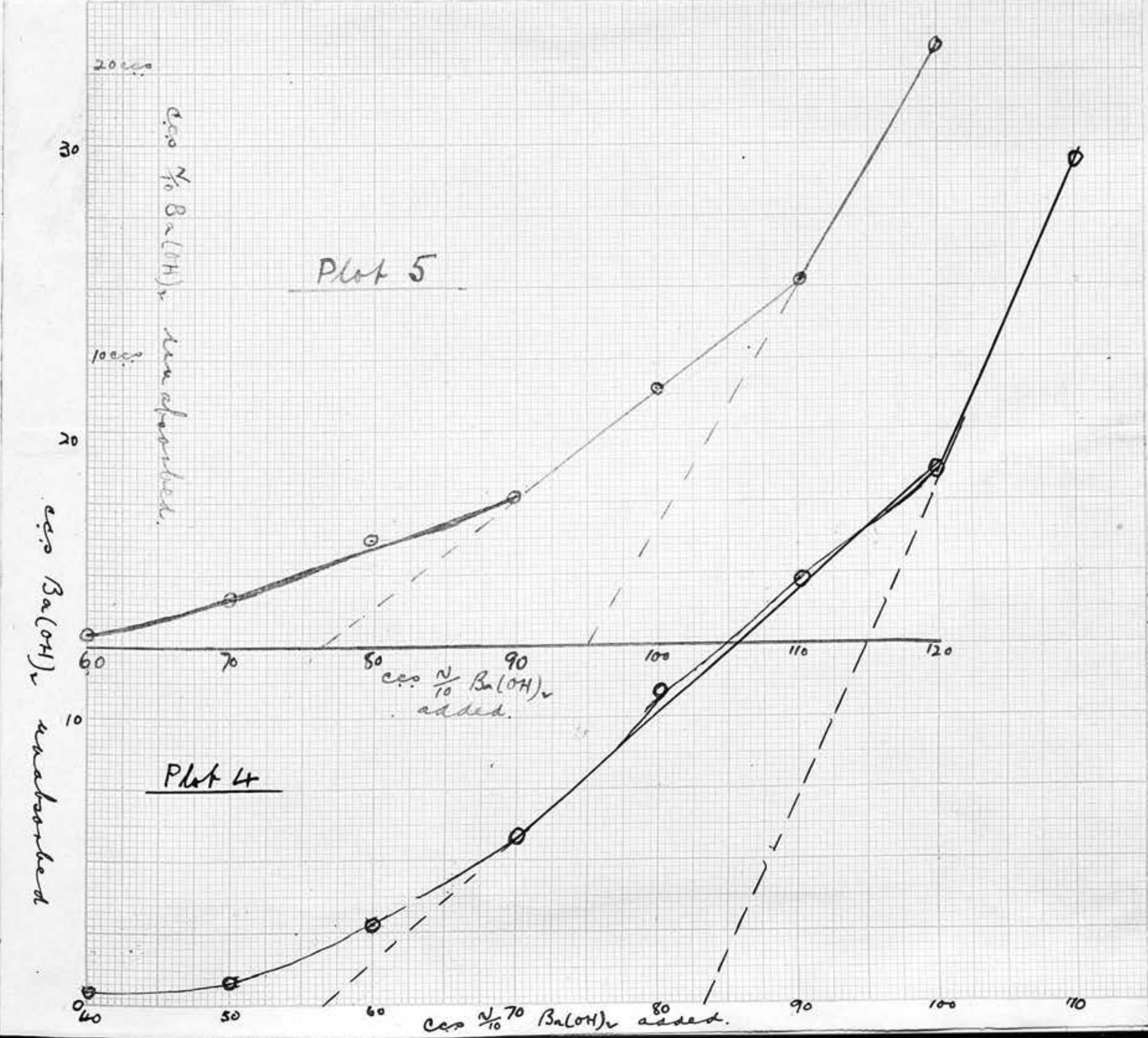


Table 26 shows T - S, S & T in m. eqs. per 100 gms. of soil and V for each plot, but it is probable that T is much too high.

Table 26.

Plot	T - S.	S.	T.	$V = \frac{100\,S}{T}$
1	58	7.2	65.2	11
2	58	7.3	65.3	11.1
3	63	5.7	68.7	8.3
4	83.5	5.4	88.9	6.1
5	94.5	4.4	98.9	4.5
6	93.5	6.9	100.4	6.9
7	82.5	5.7	88.2	6.5
8	67	6.5	73.5	8.8
9	67.5	7.8	75.3	10.4
10	56	11.2	67.2	10.6

The results show that the degree of saturation is very low and while the results may not be accurate, they show the same variation as the acidity measurements previously described, i.e. the greatest acidity corresponds to lowest degree of saturation and highest amount of exchangeable hydrogen.

Kelley's method, saturation with ammonium and method of Bobko and Askinasi, saturation with barium.

Kelley (41) - 25 gms. soil and 100 c.cs. normal ammonium chloride are left over night in an oven at 70°C. The soil is then transferred to a filter paper and leached with ammonium chloride to 1000 c.cs. It is then washed free from chloride, transferred to a flask, sodium hydroxide added and the ammonia distilled into standard sulphuric acid. In this work the leaching was continued to almost two litres and as it was discovered impossible to distil the ammonia from the soil itself, owing to frothing and bumping, the ammonium was leached out with sodium chloride and distilled using magnesium oxide instead of sodium hydroxide. The amount of ammonium obtained expressed as milligram equivalents per 100 gms of soil gives the absorption capacity of the soil.

<u>Babko and Askinasi</u> (8, 9) - 10 gms.(1 mm)air-dry soil are worked up in a porcelain basin with a small quantity of normal barium chloride and are then washed on to a filter paper. Leaching is continued until no more calcium is detected in the filtrate - in this case to almost two litres to remove the exchangeable hydrogen. The soil is then washed free from chloride and the barium leached out with normal hydrochloric acid and estimated. The amount of barium expressed in milligram equivalents per 100 gms soil gives the absorption capacity of the soil. The method is not suitable for soils containing free calcium carbonate as part of the barium chloride goes into barium carbonate and is dissolved out by the hydrochloric acid. To avoid this sodium chloride has been suggested as the leaching agent.

Table 27 shows the results of both methods in milligram equivalents per 100 gms. soil.

Table 27 (see over)

Table 27

Plot	Milligram Equivalents NH_4	Milligram Equivalents Ba
1	10.36	10.74
2	10.24	10.86
3	11.64	10.90
4	10.11	10.91
5	13.03	16.39
6	14.81	18.23
7	13.58	16.65
8	12.14	15.17
9	12.67	14.21
10	11.85	13.84

The Table shows that while fairly good agreement exists between the two methods, the results are very much smaller than those obtained by Hissink's method.

Gehring and Wehrmann's Method (23, 24)

100 c.cs. saturated Calcium Hydroxide were added to 10 gms. soil (not 25 gms as recommended by the Authors) and the whole heated to 60°C. with a thermometer in the liquid. The thermometer is then washed down with 5 c.cs. of water. After standing for 24 hours phenolphthalein is added and CO_2 led in until the colour is discharged. The whole is then well boiled to decompose any bicarbonate formed and sufficient sodium chloride added to give a normal solution. After standing for 12 hours the soil is filtered and leached with sodium chloride to 2 litres, the calcium in each litre being determined. The difference gives the maximum amount of calcium the soil is capable of holding. The degree of

saturation is defined as ratio of calcium present in the soil to the amount it is capable of holding. The results are shown in Table 28.

Table 28

Plot	Exch. Ca. C_1	Ca (Gehring) C_2	$\frac{100 C_1}{C_2}$ (Degree of Saturation)
1	5.2	35.0	14.9
2	4.2	37.1	11.3
3	3.6	35.2	10.2
4	3,5	35.2	10.0
5	3.2	38.9	8.2
6	4.2	36.8	11.4
7	3.5	33.7	10.3
8	4.5	35.8	12.6
9	5.7	35.3	16.1
10	8.8	37.6	23.4

The results given here are higher than the ammonium and barium results, but considerably lower than Hissink's. It will be seen that there is no great difference in the absorptive capacity of plots 5 - 8 an increase which would be expected from the other results and also from the measurements of acidity already given. This is almost certainly due to insufficient calcium being added as 100 c.cs. saturated calcium hydroxide = approx. to 4 m. equivalents = 40 m. Eqs. calcium per 100 gms. soil practically all of which has absorbed by the soil as shown by 5 and 6, so that decreasing the amount of soil from 25 gms. to 10 gms. is apparently not enough. This conclusion is borne out by the results obtained by the next method.

Page & William's Method - Original method (53)

25 gms. soil were mixed with 1 gm. Calcium Carbonate and the whole treated with hot Sodium Chloride and allowed to stand over night. The mixture is then leached with normal sodium chloride to two litres, the calcium in each litre being determined. In this method the hydrogen ions of the soil are replaced by sodium, the hydrogen ions reacting with the calcium carbonate to give carbonic acid, which escapes so that in time complete replacement of the exchangeable hydrogen takes place. Thus we have in solution not only the calcium ions displaced by the sodium, but also calcium equivalent to the hydrogen which has been displaced. The technique of the method has been criticised by Turner(68) who found that leaching to two litres was not enough: from 9.2 - 21.8% of the total calcium being found in the second litre. He found also that the amounts of calcium carbonate dissolved by the sodium chloride under the conditions of the experiment(no details as to method are given)in the first and second litres were equivalent to .038 and .036 gms. Calcium Oxide respectively. As a litre of sodium chloride saturated with calcium carbonate contains .038 gms. calcium oxide the leaching solution apparently remains long enough in contact with the calcium carbonate to become saturated.

The method adopted by Turner was as follows:- 25 gms. soil were moistened and thoroughly mixed with excess calcium carbonate and then 100 c.cs. hot sodium chloride solution added with thorough stirring. The mixture was allowed to stand for seven days at least and frequently shaken to assist the escape of the CO_2 formed. Finally the supernatant liquid was poured through filter paper, the soil brought on the the paper and leached to two litres. The total amount Calcium found in the two litres less the amount of Calcium dissolved, as given above, gives the saturation capacity of the soil. In this work the same method was adopted using, however, only 10 gms. soil and 2.5 gms. Calcium Carbonate and it was decided to leach to four litres in each case determining the amount of calcium in each 500 c.cs. . It was found that, in some cases, 2 litres were sufficient, but in others 2½ and 3 litres were required before the amount of calcium obtained in each 500 c.cs. became constant. Table 29 shows typical examples of the results obtained. The complete results are given in the appendix.

Table 29

Amount Ca in each 500 c.cs.

	Plot 1	Plot 3	Plot 7
1st 500 c.cs.	.0748	.066	.0913
2nd " "	.0184	.021	.0191
3rd " "	.0139	.016	.0194
4th " "	.0134	.0144	.0165
5th " "	.0119	.0134	.0186
6th " "	.0124	.0121	.0184
7th " "	.0019	.0127	.0138
8th " "	.0123	.0121	.0126

When the amount of Calcium in each 500 c.cs. had become practically constant, it was found that this was equal on the average to .012 gms. Calcium or .035 gms. Calcium Oxide per litre, which agrees very closely with the figures given by Turner. As the percentage of humus increased, the amount of leaching required became greater.

Thus for plots 1, 2, 9 and 10, 2 litres; plots 3 and 4, $2\frac{1}{2}$ litres and in plots 5 - 8, 3 litres were required(Examples of each are given above) The amount of Calcium absorbed by the soil was calculated by adding together the amounts obtained in each 500 c.cs. until the amount of Calcium became constant, and subtracting from this sum 4, 5 or 6 times .012 gms calcium as was necessary. The results are given in Table 30.

Table 30

Plot	Ca absorbed by soil in milligram equivalents per 100 gms. soil
1	36.2
2	33.2
3	35.4
4	35.0
5	47.2
6	62.0
7	56.5
8	41.0
9	37.5
10	32.0

These figures agree fairly well with those obtained by Gehring's method except in the plots 5, 6 and 7 for which a probable explanation was given earlier. Harada(28) is a comparison of these methods found Gehring's results smaller, but that when Calcium Carbonate was added to the soil after the treatment with calcium hydroxide, the two methods agreed very well. i.e. the soil was not saturated with calcium by addition of calcium hydroxide. This may have been due either to the fact that insufficient was added or that complete replacement of the hydrogen is not possible by this method.

After this work had been completed, it was pointed out by Crowther and Basu, [Advance Note in Technical Communications No. 12 Imp. Bur. of S.S., also private communication from Dr. Crowther,] that the method was inaccurate in so far that in a suspension of an acid soil, calcium carbonate and sodium chloride solution there must be some calcium bicarbonate formed owing to the action of the CO_2 formed by the interaction of the soil and the calcium carbonate. This is true, the authors state, even if as in Turner's method some days are allowed to elapse to allow the escape of the CO_2 The result is that hydrogen equivalent to this amount of Bicarbonate is thus counted twice and to obviate this they estimate the bicarbonate as well as the calcium in the leaching solution. The method adopted is, as follows:-

10 hms. soil (1mm) and 2.5 gms. calcium carbonate are made into a paste with a small amount of normal sodium chloride in a conical flask. By suitable rotation the paste is spread out as a thin film on the sides of the flask and allowed to stand until it is nearly dry. The soil is now shaken with 100 c.cs. normal sodium chloride at 70°C. and allowed to stand 45 minutes with occasional shaking and exposed to the air. This allows escape of the CO_2 thus reducing the amount of the correction and accelerating the approach to equilibrium. The clear liquid is decanted through a filter into a 500 c.c. flask and the extraction repeated in the same way until two or three successive lots of 500 c.cs. are obtained.

200 c.cs. are titrated with 0.1N hydrochloric acid to a boiling methyl red end point and the bicarbonate content subtracted from the total calcium content of the extract. It is

advisable to run a blank with all determinations as the results may be affected in a laboratory where there is a considerable amount of CO_2 present. The authors consider that estimations of the carbonate - bicarbonate and calcium in the first two half litres are sufficiently accurate for most purposes. This method was used for the soils under investigation, leaching being carried out to 4 lots of 500 c.cs. N Sodium Chloride.

The results per plots 1, 4, 7 & 10 in milligram equivalents per 100 gms. soil and a blank experiment are given in Table 31 the remaining results being given in the appendix. (pp 83-85)

Table 31.

Plot 1			Plot 4			Plot 7			Plot 10		
Ca	HCO_3	Diff.	Ca	HCO_3	Diff.	Ca	HCO_3	Diff	Ca	HCO_3	Diff.
27.9	5.8	22.1	32.5	6.5	26.0	44.7	7.5	37.2	31.8	6.7	25.1
9.7	5.2	4.5	12.3	5.7	6.6	14.0	6.5	7.5	10.6	5.5	5.1
6.8	4.3	2.5	9.6	5.7	3.9	11.1	6.4	4.7	9.0	5.8	3.2
7.3	4.7	2.6	8.8	5.5	3.3	11.1	6.3	4.8	8.1	5.3	2.6
		31.7			39.8			54.2			36.0

Blank

Ca.	HCO_3	Diff.
4.4	3.4	1.0
3.8	3.6	.2
4.0	3.6	.4
4.2	3.5	.7
		2.3

As mentioned above Crowther and Basu have stated that for most purposes determinations of the bicarbonate and calcium in the first two half-litres would be sufficient, but for such acid soils as above it is doubtful if this would suffice as Table 31 shows. It may be that four 500 c.cs. lots are not sufficient, but by subtracting the blank from the total amounts of the difference columns in the first four 500 c.cs., one should obtain a good approximation at least to the saturation value. The values obtained by this method are shown in Table 32 in m. eqs. per 100 gms. Soil with the values previously obtained by Turner's and Gehring's method.

Table 32

Plot	Crowther & Basu	Turner	Gehring
1	29.5	36.2	35.0
2	33.0	33.2	37.1
3	34.0	35.4	35.2
4	37.5	35.0	35.2
5	44.3	47.2	38.9
6	49.5	62.2	36.8
7	52.9	56.5	33.7
8	41.6	41.0	35.8
9	37.3	37.5	35.3
10	33.7	32.0	37.6

Apart from the discrepancy in soils 5 and 8 in Gehrings column, the results show good agreement which in the case of Crowther & Basu and Turner is rather surprising. One can only assume that in Turner's method as the suspension of soil , calcium carbonate and sodium chloride is allowed to stand for seven days the greater part of the CO_2 has escaped and that therefore the amount of calcium bicarbonate formed is extremely small, thus giving no difference between the two results. That this agreement occurs in this case is not to say that the two methods are equally correct, as it is obvious that Crowther & Basu's method will give the more accurate results. A short discussion on all the results is given in the final section - the summary.

Effect of Liming on Crop Yield and the amount of Calcium in the grain

The yield from each plot, the pH and notes on the crop are given in Table 33.

Table 33.

Plot	Liming Lbs $Ca(OH)_2$	pH 10/4/30	Grain Lbs.	Straw Lbs.	Total Lbs.	Notes
1	0	-	-	-	-	-
2	24	5.5	1	5.5	6.5	Straw short
3	48	5.7	1.2	6.7	7.9	do.
4	72	6.2	1.1	6.5	7.6	do.
5	96	6.2	1	4.4	5.4	do & thin
6	0		Nil	Nil	Nil	-
7	24	4.9	.1	.7	.8	Poor growth stunted
8	48	5.4	.8	3.8	4.6	do.
9	72	6.2	2.2	15.4	17.6	Good
10	96	7.2	1.8	12.8	14.6	Good

As the chief object of the investigation was the effect of lime on the soil no artificials of any kind were applied and as can be seen the results in the first year were very poor. If one takes 35 cwts. (straw & grain)as an average yield per acre, then only plots 9 and 10 give results which approximate to this; being at the rate of 38 and 31 cwts. per acre respectively. None of the other plots have given satisfactory growth, not even plots 4 and 5, which were also heavily limed.

The results for the second year are given in Table 34. Only 9 and 10 were ripe when the plots were cut at the end of September, the rest being still fairly green, owing partly to the wet season. As it was unlikely that they would ripen further, they were brought inside after cutting, dried, and the weight taken. As the grain was in most cases very poor, no attempt was made to obtain separate weights for the grain and the straw.

Table 34 gives the yield and the pH of the plots.

Table 34

Plot	pH	Yield (Straw Grain)	Notes
1		Nil (control)	
2	5.1	2½ lbs.	Poor
3	5.3	4¼ "	"
4	5.8	6 "	"
5	6.0	8 "	"
6	–	Nil(control)	
7	4.8	1 lb.	"
8	5.3	5 lbs.	"
9	5.9	13¾ "	Fairly good
10	6.8	19 "	Good

Only plots 9 & 10 gave satisfactory results in the second year as in the first. The failure of the plots 2, 3, 7 and 8 was probably due to the acidity, the pH being below 5.3 Plots 4 and 5 in spite of being heavily limed did not give satisfactory results and this may have been due partly to the lack of artificial manures and also to the fact that these plots which lay in a part of the field which was not well drained and they may have become slightly waterlogged owing to the wet season.

The chief factor was probably due to the want of artificials the failure to ripen and poor grain formation pointing to lack of phosphates. Owing to this, it is not possible to draw any satisfactory conclusions from the results, but it would seem that acidity below pH 6 is not suitable for barley.

Calcium in the Grain.

The Calcium in the grain of the first and second years crop was estimated and the results are given in Table 35

Table 35

Plot	Lime applied	% Ca in Grain	
		1st Year	2nd Year
2	24 lbs.	.039	.045
3	48 "	.041	.045
4	72 "	.042	.046
5	96 "	.045	.053
7	24 "	.040	.044
8	48 "	.043	.049
9	72 "	.045	.047
10	96 "	.043	.043

The amount of lime applied seems to have made little or no difference to the calcium present in the grain. In the first year there is a slight increase in the Calcium as the lime applied is increased, but in the second year there is practically no difference between the plots except in the case of Plot 5, which is higher than the others and which has had the heaviest dressing of lime. The yield of grain, however, in the second year was so poor that it would not be correct to draw any conclusions from the above results.

Summary and Conclusions.

The chief objects of the investigation were (1) to compare the "lime requirements" of certain acid soils as determined by methods in use in various countries and to compare the effects of adding lime in the laboratory and in the field (2) to compare the results obtained by the various methods which have been proposed for the determination of the saturation value of the soil and (3) to determine the amount of Calcium absorbed in the field, its effect on the other bases of the soil and on the crop yield.

For this purpose 10 plots were laid down, 5 in duplicate, the soils all containing practically the same amount of clay 22 - 25%, but varying amounts of organic matter 10 - 21%. A short discussion on the methods of estimating organic matter is given, the method used being that of Robinson's, i.e. reduction of sulphuric acid to sulphur dioxide by the carbon of the organic matter and estimation of the sulphur dioxide evolved. The results agree well with the "loss on ignition" and the method would appear to be very useful in routine work. The total nitrogen was also estimated, but no definite ratio could be established between the carbon and the nitrogen - the ratio carbon to nitrogen varied between 13 and 17 - or between the nitrogen and the organic matter.

The pH of the plots in water solution varied between 4.5 and 5 and between 3.7 and 4.2 in N Kcl solution, i.e. they were highly acidic.

The various methods used in determining the "lime requirements" were (1)Christensen-Jensen - lime required to give pH 7 found by titration with $Ca(OH)_2$. The buffer power of the soils calculated according to his method is given.

(2) Kappen's - Lime required to remove the "hydrolytic acidity" found by shaking soil with calcium acetate or sodium acetate and titration of filtrate with sodium hydroxide. More acidity was liberated by treatment with calcium than with sodium acetate.

(3) Daikahura's - Lime required to remove "exchange acidity" found by shaking soil with normal potassium chloride and titration of filtrate with standard sodium hydroxide. (Kappen's types of acidity : "Hydrolytic Acidity", "Exchange Acidity", "Neutral Salt Decomposition", and "Active Acidity", and also Page's theory that these are not different types, but are all of one kind differing only in degree are discussed. The various phenomena can be explained by assuming greater amounts of replaceable hydrogen present in the soil complex as the acidity increases).

Hutchison and McLennan - Lime requirement by determining the amount of calcium absorbed by soil from a solution of calcium bicarbonate. The errors of the method pointed out by various observers are given.

The results show that most lime is required to give pH 7, the hydrolytic acidity method less, Hutchison-McLennan still less, and least of all by exchange acidity method. It is pointed out that pH 7 is perhaps unnecessarily high for many crops so that the amount of lime could be decreased. It was also found that time taken for suspension of soil and calcium hydroxide to reach equilibrium was longer than 48 hrs, 96 hours and 120 hours being necessary in some cases. This makes the method too long for routine use.

The exchange acidity methods give amounts of lime which are too low for practical purposes.

The Hutchison-McLennan and Kappen's method give results which appear to be suitable. Kappen's method would be useful in practice as being quicker than Hutchison-McLennan, but the amount of soil used 100 gms. could be decreased and 200 c.cs. solution taken.

A comparison of the 4 methods, the "buffer power" and the amount of organic matter present is given in the following table. In each the value for plot 6 has been taken as 100 and the other values calculated in proportion to this figure.

Plot	Organic matter	c.cs. $Ca(OH)_2$ to give pH 7	Hyd. Acid	Exch. Ac.	Hutch.- McLennan	Buffer Power
1	48	44	51	47	56	44
2	64	59	63	65	66	50
3	71	59	74	64	73	50
4	72	67	73	63	73	64
5	93	98	98	87	102	96
6	100	100	100	100	100	100
7	99	96	96	105	91	93
8	75	71	79	78	73	64
9	71	61	67	60	61	58
10	59	43	45	36	43	-

The clay has not been taken into account as the soils have practically all the same content. There is a good correlation between the amount of organic matter and the different values, showing that the humus is the chief factor in the various results obtained, i.e. when the clay content is constant.

The pH to which the soil would be raised in the laboratory by adding the amounts of lime determined by the various methods were Jensen 7, Hyd. Ac. 6.5, Exch. Acidity 5.5, H. McLennan 6.2 - 6.3.

Effect in the Field :- The effect in the field was found to lie between one-half and one-third of that in the laboratory. In Jensen's method the amount of lime necessary to give a pH of 7 in the field and in the laboratory is compared. The pH in the field is affected in two ways:-

(1) by the time which elapsesbetween liming and sampling and (2) by the growing plant. It is suggested that a suitable time for sampling would be one year after the application of the lime and, if possible, either in the Spring or Autumn when no plants are growing. The changes noted in the pH during the growing season are given.

Exchangeable bases The bases Calcium, Magnesium, Potassium, Sodium, Ammonium were determined, the amounts were small with Calcium about 80% of the total. Aluminium was not included in the replaceable bases as its position is doubtful. Its effect as a toxic agent on plants is discussed. It was found from a number of samples taken from a field in which barley had partially failed that the chief factor in crop failure appeared to be lack of calcium and that the plant could tolerate larger quantities of aluminium if sufficient calcium were present. The results of other workers on this subject are given.

Effect on other bases. The Calcium was adsorbed at the expense of the exchangeable hydrogen . There was a slight decrease in the amount of magnesium, but little or no difference in the others. The amounts of the bases other than calcium and hydrogen were so small that it was not possible to draw any definite conclusions. No aluminium was obtained in plots with pH above 5.3.

The amount calcium absorbed was about 70% of that applied.

The Exchangeable Hydrogen is dealt with in section under Saturation Value. Gedroiz's method of determining the Hydrogen, i.e. leaching with barium chloride and titration with sodium hydroxide was attempted, but was abandoned. The end point of titration, when titrating large quantities of liquid with very dilute alkali, is too indefinite.

Exchangeable Hydrogen and Saturation Value.

The methods used were those of Hissink's, Kelley, Bobko and Askinasi, Gehring and Wehrmann, Page and Williams Turner's modification) and Crowther and Basu.

The Saturation Value V is defined as $V = \frac{100\ S}{T}$ S = bases present; T = total amount soil can absorb.

Hissink's method gives the hydrogen, i.e. T - S to which is added S giving T. The results are probably not an accurate measure of T - S, being too high. Reasons for this and certain other disadvantages are given.

In Kelley's method - leaching with ammonium chloride- and Bobko and Askinasi-leaching with Barium Chloride - until all other bases are replaced and amounts absorbed estimated, the results obtained were low. This may be due to insufficient leaching. If this is so, then method is not suitable for routine use as the leaching with ammonium chloride or barium chloride would require to be much greater than two litres (the amount used here). This coupled with subsequent washing and a second leaching to obtain the adsorbed ions would make a long and expensive process. Other workers have found low results by above methods.

In Gehring's method the hydrogen ions are replaced by Calcium by treatment with $Ca(OH)_2$ and total calcium present estimated. The degree of saturation is given by the ratio of the replaceable calcium to the total calcium. The other bases in acid soils are in very small amount and would not greatly affect the result. It was found that the results for the total calcium were lower in the more acid soils than by the two final methods . Harada found similar results and suggested the addition of Calcium Carbonate after treatment with calcium hydroxide to remedy this. A larger quantity of calcium hydroxide might also be used.

Page and William's (Turner's modification). The soil is treated with calcium hydroxide and sodium chloride. The amount of leaching required was found to be more than two litres - in the case of the more acid soils 2½ and 3 litres were necessary. In Crowther & Basu's method, which is a modification of the previous method, the bicarbonate formed by the action of CO_2 on the calcium carbonate is estimated. Otherwise the calcium of the calcium bicarbonate is estimated as adsorbed calcium giving too high a result. Little difference was found between the two methods and it is through that most of the CO_2 had escaped in Turner's method, thus giving results which were similar to Crowther's method, which, however, is theoretically more accurate.

Of the six methods described, those of Gehring & Wehrmann, and Crowther & Basu would appear to give most satisfactory results. Though shorter than the other methods, they are still somewhat long for routine use.

Effect of liming on Crop Yield and amount of Calcium in the Grain.

Though the best results were obtained with highest liming, the yields except in two cases were not satisfactory. This was probably due to the want of artificial manures chiefly it is thought to the lack of phosphates. The barley was not good below pH 6. The amount of Calcium in the grain varied little throughout the plots.

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Appendix:-

Complete results for Page & William's Method (Turner's Modification).

Amount Calcium in each 500 c.cs.

	Plot 1	Plot 2	Plot 3	Plot 4	Plot 5	Plot 6
1st 500 c.cs.	.0748	.0618	.0660	.0655	.0772	.0991
2nd 500 c.cs.	.0184	.0200	.0210	.0207	.0226	.0261
3rd " "	.0139	.0168	.0160	.0163	.0203	.0237
4th " "	.0134	.0159	.0133	.0137	.0160	.0170
5th " "	.0119	.0129	.0144	.0137	.0158	.0150
6th " "	.0124	.0125	.0121	.0116	.0144	.0153
7th " "	.0119	.0122	.0127	.0133	.0138	.0130
8th " "	.0123	.0122	.0121	.0137	.0126	.0134

	Plot 7	Plot 8	Plot 9	Plot 10.
1st 500 c.cs.	.0913	.0748	.0720	.0623
2nd " "	.0191	.0200	.0205	.0196
3rd " "	.0194	.0158	.0153	.0189
4th " "	.0165	.0147	.0154	.0142
5th " "	.0186	.0154	.0133	.0129
6th " "	.0184	.0140	.0126	.0129
7th " "	.0138	.0130	–	–
8th " "	.0126	.0126	–	–

Complete Results for Crowther's and Basu's Method

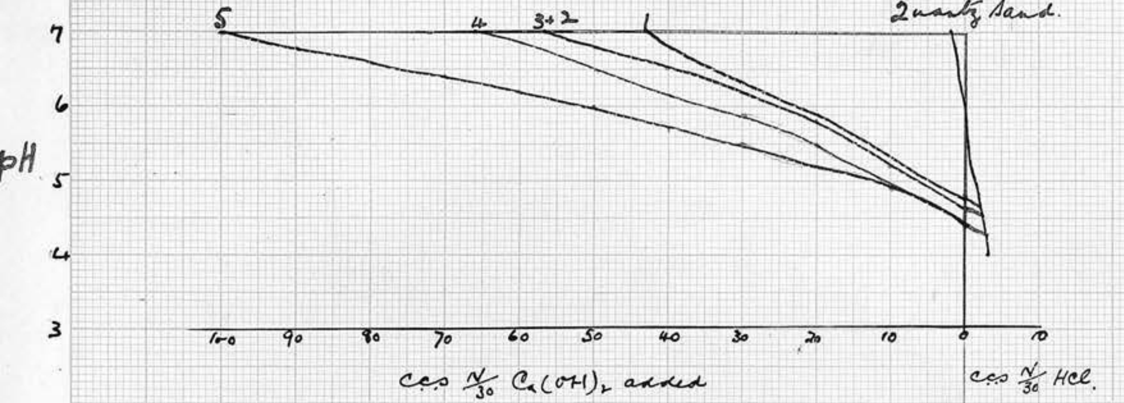
for Estimation of the Saturation Capacity of the Soil.

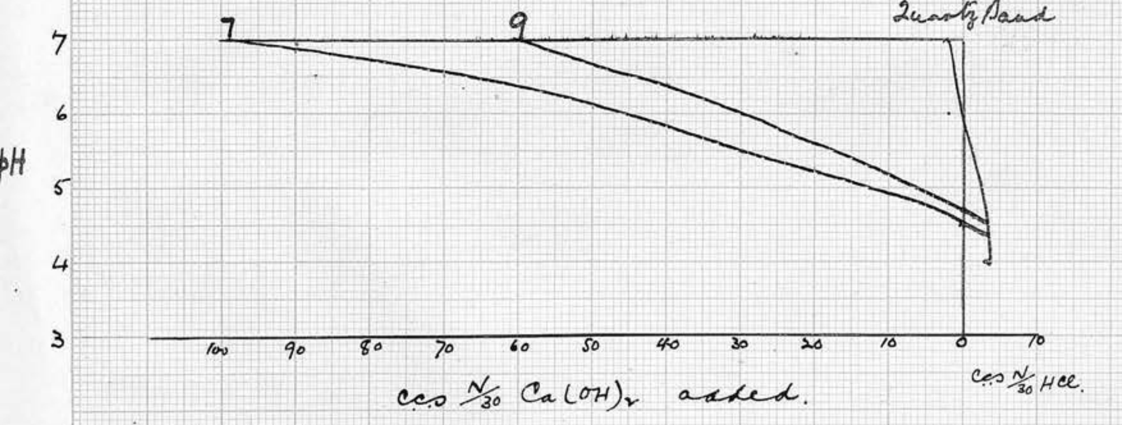
	Plot 1			Plot 2			Plot 3		
	Ca.	HCO_3	Diff.	Ca.	HCO_3	Diff.	Ca	HCO_3	Diff.
st 500 c.cs.	27.9	5.8	22.1	29.7	5.9	24.2	29.2	5.8	23.4
2nd 500 c.cs.	9.7	5.2	4.5	11.1	5.7	5.4	11.1	5.4	6.3
3rd 500 c.cs.	6.8	4.3	2.5	8.7	5.5	3.2	8.8	5.0	3.8
th 500 c.c.s	7.3	4.7	2.6	7.9	5.4	2.5	7.9	5.1	2.8
	Total		31.5			35.3			36.3

	Plot 4			Plot 5			Plot 6		
	Ca.	HCO_3	Diff.	Ca.	HCO_3	Diff.	Ca.	HCO_3	Diff.
st 500 c.cs.	32.5	6.5	26.0	36.5	6.1	30.4	43.1	7.8	35.3
2nd 500 c.cs.	12.3	5.7	6.6	13.4	6.3	7.1	13.8	6.7	7.1
3rd 500 c.cs.	9.6	5.7	3.9	10.2	5.6	4.6	11.1	6.4	5.3
th 500 c.cs.	8.8	5.5	3.3	9.6	5.2	4.4	10.6	6.5	4.1
	Total		39.8			46.5			51.8

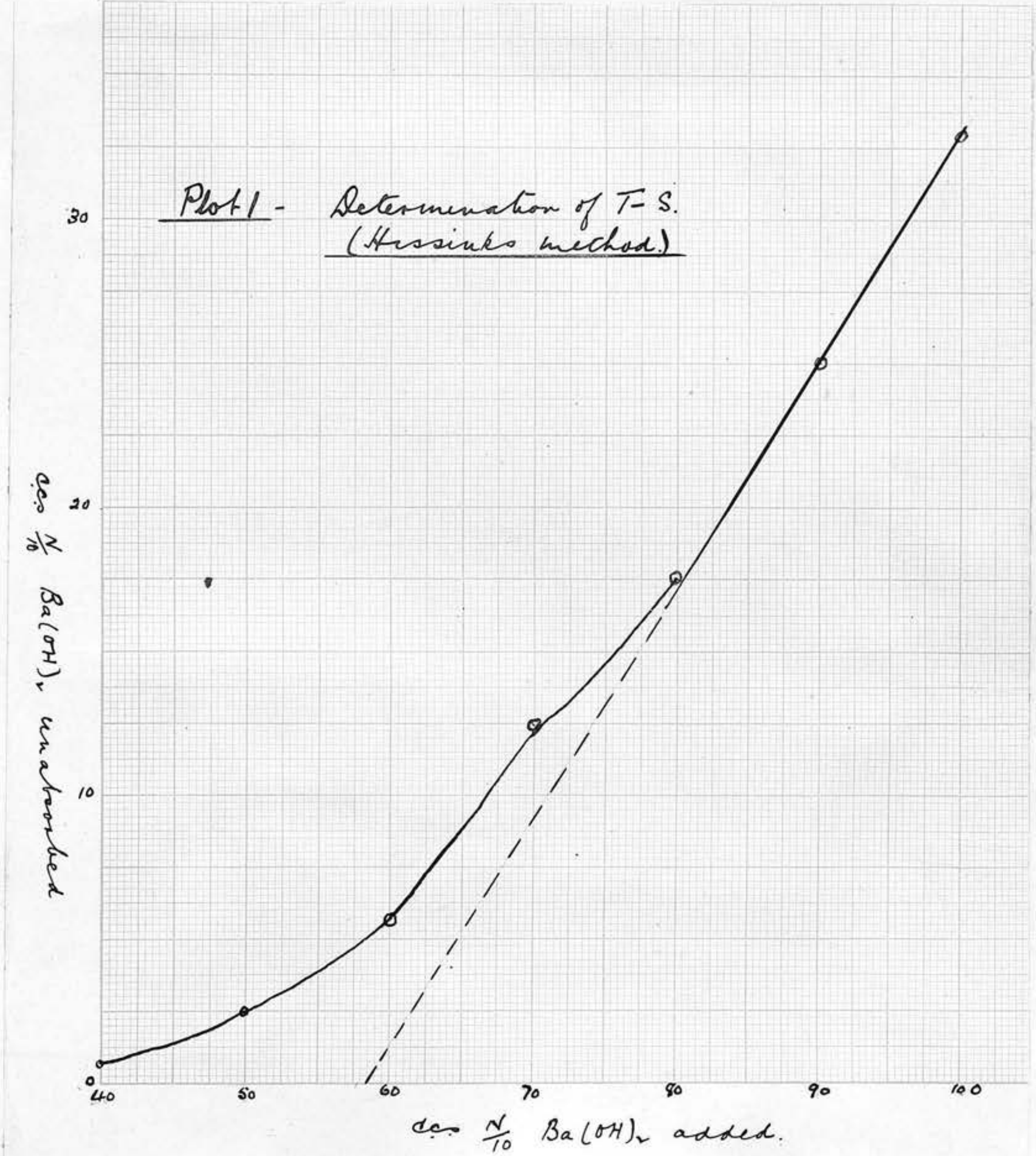
	Plot 7			Plot 8			Plot 9		
	Ca	HCO_3	Diff.	Ca.	HCO_3	Diff.	Ca.	HCO_3	Diff.
1st 500 c.cs.	44.7	7.5	37.2	36.2	7.0	29.2	34.7	6.2	28.5
2nd 500 c.cs	14.0	6.5	7.5	12.5	6.5	6.0	11.0	5.8	5.2
3rd 500 c.cs.	11.1	6.4	4.7	11.5	6.2	5.3	8.8	5.7	3.1
4th 500 c.cs.	11.1	6.3	4.8	9.2	5.7	3.4	8.4	5.6	2.8
	Total		54.2			43.9			39.6

"Buffer Space" curves of Plots 1, 2, 3, 4, 5, 7 and 9.

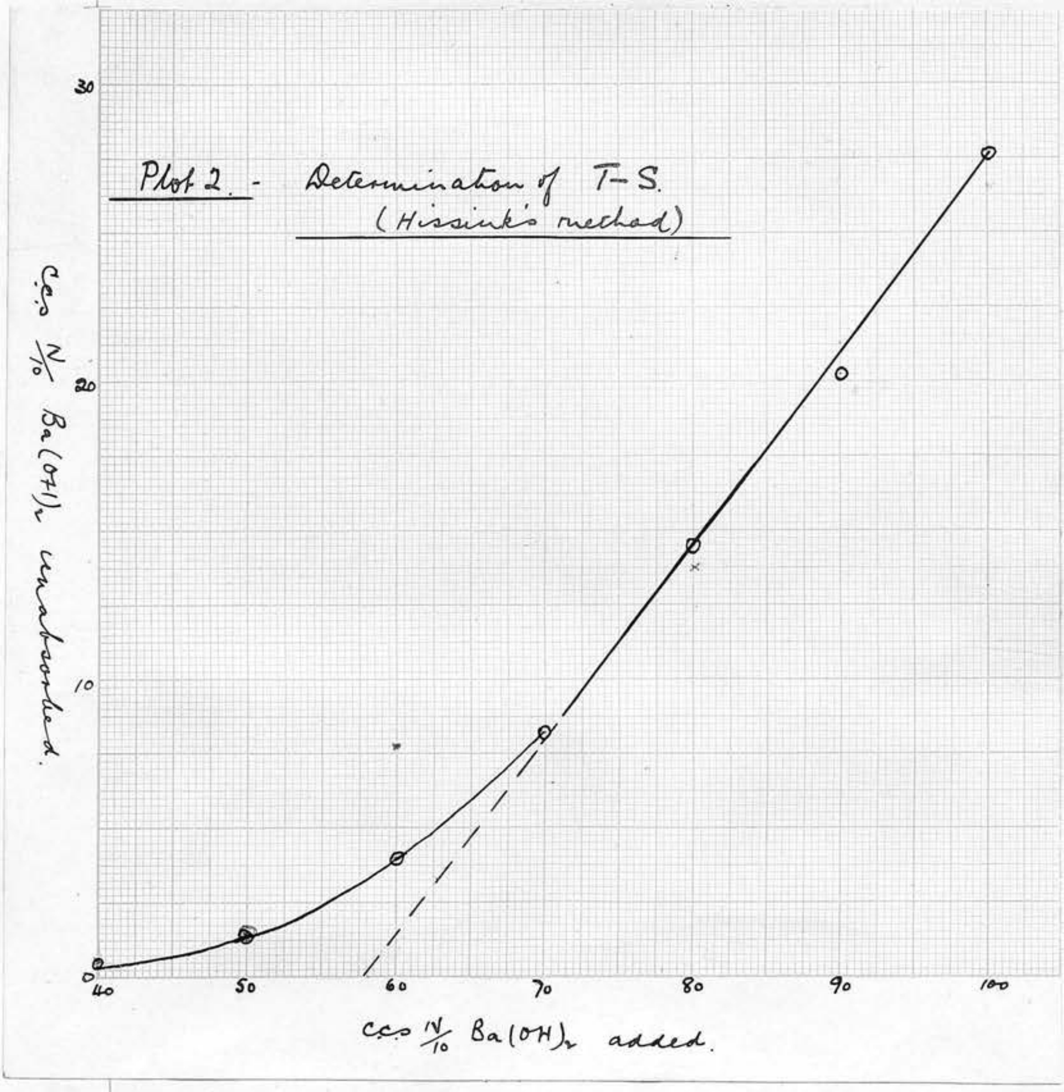




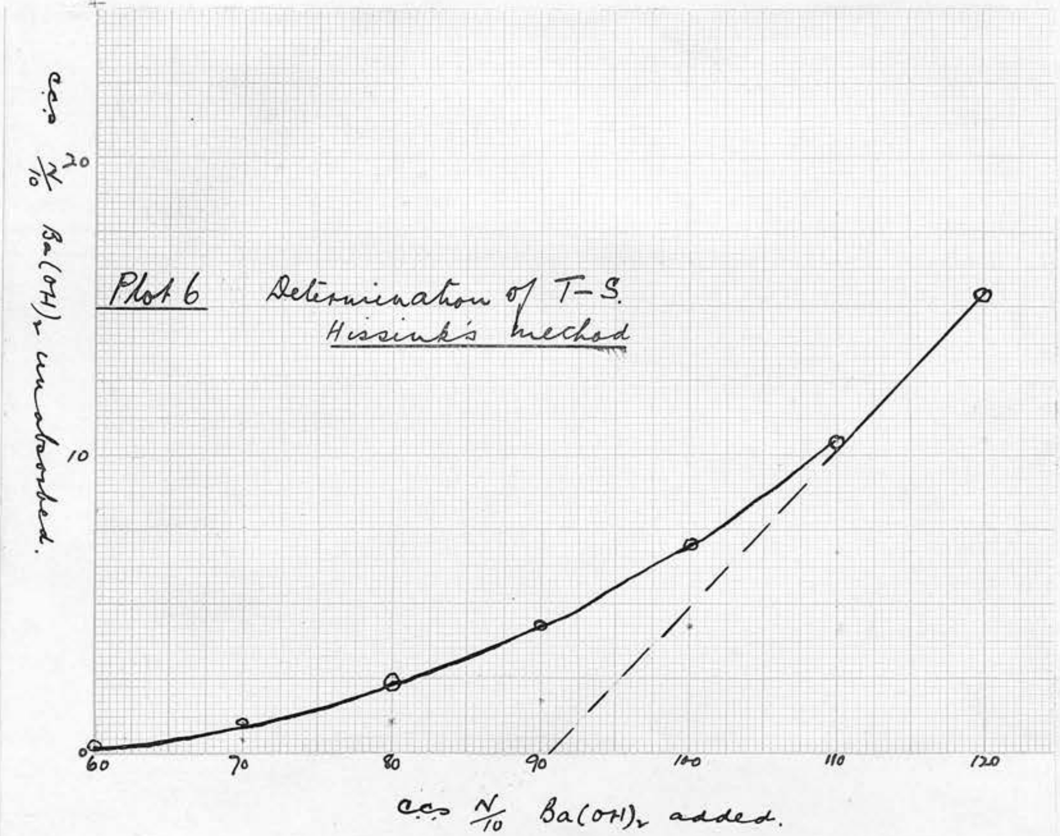
	Plot 10			Blank.		
	Ca.	HCO_3	Diff.	Ca.	HCO_3	Diff.
1st 500 c.cs.	31.8	6.7	25.1	4.4	3.4	1.0
2nd " "	10.6	5.5	5.1	3.8	3.6	.2
3rd " "	9.0	5.8	3.2	4.0	3.6	.2
4th " "	8.1	5.3	2.6	4.2	3.5	.7
		Total	36.0			2.1



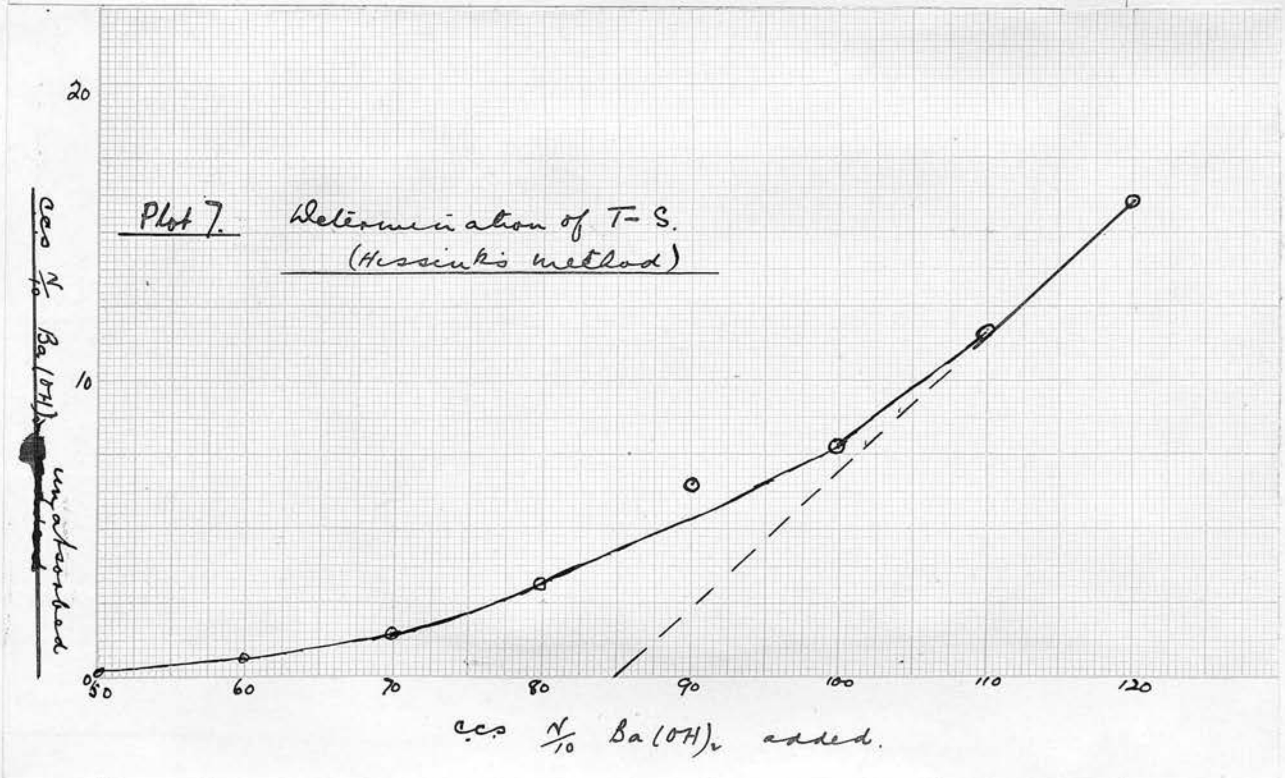
Plot 1 - Determination of T-S.
(Hessinks method.)



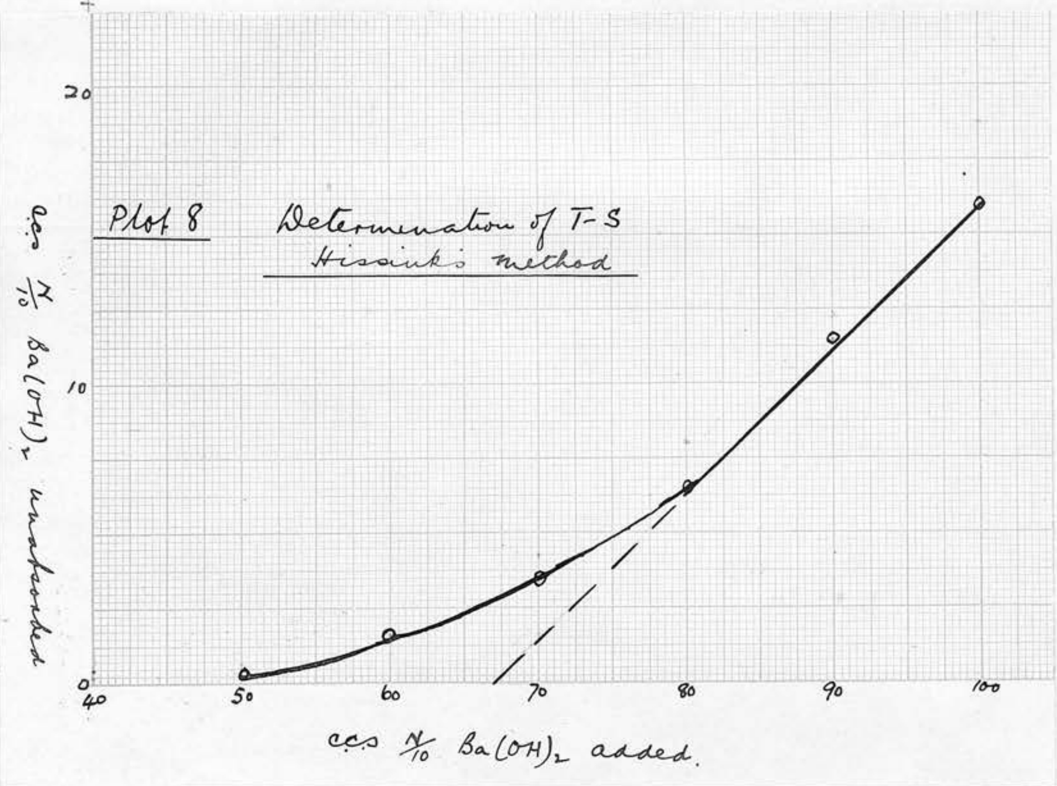
Plot 2. - Determination of T-S. (Hissink's method)

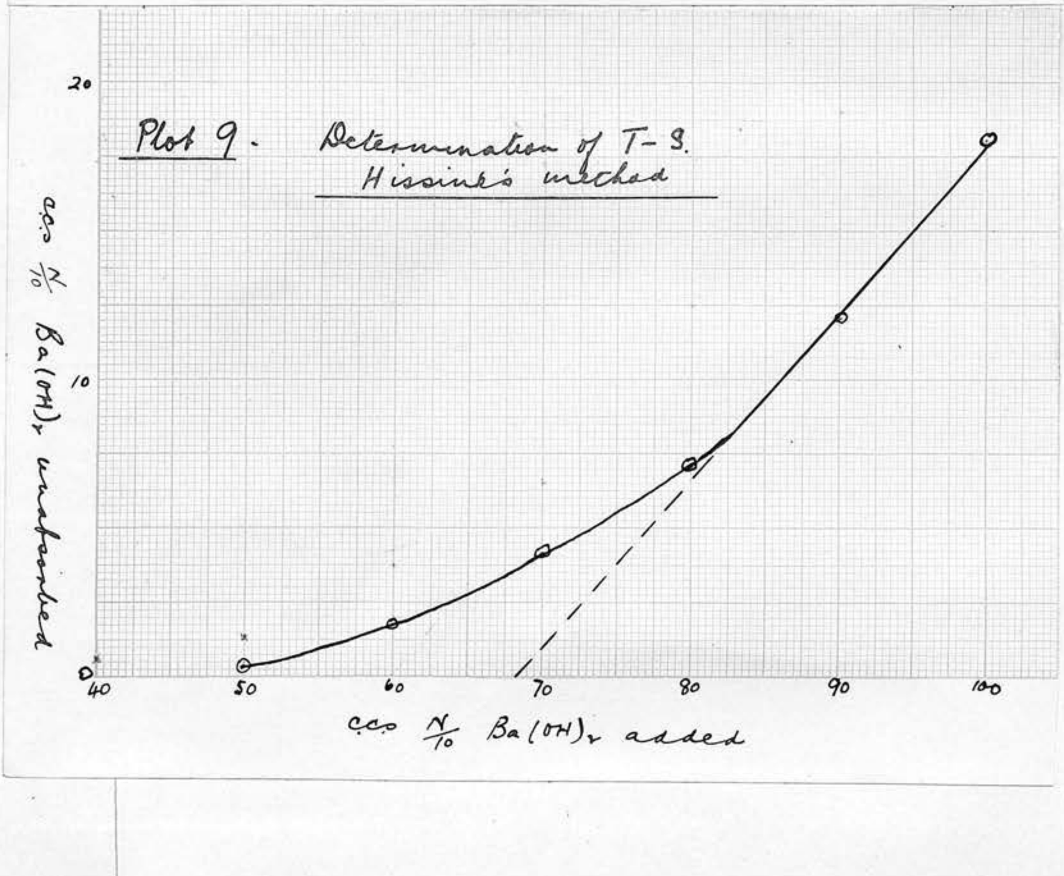


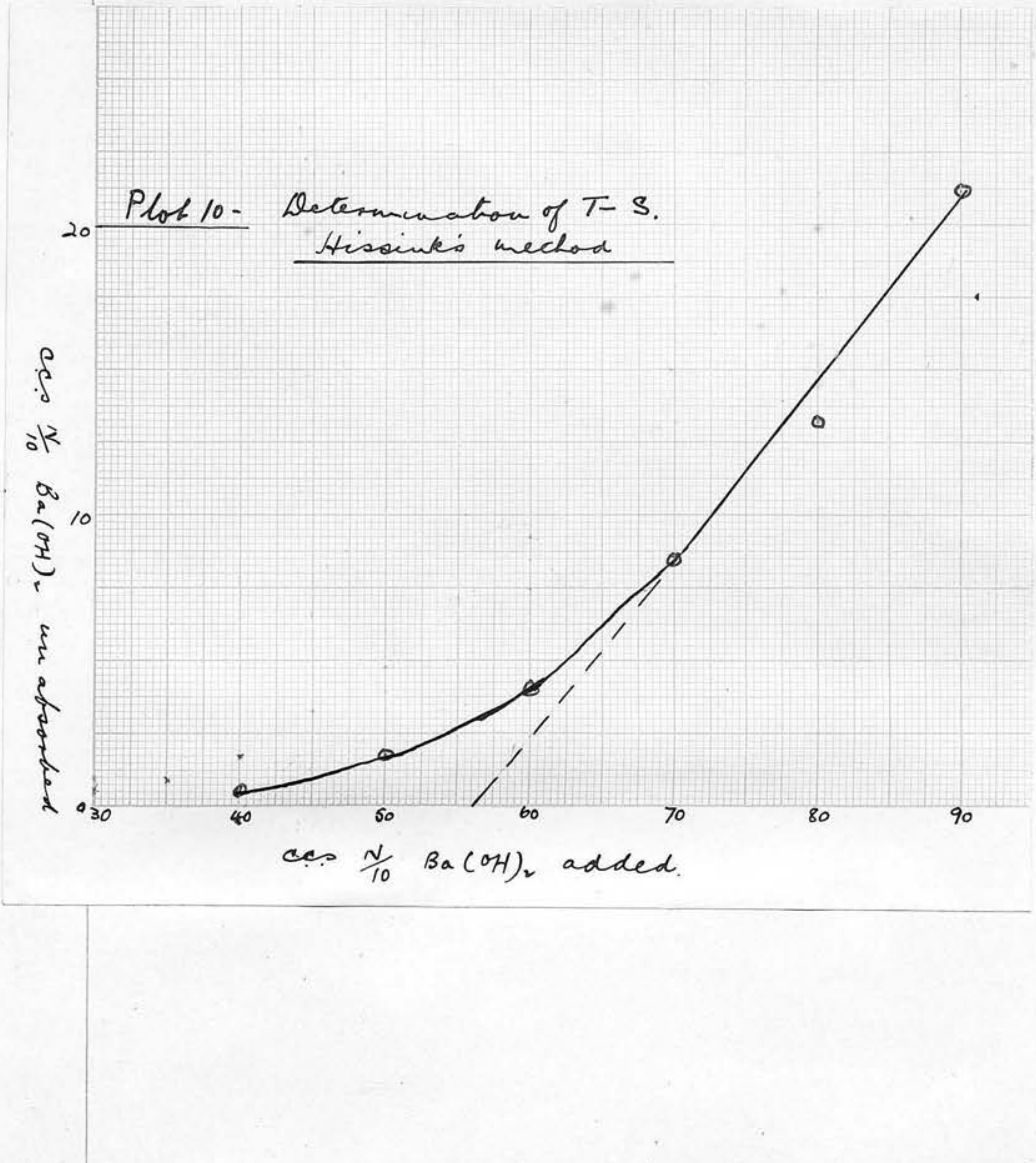
Plot 6 Determination of T-S. Hissink's method



Plot 7. Determination of T-S. (Hissink's method)


Plot 8
Determination of T-S
Hissink's method
c.c.s $\frac{N}{10}$ $Ba(OH)_2$ unabsorbed
20
10
0
40
50
60
70
80
90
100
c.c.s $\frac{N}{10}$ $Ba(OH)_2$ added.


Plot 9.
Determination of T-S.
Hissink's method
c.c.s $\frac{N}{10}$ $Ba(OH)_2$ unabsorbed
20
10
0
40
50
60
70
80
90
100
c.c.s $\frac{N}{10}$ $Ba(OH)_2$ added



Plot 10 - Determination of T-S. Hissink's method