# Results of the investigation of the seven Standard Soil Samples No. I–VII of the International Society of Soil Science

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#### I. Object of the investigation

At the Congress at Oxford (1935) Dr. H. Greene (Sudan) pointed out the desirability of comparing methods of determining exchangeable bases. Dr. E. M. Crowther (England) suggested that this object could best be attained by collecting a limited number of Standard Soil Samples at a particular place, to be sent on request to those persons who wished to make cooperative studies in the domain of exchangeable bases. The Congress charged me to collect and distribute a series of standard soil samples for this purpose.

The main object of this cooperative work is to obtain a satisfactory expression for the exchangeable base content of the natural soils. This seems to necessitate studying the displacement of bases by a variety of methods as e.g. treatment with neutral salts or weak acids in various amounts and at various soil-water ratios.

The second objective of the cooperative work is to measure the exchangeable base content of the soils when brought to "saturation" by some specified treatment. This treatment may involve the strongly alkaline conditions produced by a hydroxide (e.g. barium hydroxide, Hissink), less alkaline conditions, such as were used by Bradfield and Allison (1933, Transactions International Society of Soil Science, Commission 2, Volume A, Copenhagen), or a range of pH conditions, giving a titration curve.

Determinations may be made either by recognized methods or by new ones, but in every case the precise details should be given clearly. It is not sufficient merely to give the name of the original author of 1

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the method. Other determinations, mechanical analysis, humus, calcium carbonate, pH etc., may of course be included at the discretion of the investigator.

The following Standard Soil Samples are at present available for distribution at the Institute of Soil Science, Groningen, Holland:

- SS I Gezira (Sudan), heavy clay surface soil, passing 1 mm. sieve, pH between 9 and 10; contains neither sulphates nor chlorides soluble in water;
- SS II Young Dutch marine heavy clay soil, with about 8% CaCO<sub>3</sub>, pH about 7.7. Contains neither sulphates nor chlorides soluble in water;
- SS III Old Dutch marine clay soil, free from CaCO<sub>3</sub>, pH about 5.5. Contains neither sulphates nor chlorides soluble in water;
- SS IV Roseworthy (Australia), fairly sandy clay surface soil of the Mallee type, with about 10 % CaCO<sub>3</sub>, pH about 9. Contains a small amount of salts soluble in water;
- SS V Curlwaa (Australia), very heavy clay surface soil, being a River Murray alluvium from a fruit-growing irrigation area, with less than 1% CaCO<sub>3</sub>, pH about 8. Contains sulphate and chloride soluble in water;
- SS VI Podzol from Russia, from the upper layer (1-13 cm.), passing 2 mm. sieve;
- SS VIIFairly heavy Tschernozem from the Woronesch region, Russia, from the uper layer (1-12 cm.), passing 2 mm. sieve.

In the Proceeding of the International Society of Soil Science (green Journal), Vol. XII (1937), No. 2, p. 66—67, it was stated that 2½ kilograms of any of these samples would be forwarded on request to those interested, on payment of the expenses connected therewith. Furthermore it was agreed that the results should be communicated to me for publication in order that the samples may become standards by which members can compare their own methods or technique with those of other workers. After my departure from Groningen, these results are to be sent to my new address (Dr. D. J. Hissink, Ruychrocklaan 164, The Hague, Holland).

So far requests for the S. S. Samples have been received from some 8 colleagues. Of these 8, two, viz. Dr. Liatsikas, Athens, and Dr. Meyer, Hamburg, have furnished particulars of the results of their investigations. Now that in the meantime the investigation of the 7 samples at the Institute of Soil Science in Groningen has been concluded, it would seem advisable first to publish the results obtained

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in Groningen. I now do so, with thanks to the late Mr. M. Dekker, under whose supervision the investigation was carried out, and who also worked out the results.

Although therefore, as stated above, all that is required is a communication of the methods of investigation employed and of the results obtained, it seemed desirable to add here and there a few remarks regarding the figures found.

### II. Methods employed at the Institute of Soil Science Groningen

The methods of investigation are given in the "Erster Bericht über die Arbeiten und über die Tagung der Arbeitsgemeinschaft zur Prüfung der Laboratoriumsmethoden für die Bestimmung des Kaliund Phosphorsäurebedürfnisses der Böden", Transactions of the 2nd, 3rd, and 4th Commissions of the International Society of Soil Science, Meeting July 1936, Königsberg, pp. 135 and 136. As this Report is written in the German language, and moreover is in the possession of a small number of members only, a translation is given here.

Notes on Tables V to VIII by D. J. Hissink (Transactions Königsberg)

CaCO<sub>3</sub>. This was determined by Passon's volumetric method, modified by the Institute of Soil Science at Groningen. The carbonic acid is expelled with hydrochloric acid (2 vol. HCl spec. grav. = 1.195 + 1 vol. H<sub>2</sub>O) at room temperature. For the correction of differences of temperature and air-pressure a standard determination with a known amount of CaCO<sub>3</sub> is made at the same time in the case of each series.

Humus. This determination was made by means of Ter Meulen's elementary analysis (1). For the recalculation of the amount of carbon (C) found on the basis of the humus content, the C-content of the humus was assumed to be 58%.

Clay and sand. By clay and sand was understood particles with a diameter of less and more than 16 micra respectively. For the pre-treatment of the soil see the Communications of the International Society of Soil Science E (2). The separation of clay and sand was performed by washing in the Atterberg cylinder. The duration of sedimentation for particles with a diameter larger than 16 micra is  $7\frac{1}{2}$  minutes per 10 cm. By means of a sieving method the sand is divided into 12 subfractions. From these the U-value per 100 gr sand was calculated. For further particulars see S. B. Hooghoudt (3).

Nitrogen. This was determined by the Kjeldahl method and refers to the organically bound nitrogen. The table also mentions the number of grammes of nitrogen (N) per 100 gr humus.

Phosphoric acid. See Int. Agr. Wiss. Rundschau, 2, 364, 1926.

Potassium. See Intern. Mitteil. f. Bodenkunde, V, 1, 1915.

Weathering silicate A. For this method of determination see Hissink's paper: "Über die Bedentung und die Methode der chemischen Bodenanalyse mit starker heißer Salzsäure" (4). The analytical part has been altered here and there.

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Inter alia boiling is now carried out in a glycerine bath at 125 to 130 degrees C. In the hydrochloric acid extract the sum of  $Al_2O_3 + Fe_2O_3 + P_2O_5$  is determined gravimetrically. Then follows the determination of the  $P_2O_5$  (according to Lorenz) and of the  $Fe_2O_3$  (titrimetrically with KMnO<sub>4</sub>, after reduction with zinc powder). This sum minus ( $Fe_2O_3 + P_2O_5$ ) =  $Al_2O_3$ . In addition to the content of  $Al_2O_3$ ,  $SiO_2$  and  $Fe_2O_3$  in percentages, the table shows the number of millimoles of these constituents per 100 gr dry soil. From these latter figures, finally, the molecular ratio is calculated.

Exchangeable bases and S-value, T-S-value, T-value and V-value. For the method for the determination of exchangeable bases see Hissink's paper: "Beitrag zur Kenntnis der Adsorptionsvorgänge im Boden" (5). This table gives the amount of exchangeable CaO, MgO,  $K_2O$  and  $Na_2O$  in percentages of dry matter. From this the number of milligram-equivalents (mge) of these bases per 100 gr dry matter is calculated. The sum of the number of mge CaO + MgO +  $K_2O$  +  $Na_2O$  gives the S-value in mge per 100 gr dry matter. Finally the molecular proportion (to S = 100) was calculated from these results; in cases where the S-value is less than 4, this proportion was not calculated.

The method for the determination of the T minus S-value is described i. a. in "Base Exchange in Soils, a general discussion held by the Faraday Society", December 1924, pp.560—562. The sum of S and T—S = T. From this V is calculated according to the formula:

$$\frac{100 \text{ S}}{\text{T}} = \text{V}$$

pH. This was determined with the quinhydrone electrode in a suspension of 10 gr soil + 26 cc distilled water free from carbonic acid.

The following additions can be made here.

Mechanical Soil Analysis. The time for sedimentation of fraction II (particles with a diameter of from 2 to 16  $\mu$ ) is 8 hours per 10 cm. The syphoning off of fraction I in the Atterberg cylinders gave rise to some difficulties in the case of sample No. V. After decanting of the electrolytes with water, this soil flocculated again with NH<sub>4</sub>OH + + NaOH. The result was that the syphoning off of fraction I of this sample took from 3 to 4 weeks.

Fractions I and II of samples II and V were also determined by the pipette method. After washing out the electrolytes we do not in that case treat the soil with  $NH_4OH + NaOH$ , but simply with  $NH_4OH$ . In the following table the results obtained by both methods are given.

No	Smaller	than $2\mu$	Upto	$16\mu$
140.**	pipette	Atterberg	pipette	Atterberg
II V	<b>44</b> .8 <b>43</b> .5	47.4 43.5	65.3 58.1	65.8 57.4

The agreement of the results is on the whole very satisfactory. Sample No. II, however, shows a lower content of particles smaller than  $2 \mu$  by the pipette method than by the Atterberg method. Presumably the electrolytes had not been sufficiently washed out in the pipette method and still had a certain flocculating effect.

Organic matter. It was difficult completely to analyse the organic matter of sample No. VII by dry combustion. With the elementary analysis this sample therefore required an abnormally long period of ignition. The humus content of No. VII was also determined by the "loss on ignition" method, the content of water bound being assumed to be 6 gr per 100 gr clay (particles smaller than 16  $\mu$ ). The humus content according to this latter method was found to be 11.9%, as against 11.8% as found by the Ter Meulen method (elementary analysis).

Soil Acidity. The pH was determined not only with the quinhydrone electrode, but also with the glass electrode. In both cases measurement was performed in a suspension of 10 gr soil and 25 cc distilled water free from carbonic acid. With the quinhydrone electrode samples V and VI showed a marked drift in the alkaline direction. With the exception of No. VII, all the quinhydrone figures are higher than those obtained with the glass electrode; the differences are largest in the case of nos. V and VI.

Exchangeable Bases. For the purpose of determining the contents of exchangeable lime and magnesia, 15 gr instead of 25 gr of soil were used from samples I and VII. In spite of this the 2nd litre of the extract of sodium chloride of No. VII was found still to contain lime. As this sample is free from calcium carbonate and the lime found in the 2nd litre therefore does not come from the calcium carbonate, this lime should not be deducted from the lime of the first litre, but should be added to it, which was in fact done. The exchangeable potassium and sodium were determined by newer methods (6). In so far as the samples contained sulphates and chlorides soluble in water, thé analysis of the sodium chloride and the ammonium chloride extracts yields the sum of the exchangeable bases and the bases soluble in water (CaO, MgO, K<sub>2</sub>O and Na<sub>2</sub>O). The bases soluble in water should in such cases be determined separately. For this investigation only the samples IV, V, and VI called for consideration. In our salty Zuyder Zee soils this determination is at present made by a method worked out by Dr. Zuur, in the press-juices obtained from fresh, fairly moist samples. The S. S. Samples IV, V and VI are, however, in an air-dry condition. Before pressing out, therefore, a certain amount of water had to be added; to 1200 grammes of air-dry soil enough distilled water was added to bring it to the water content shown in the second column of Table II.

1st part (30.8—34.2—32.8). Soil and water were well kneaded several times in a dish and after a period of about 48 hours, the soil solutions, with the constituents dissolved in it, were pressed out in a hydraulic laboratory press at a pressure of 400 atmospheres.

Determination of T—S. During the determination of the T—S value by the baryta method, sample VI behaved differently from the others. A white, flocculent precipitate was produced during the retitration of the excess baryta with hydrochloric acid, approximately at the neutralisation point. This precipitate was found to consist of iron, aluminium and presumably of still other constituents. This sample was investigated in triplicate, and the points of the three T-S lines drawn were on the whole less satisfactory.

Potentiometric lime titration. In the three acid reacting samples III, VI and VII a potentiometric lime titration was performed. For the method here employed see pp. 72 to 93 of Vol. B of the Transactions of the Second Commission of the International Society of Soil Science, Groningen Meeting, 1926. In the method of investigation there described an alteration was made; instead of making use of a particular amount of soil, a particular amount of adsorbing material was employed. For clay soils this amount is 2.25 gr clay + humus (as clay) and for the organic soils 0.5 gr humus + clay (as humus). To this, as before, 20 cc liquid was added in all cases, whilst the period of action was fixed at three days. Another difference from the method previously used is that the pH was not determined with the quinhydrone electrode, but with the glass electrode.

N,  $P_2O_5$ ,  $K_2O$ . The investigation of the contents of nitrogen, phosphoric acid and potassium caused no difficulties. The extract for the determination of the potassium soluble in 0.1 normal hydrochloric acid was prepared by shaking 60 gr soil with 600 cc 0.1 normal hydrochloric acid for 1 hour. Additional hydrochloric acid was also added in amounts equivalent to any calcium carbonate present.

#### **III.** Results of the investigation

The results of the investigation will be found collected in Tables I to V inclusive. Each of these Tables will be discussed separately below.

#### a) Table I; mechanical composition

In so far as the figures of this supplement express specific percentages, they call for no further remarks. We shall restrict ourselves to a discussion of a few figures derived from them. From the contents of fractions I and II their relative proportions were calculated (column 9). These proportions vary greatly, viz. from 0.14 to 2.0. The clay fraction (fractions I and II) of samples I and IV is, relative to the other samples, very rich in fraction I (1:0.14 and 1:0.18). A similar preponderance of fraction I is so far not found in our Dutch clay-soils. For our marine clay soils a proportion between 0.4 and 0.6 (as in Nos. II and III) is normal. The proportion for No. VII is of the same nature (0.51); that for No. V (0.32) is somewhat lower than that for the Dutch marine clay soils. Quite a different picture is shown by No. VI, with a proportion of 2.0; in this podsol fraction II occupies by far the most important place (fraction I = 13.4; fraction II = 27.1). It is obvious that these great differences in the relation between fractions I and II must have an effect on the adsorptive capacity for bases of what I have called the clay substance (fraction I + II). When discussing this subject I will deal more fully with this point also.

Column 10 of Table I shows the connection between the content of humus and that of clay (fractions I and II). This shows that the tropical soil from the Sudan (No. I) and the "Curlwaa" from Australia (No. V) are very poor in humus in proportion to their clay content (1.0 and 1.7). From this point of view the Russian Podsol is likewise fairly poor in humus (No. VI with 3.2%). For Dutch marine clay soils from 5 to 7 gr humus per 100 gr clay (fractions I and II) is a normal figure. Samples IV (Australia) and VII (Chernozem, Russia) are comparatively rich in humus.

U-values of the sand fractions. The U-values of the sand fraction (particles between 0.016 and 2.0 millimetres diameter) vary from 113 to 360. According to a classification made for Dutch soils the sand fraction of No. IV (U = 113) is very fine, that of the other samples extremely fine (7).

## b) Table II. Constituents soluble in water

Before pressing, the air-dry soil samples IV, V, and VI were brought to water contents of 30.8-34.2-32.8 (see table II, first part, column 2). Slight amounts of bicarbonate were found in the press-juices (about 46.0-62.8 mg per 100 cc press juice). Similar small amounts also occur in soils which are absolutely free from chlorides and sulphates. We take it that the water containing  $CO_2$  dissolves small quantities of lime out of the calcium carbonate or out of the clay-humus complex and forms calcium bicarbonate with these. We therefore include this calcium bicarbonate not in the salts which are really soluble in water,

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## Table 1

			Percenta so	ges in ov il (105° C	en-dried ')			:	8
No. S.S.S.	water-soluble substances	CaCO <sub>8</sub>	Humus (dry combustion; Ter Meulen-method)	Fraction I; particles smaller than $2 \mu$	Fraction II; particles from $2-16\mu$	clay substance (fraction I + II)	Sandfraction (parti- cles from 0,016 —2 m M)	Ratio fraction ] fraction II = ]:	G humus per 10 clay substanc
7						;	· ·		
Ι	0	2.4	0.7	64.3	8,8	73.1	23.8	0.14	1.0
II	0	8.7	3.2	47.4	18.4	65.8	22.3	0.39	4.9
ΪΠ	0	0	5.1	47.1	23.4	70.5	24.4	0.50	7.2
IV	0	11.9	2.7	17.2	3.1	20.3	65.1	0.18	13.3
v	0.3	0	1.0	43.5	13.9	57.4	41.3	0.32	1.7
VI	· 0	0	1.3	13.4	27.1	40.5	58.2	2.0	3.2
VII	0	0	11.8	47.3	24.0	71.3	. 16.9	0.51	16.5

and do not deduct the amount of CaO equivalent to the bicarbonate from the sum of the CaO soluble in water plus the exchangeable CaO. It is obvious that this reasoning does not hold good in the case of typical soda soils, but no soil of that kind is present in the collection of the Standard Samples.

#### Table II

## Water-soluble constituents of the press juice

-	$g H_2 O per$ 100 g oven-	Milligrammes per 100 cc press-juice							
No.	dried soil (105°C) be- fore pressing	HCO3	CI	SO3	CaO	MgO	Na <sub>2</sub> O		
IV V VI	30.8 34.2 32.8	$62.8 \\ 51.8 \\ 46.0$	14.6 229.9 9.4	4.0 338.2 6.0	83.9 111.6 21.2	9.8 83.5 10.0	<sup>č</sup> 7.4 241.7 7.6		

·	i.	•	g per	: 100 g o	ven-dried	l soil (10	5° C)		
No.	ca	lculated f	wate	r-soluble	(after				
	πoo			0.0	M~0	No			<u>.                                    </u>
•	HUO3	1.01	€Ua	CaU	J mgo		CaO	MgO	Na <sub>2</sub> O
IV.	0.019	0.004	0.001	0.010	0.003	0.002			
V .	0.018	0.079	0.116	0.038	0.029	0.083	0.028	0.027	0.077
Υ١.	0.015	0.003	0.002	0.007	0.003	0.002		· ·	

**Mechanical** Composition

	Subfractions of the sandfraction (diameter in micra)											
16— 43	43 74	74—- 104	104 147	147 208	208 295	295 417	417— 589	589 833	833— 1168	1168— 1651	(specific surface) calculated per 100 g sandy fraction	
91	50	.99	18	90			0.8	0.1	0	6	994	
14.2	5.5	1.1	0.4	0.4	0.3	0.0	0,5	0.1	0 0	l d	307	
18.9	2.6	0.9	0.7	0.6	0.4	0.1	0.1	0.1	0	0.	336	
6.5	7.0	10.3	12.5	14.6	8.1	3.9	1.6	0.6	Ö	Ŏ	113.	
16.6	11.0	7.3	4.0	1.8	0.3	0.2	0.1	0	0	0	239	
49.7	5.6	0.4	0.3	0.3	0.3	0.4	0.5	0.4	0.3	· 0 ·	360	
12.8	1.0	0.6	0.5	0.7	0.5	0.3	0.3	0.1	0.1	· 0	323	

It is now necessary to calculate the CaO equivalent to the bicarbonate. For Nos. IV, V and VI, with respectively 0.019 %, 0.018 % and 0.015 % HCO<sub>3</sub> of dry soil (table II, second part, col. 2), this is 0.009 %, 0.008 % and 0.007 % CaO. Practically all the CaO (respectively 0.010 % and 0.007 %; see table II, second part, col. 5) found in the press-juices of Nos. IV and VI is therefore present in these in the form of calcium bicarbonate. The press-juice of these two samples further contained only a few thousandths per cent MgO and Na<sub>2</sub>O (0.003-0.002), whilst analysable quantities of K<sub>2</sub>O were not found in any of the three pressjuices. It will perhaps also be possible to find such small amounts of bases in a press-juice of a soil that is practically free from chloride and sulphate. The content of bases soluble in water (CaO, MgO, K<sub>2</sub>O and Na<sub>3</sub>O) of samples IV and VI may therefore safely be taken as nil.

Soil Sample No. V, on the other hand, does contain chlorides and sulphates soluble in water. The amounts of CaO, MgO, and Na<sub>2</sub>O (where necessary that of K<sub>2</sub>O also) equivalent to these were calculated as follows. From the 0.038 % CaO found in the press-juice, 0.008 % CaO must be deducted (equivalent to the  $\text{HCO}_3$ , i. e.  $28 \times 18:61 = 8$ ). The remaining 0.030 % CaO and likewise the 0.029 % MgO and 0.083 % Na<sub>2</sub>O must now be corrected for the so-called "negative adsorption". For if soil is put into a salt solution (e. g. of NaCl), a zone poorer in anions forms around the particles. The result of this is that the solution itself becomes richer in sodium chloride. This increase of the concentration in NaCl will depend on the proportion of soil to liquid. When the ex-

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changeable bases + those soluble in water are calculated, the soil is lixiviated with considerably more water than it contains when pressed. Per 100 gr soil No. V, when pressed (present 34.2 cc water; see table II, first part, col. 2), 0.079 gr Cl were found, whilst when 100 gr soil No. V were shaken with 1200 cc water, after filtration 0.073 gr Cl was found (8). The amount of bases, 0.030 % CaO, 0.029 % MgO and 0.083 % Na<sub>2</sub>O found in the press-juice of No. V was therefore multiplied by the factor 73: 79 = 0.92. In this way we calculated that soil sample No. V contained 0.028 % CaO (0.92 × 0.030 = 0.028), 0.027 % MgO, and 0.077 % Na<sub>2</sub>O (table II, second part, last columns) as bases soluble in water. The sum of the CaO, MgO and Na<sub>2</sub>O soluble in water plus the exchangeable CaO, MgO and Na<sub>2</sub>O found with the extraction was reduced by these small amounts. When the contents of exchangeable bases of soil sample No. V, as shown in table III (0.274 - 0.182 - 0.046 - 0.039) were calculated, this reduction had already been taken into account.

#### c) Table III. Soil Acidity (pH) and Adsorption Values (S, T, V).

With the exception of sample No. VII, the glass electrode invariably yielded a lower pH value than the quinhydrone electrode. The difference was greatest with samples V and VI, which showed a marked drift in the alkaline direction with the quinhydrone electrode. In these cases the values found with the glass electrode are certainly to be preferred. As a matter of fact this holds good in general, and especially with those samples of which the pH is higher than 8. Three of the samples (III, VI, and VII) show an acid reaction; the others an alkaline one. There are, however, no abnormally strongly acid or strongly alkaline reacting types, such as soils containing Fe-Al-SO<sub>4</sub> or alkali soils.

The remaining figures of the first part of this table refer to the content of adsorptively bound bases. These are expressed in percentages of dry soil, in milligramequivalents (mE) per 100 gr dry soil, in percentages of clay + humus (as clay), and in mE per 100 gr clay + humus (as clay) respectively. The sum of the mE of exchangeable CaO + MgO + K<sub>2</sub>O + Na<sub>2</sub>O gives the S value, which is therefore expressed per 100 gr dry soil and per 100 gr clay + humus (as clay) respectively. The base binding capacity of the humus substance was assumed to be 4.545 times larger than that of the clay substance (fraction I + II). The 3.2 gr humus of sample No. II therefore has a base binding capacity equal to  $3.2 \times 4.545 = 14.6$  gr clay substance (fraction I + II); for the clay + humus of sample II the base binding capacity is equivalent to that of 65.8 clay substance + 14.6 clay substance = 80.4 clay substance (fraction I + II) (9).

This conversion is only approximately correct, and it will be advisable not to apply it to soils with too much humus; it would, for instance, be better not to take into account sample No. VII, with 11.8% of humus.

The second part of Table III contains the relative proportion of the exchangeable bases to S = 100. Then follow the values T—S and T, expressed in mE per 100 gr soil and per 100 gr clay + humus (calculated as clay). Finally comes the value V (= 100 S: T).

Value T. The calculation of the value T per 100 gr clay substance (+ humus) therefore gives the total base binding capacity of 100 gr clay substance (fraction I + II) in the 6 mineral soils (samples I - VI). If this 100 gr clay substance (fraction I + II) in all the 6 mineral soils possessed the same total base binding capacity, the values T would be equal. They are, however, not so; these values range from 139.5 to 43.2. It is worth while trying to determine the cause of these very great differences. It is not very likely that these are to be ascribed to inaccuracies in the small correction for the humus contents. It should much rather be sought for in what I have called the clay substance (fraction I + II), that is, in differences in the mineral soil complex. As far as the available data are concerned, these differences are only manifested in the proportion figures of fraction I and fraction II (see table I, column 9). It is perhaps still clearer to indicate how much per cent fraction I is of the clay substance (fration I + II); that is: 88-72-67-85-76-33 for the six mineral soils respectively.

In table III (second part) an attempt has been made to split up the total T values in 100 gr dry soil (106,5 - 66.8 - etc.) into the T values for the humus substance, for fraction I and for fraction II. The data for this splitting up are, however, taken from investigations of Dutch soils, and even for these soils they are only comparatively accurate. They were calculated in the following way.

According to an investigation of a large number of Dutch soils of various types, an average of 519 mE of bases are bound by 100 gr humus, with a total saturation (T), or 1 mE base by 193 mg humus (10). Sample No. I contains 0.7 gr humus per 100 gr dry soil, which therefore bind 700: 193 = 3.6 mE bases when totally saturated. For the other mineral soils this is 16.6 - 26.4 - 14.0 - 5.2 - 6.7.

For the clay fraction II (particles from 0.002–0.016 mM diameter) the base binding capacity per 100 gr fraction II with total saturation (T) is assumed to be 14 mE (11). The sand fraction (particles greater than 16  $\mu$ ) also possesses the power of binding bases (see same paper), but the figures concerned are too divergent to admit of an average

					Table
Exchangeable	bases	(S-value);	total	base	binding

No.	pH in aqueous suspension suspension quin-			excheangeable bases per in grammes				100 gr oven-dried soil (105° G) in milligrammequivalents				
	hy- dron electr.	glass- electr.	gr clays humus (c clay) per dried se	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgÖ	. K <sub>2</sub> 0	Na <sub>2</sub> O	Som = S
I · II	8.9 7.8	8.6 7.5	76.3 80.4	1.248 0.742	0.159 0.056	0.073 0.057	0.137 0.010	44.6 26.5	7.9 2.8	1.6 1.2	4.4 0.3	58.5 30.8
III IV	5.4 8.3	5.2 8.1	93.7 32.6	$0.452 \\ 0.451$	0.124 0.105	0.038	0.009 0.009	16.1 16.1	6.2 5.2	0.8 0.6	0.3 0.3	$\begin{array}{c} 23.4\\ 22.2 \end{array}$
V VI	7.9 5.5	7.5 4.9	61.9 46.4	$0.274 \\ 0.026$	0.182 0.012	0.046 0.002	0.039 0.014	9.8 0.9	9.1 0.6	$\begin{array}{c} 1.0 \\ 0.1 \end{array}$	1.3 0.5	21.2 2.1
VH	6.3	6.4	124.9	1.376	0.164	0.035	0.007	49.1	8.2	0.7	0.2	58.2

No S.S.S.	relati	ve propor geable per 100 1 are pres	tion of ex bases nE bases sent mE	chan-	mE pe oven- soil (10	er 100 gr •dried 95°C)	mE per 100 gr clay + humus (calculated as clay)		V = 100 S
	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	T—S	т	T-S	Т	
			-						
Ι	76.2	13.6	2.6	7.6	48.0	106.5	62.9	139.5	55
· II	86.1	8.9	4.0	1.0	36.0	66.8	44.8	83.1	46
III	68.8	26.4	3.6	1.2	48.5	71.9	51.8	76.8	33
IV	72.3	23.5	2.9	1.3	21.5	43.7	66.0	134.4	51
V	46.3	43.1	4.7	5.9	34.5	55.7	55.7	89.8	38
VI	_	°	_	· · · · · · · · · · · · · · · · · · ·	18.0	20.1	38.8	43.2	10
VII	84.4	13.9	1.3	0.4	63.5	121.7	50.8	97.5	48

being calculated for the sand fraction. Moreover the share which this fraction has in the total base-binding capacity of the soil is only a very slight one. For these reasons the sand fraction is here left out of account. Sample No. 1 contains 8.8 gr of fraction II per 100 gr dry soil, to which with total saturation (T)  $0.14 \times 8.8 = 1.2$  mE bases are bound. For the remaining samples this is 2.6 - 3.3 - 0.4 - 1.9 - 3.8. For fraction I there then remains: 101.7 - 47.6 - 42.2 - 29.3 - 48.6 - 9.6.

In the last column but one of table III the T value of the mineral particles (Fraction I + II = a) is calculated per 100 gr fraction I + II. There is a striking connection between these latter T values (141 - 76 - 65 - 146 - 88 - 33) and the ratios of fraction I to fraction II, resp.

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•	in gr	ammes			in mill	igrammequ	livalents	;
CaO	MgO	K20	Na <sub>2</sub> O	CaO	MgO	K20	Na2O	Som = S
1.636	0.208	0.096	0.180	58.4	10.4	2.0	5.8	76.6
0.923	0.069	0.071	0.012	33.0	3.4	1.5	0.4	38.3
0.482	0.132	0.041	0.010	17.2	6.6	0.9	0.3	25.0
1.384	0.322	0.092	0.028	<b>49.4</b>	16.1	2.0	0.9	68.4.
0.443	0.294	0.074	0.063	15.8	14.7	1.6	2:0	34.1
0.056	0.026	0.004	0.030	2.0	1.3	0.1	1.0	4.4
1.102	0.131	0.028	0.006	39.4	6.5	0.6	0.2	46.7
	-						-	•
	mE	per 100 g o (1059	oven-dried 'C)	soil		T-va	alue of fr	action
<u>, , , , , , , , , , , , , , , , , , , </u>	mE adsorbe	per 100 g d (105 ed at total	oven-dried 'C)	soil (T) in		T-va I + II (= calculat	alue of fra = a)   and   c	act  I ( alc

in fraction II

1.2

2.6

3.3

0.4

1.9

3.8

3.4

Capacity (T-value); degree of saturation (V-value)

111

the humus

3.6

16.6

26.4

14.0

5.2

6.7

61.1

I + II (= a)

102.9

50.2

45.5

29.7

50.5

13.4

60.6

the percentages of fraction I of the clay substance (fraction I + II), as is shown by the following.

 $\mathbf{I} = \mathbf{b}$ 

101.7

47.6

42.2

29.3

48.6

9.6

57.2

fraction I+II

141

76

65

146

88

33

85

fraction I

158

100

90

170

112

121

72

As the percentage of fraction I increases the T value of the mineral particles (calculated per 100 gr fraction I + II) rises. This must obviously be the case. The T value depends, at least partly, on the base binding surface of the soil particles and this base binding surface occurs, at any rate for the greater part, in the finer particles of fraction I. The differences in the T values, for instance of samples No. I (141) and No. II (76) are, however, too great, to be ascribed only to the differences in the percentages of fraction I of the clay substance (fraction I + II), viz. 88 and 72. Now the data of table III permit us to calculate the T

Sample	I	IV	v	II	ш	VI .
ratios fraction I : fraction II fraction I as par-	} 0.14	0.18	0.82	0.39	0.50	2.0
centage of frac-	88	85	76	72	67	33
T value (of frac- tion I + II) per 100 gr fraction I + II	) } 141	146	88	76	65	<b>33</b> <sup>°</sup>
Tvalue (of fraction I per 100 gr frac- tion I	$\left. \right\}$ 158	170	112	100	90	72

values of fraction I per 100 gr fraction I (see table III, last column), which are 158-100-90-170-112-72. From these latter data follows that the base binding capacity of 100 gr fraction I of samples I (158) and IV (170) is a good deal larger than that of 100 gr of fraction I of samples V (112), II (100) and III (90) and of sample VI (72). Not only therefore do samples I and IV contain more fraction I per 100 gr clay substance, but this fraction also has a larger base binding capacity. This latter value finds its expression in the T values of fraction I calculated per 100 gr fraction I (158-100-etc.) (12).

The six mineral soil samples can be assembled into three groups, namely:

- Sample	I and IV	V, II, III	VI
ratio fraction I : fraction II	0.16	0.40	2.0
fraction I on % Fraction I + II	86	72	33
T value (fraction I + II) per fraction I + II	144	76	33
T value (fraction I) per fraction I	164	101	72

It follows from the above that the total base binding capacity (T value) of the mineral soil complex neither calculated per 100 gr clay substance (fraction I + II), nor per 100 gr fraction I, has a general significance. For Dutch soils, which — as far as our investigations show — have a fairly regular composition of the mineral soil complex, both as regards the mechanical and the chemical composition, this is approxi-

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mately the case, but thisholds good both for a calculation per fraction  $\cdot I + II$  and per fraction I. For practical reasons a calculation per fraction I + II was chosen; for soils with fairly high percentages of fraction II (about 60 to  $50^{\circ}/_{0}$  of fraction I + II), as SSSVI, this seems to me more correct even on principle.

Value S. The S values per 100 gr dry soil are between 58.5 and 2.1. These S values depend on the composition of the base adsorbing soil complex and on the degree of saturation of this complex with bases. Table III (first part, last half) contains the calculation of the contents of exchangeable bases and of the S values on clay (+ humus). The same objections hold good with regard to the S values per 100 gr clay (+ humus) as against the T values per 100 gr clay (+ humus). The influence of the degree of saturation on the S value is best seen from the S values of the two Dutch clay soils, which are of the same type. The young soil No. II (pH = 7.5), which is well saturated with bases and contains CaCO<sub>3</sub>, has an S value (per 100 gr clay) of 38.3, which is about the normal value for Dutch soils of this type; soil No. III (pH = 5.2), which already gives an acid reaction, has an S value = 25.0. Samples I and IV give the very high S values 76.6 and 68.4 (per 100 gr clay). These S values, which from the point of view of Dutch soils are high, can be partly explained by the fairly high pH values (8.6 and 8.1), which will doubtless be connected with the more or less arid climate; but the mechanical, and possibly also the chemical, composition of the mineral soil complex also no doubt play a part in this. Sample No. VI gives a fairly strong acid reaction (pH = 4.9) and has the extremely small S value of 4.4 per 100 gr clay. Such low S values do not occur in the Netherlands with soils with pH values of about 5; here, too, the mechanical composition of the mineral soil complex (high content of fraction II) probably plays a part.

Value V. The degree of saturation (value V) expresses the percentage of the bases which the soil can bind (T) which are present in exchangeable form (S). As far as I can judge at present, this V value is independent of the mechanical and chemical composition of the mineral adsorbing complex. The V values range between 55 and 10. For the Dutch clay soils (sample No. II), which are well saturated with bases, a V = 46 is a normal value; the other type (No. III) gives an acid reaction (pH = 5.2) and has a V = 33. According to Dutch ideas samples I and IV have fairly high V values (55 and 51); this will no doubt be connected with the more or less arid climate.

There must be a connection between the V values and the pH values. But the nature of the bases also has an effect on the pH;

if the adsorptively bound CaO is replaced by  $Na_2O$ , the pH rises. This means that also the relative proportions of the exchangeable bases (per 100) plays a role.

Relative proportion of the exchangeable bases. Only two samples (I and V) contain more than small amounts of exchangeable Na<sub>2</sub>O (7.6 and 5.9). Samples III and IV, and especially V, further contain a good deal of MgO.

Relation between V and pH. This relation is shown by the following table:

No. SSS	VI	III	V	II	IV	I
рН	4.9	5.2	7.5	7.5	. 8.1	8.6
	10	33	38	46	51	55

The high pH value of sample V (7.5), with a V value = 38, can be accounted for by the fairly high content of Na<sub>2</sub>O (5.9).

d) Table IV. Potentiometric lime titration

The adsorption of lime by potentiometric lime titration was determined only in the case of the acid samples III, VI, and VII. In the first part of table IV, columns 2 to 6 inclusive contain particulars of the manner in which the investigation was carried out and of the pH values found on giving the successive doses of lime. With the aid of these pH values titration curves were plotted, the dose of lime being set out on the horizontal axis in mE CaO per 100 gr clay (+ humus). It was then determined where these titration curves and the pH lines 6.5 - 7.0 - 7.5 - 8.0 intersect. In the case of sample III this occurs with an adsorption of lime of 5.5 - 9.4 - 13.3 - 17.1 mE CaO per 100 gr clay (+ humus) respectively. These results are included in table IV, first part, columns 7 to 10 inclusive.

In the second part of table IV the S values in mE per 100 gr clay (+ humus) are first of all repeated. The next 4 columns contain the sum of these S values and the number of mE CaO which must be adsorbed to reach a pH value of 6.5 - 7.0 - 7.5 - 8.0 respectively (thus in the case of sample III, 25.0 + 5.5 = 30.5; 25.0 + 9.4 = 34.4; etc.). These figures therefore indicate new S values, which these soils would possess if their pH were 6.5 - 7.0 - 7.5 - 8.0 respectively. It should be remarked that these pH values were determined with a different ratio of soil to water  $(2.5 - 4.9 - 1.9 - \text{gr soil with } 20 \text{ cc } \text{H}_2\text{O})$  from that for the ordinary pH-determination (10 gr soil with 25 cc H<sub>2</sub>O).

No. S.S.S.	r air-dry soil used = 2,25 gr clay + humus as clay)	cc lime solution 1 == 0,0433) added	cc water added	olumn 3 expressed mE CaO per 100 gr sy+humus (as elay)	pH (glass- elec- trode)	Lime adsorption, in mE per 100 gr clay + humus (as clay), to reach pH					
	<u>ରେ                                    </u>	<u>.</u>		c( as cla				1.0			
;		0	20.0		5.65			÷.,			
	•	2.5	17.5	4.8	6.41			:			
ш	2.519	5.0	15.0	9.6	7.02	5.5	9.4	13.3	17.1		
		7.5	12.5	14.4	7.65						
		10.0	10.0	19.2	8.27						
		~ .	1								
	4.988	0 ·	20.0	0	5.16						
		2.5	17.5	4.8	6.09		11.3	14.9	18.2		
VI		5.0	15.0	9.6	6.78	7.7					
		7,5	12.5	14.4	7.41				ļ		
		10.0	10.0	19.2	8.16	,	 	<u> </u>	L		
	1.962	0	20.0		6.71						
		1.0	19.0	1.9	7.00		1.9	4.7			
¥11		2.0	18.0	3.8 . 5 0	7.33				7.2		
		3.0	17.0	0.8	7.75				1		
·		4.0	10.0	1.7	0.09			,	I		
							-				
/ 9 ;	n m F n	ar Sun	of San	d lime ad	l- Tin	mEner					

Table IV

No. S.S.S.	S in m.E. per 100 g clay + humus (as clay) (see	Sum sorp 100 clay	of Sa tion in gr clay-  ) to re	nd lime m. E. -humus ach pl	ad- per s (as H ==	T in m. E. per 100 gr clay + humus (as clay) (see	V (= 100 8 : T) with a pH =				
	Table III)	6.5	7.0	7.5	8.0	Table III)	6.5	7.0	7.5	8.0	
III VI VII	25.0 4.4 46.7	30.5 12.1	34.4 15.7 48.6	38.3 19.3 51.4	42.1 22.6 53.9	76.8 43.2 97.5	40 28	45 36 50	50 - 45 53	*55 52 55	

This causes a certain difference in the pH values. The following remarks with respect to the new S values may also be made. Sample No. III, with a pH = 7.5, has an S value = 38.3 mE per 100 gr clay (+ humus), which happens to be exactly the same S value as is possessed by sample No. II, which is of the same type and itself has a pH = 7.5. The S values of No. VI and No. VII differ fairly considerably from those of Bodenkundliche Forschungen 2

No. III with the same pH values. The composition of the clay and the humus fractions plays a role here.

With the aid of the T values it is possible to calculate the V values with the pH values 6.5 - 7.0 - 7.5 - 8.0. The S value of sample No. III, for instance, with pH = 7.5 is 30.5; the T value is 76.8; this gives  $V = 100 \times 30.5$ ; 76.8 = 40 (see table IV, last columns). Since none of the three soils has more than a small amount of Na<sub>2</sub>O, so that the nature of the bases has no influence. I had expected practically equal values here. In the pH region from 7.0 to 8.0 this is pretty well the case; the differences are not great. Sample No. III has a V = 50with a pH = 7.5, whilst the same type No. II, which in itself has a pH = 7.5, shows a V value of 46. This comparatively slight difference may be caused by a difference in the method of pH determination. Sample No. VI. with a pH = 8.0, has practically the same V-value (52) as samples III and VII. With lower pH values the V-value of No. VI is lower, and this difference becomes larger according as the pH falls. The reason for this behaviour is unknown to me.

e) Table V. Nutrient Elements (N,  $P_2O_5$ ,  $K_2O$ )

Nitrogen. The content of nitrogen is expressed in grammes per 100 gr dry soil and per 100 gr humus. In the Dutch clay soils, with a normal humus content (an average of about 6 gr humus per 100 gr clay = fraction I + II) from 5 to 7 gr nitrogen per 100 gr humus is found as a rule, so that the nitrogen content of the humus, 6.8 and 6.2 gr respectively, found in Nos. II and III, would be normal for Dutch soils. Not only is the tropical soil No. I absolutely poor in nitrogen (0.026 %), but the humus also is poor in this constituent (3.7). Sample No. VII, which is rich in humus, contains a high percentage of nitrogen per 100 gr soil (0,540 %), hut the nitrogen content of the humus (4.6) is smaller than that of Nos. II and III. In Dutch soils, however, with a similar humus content, the last mentioned value is also as a rule no higher.

Phosphoric acid. The contents of phosphoric acid were determined by dissolving in 12.5 per cent  $\text{HNO}_3$ , after igniting the soil (the so-called total  $P_2O_5$ ) and in 1 per cent citric acid. From this the relative solubility of the  $P_2O_5$  is calculated (for sample I, that is,  $0.048 \times 100$ : 0.141 = 34.0). On these  $P_2O_5$  values Lemmermann's well-known limit figures are based, by the aid of which conclusions can to a certain extent be drawn as to the  $P_2O_5$  requirement of the soil. In connection with this it may be remarked that soil No. II will be able to yield a large agricultural crop for at least 200 years, without any phosphoric

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Nutrient elements (N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O)

0 soluble in 0,1 l HCl per 100 gr	tion	I	0.075	0.110	0.064	0.081	0.062	0.030	0.047	
	frac	I + II	 0.066	0.079	0.043	0.069	0.047	0.010	0.031	
gr K <sub>2</sub> norma	oven-	driedsoil	0.048	0.052	0.030	0.014	0.027	0.004	0.022	
le in 00 gr	tion	Ι	0.73	1.03	0.98	2.15	1.54	0.67	1.21	
aO solubi	frac	I + I	0.64	0.74	0.65	1.82	1.17	0.22	0.80	,
gr K 5% I	-uevo	dried soil	0.47	0.49	0.46	0.37	0.67	60.0	0.57	
relative solubi- lity of	the P <sub>2</sub> O <sub>5</sub>		34.0	20.2	14.1	28.9	15.9	11.8	4.4	
), per oven- soil .	1% ci-	tricacid	0.048	0.039	0.027	0.013	0.007	0.008	0.008	
gr P <sub>a</sub> ( 100 gr dried solub	$12^{1}/_{2}\%$	$HNO_3$	0.141	0.193	0.192	0.045	0.044	0.068	0.182	
rogen 100 gr		Sumus	3.7	6.8	6.2	4.6	6.0	4.9	4.6	
gr nit (N) per	oven-	dried soil	0.026	0.218	0.314	0.123	0.060	0.064	0.540	
J)	m-dried soil ee Table I) fraction	· I	64.3	47.4	47.1	17.2	43.5	13.4	47.3	
er 100 gr m-dried s ee Table		I + II	73.1	65.8	70.5	20.3	57.4	40.5	71.3	
s) Ala La		snernu	0.7	3.2	5.1	2.7	1.0	1.3	11.8	
No. S.S.S.			I	II	III	IV	v	VΙ	VII	

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acid fertilization. It should, however, be pointed out that the crops on the plot in question can draw their nutriment from a layer of at least 1 metre thick. The plot of sample No. III already receives from time to time a  $P_2O_5$  manuring. Samples I, IV, V, and VI are poorer in total  $P_2O_5$  than the two Dutch soils, and this is especially the case with the soils from Australia and with the Russian Podsol. In No. I the solubility in citric acid, and therefore also the relative solubility of the phosphoric acid, is high; in Nos. V and VI these values are low. Sample No. VII is fairly rich in total  $P_2O_5$ , but poor in  $P_2O_5$  soluble in citric acid, so that the relative solubility is extremely low (only 4.4). According to Lemmermann's ideas, soils III to VII inclusive must,

for normal agriculture, require phosphoric acid.

Potassium. Two potassium contents were determined, viz. soluble in 5 per cent hydrochloric acid at boiling point and in 0.1 normal hydrochloric acid at room temperature. By the former method only part of the potassium dissolves out of the weathering silicate; when boiled with 25 % hydrochloric acid a good deal more potassium is dis-The contents of potassium determined by both methods are solved. expressed in gr per 100 gr dry soil, per 100 gr clay (particles smaller than 16 micra) and per 100 gr fraction I (particles smaller than 2 micra). From these figures — in as far as the potassium soluble in 5 % hydrochloric acid is concerned — it can be concluded that sample No. VI is poor in potassium. Calculated as percentages of fraction I, the difference from the other samples, however, is not so large. The potassium figures (5 % HCl), calculated per 100 gr clay (fraction I + II) and per 100 gr fraction I, of No. IV and V are very high (2.15 and 1.54). The content of potassium soluble in 5% hydrochloric acid is determined in order to obtain a general impression as to the content of potassium; conclusions with regard to the potassium requirement of the soil are not, however, drawn from these figures. Advice as to fertilization is based by the Bedrijfslaboratorium voor Grondonderzoek, Groningen, on the content of potassium soluble in 0.1 normal hydrochloric acid. Definite norms for this have, however, not been fixed.

The Hague (Holland), November-December 1939.

#### Notes

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- 1. Spithost, C.: Verhandl. d. II. Komm. d. Intern. Bodenkdl. Gesellschaft, Teil A, 113, Kopenhagen 1933.
- 2. Washington, Conclusions of the 1st. Commission, Method A, Proceedings Intern. Soc. Soil Science IV, 216-218, 1929.
- 3. Hooghoudt, S. B.: Trans. 1st. Comm. Intern. Soc. Soil Science, entitled "Physique du Sol", 213, Versailles 1934.
- 4. Intern. Mitteil. f. Bodenkde., V, 1, 1915.
- 5. Internat. Mitteil. f. Bodenkde., XII, 104, 1922.
- Bepaling van het uitwisselbare magnesium, kalium en natrium in den grond volgens nieuw toegepaste analyse-methoden, door Dr. Jac. van der Spek en M. Dekker, Verslagen Landb. Onderzoekingen, No. 44 (13) B.
- See my paper in the Transactions of the First Commission of the Int. Soc. of Soil Science, Bangor, Vol. A, 1938, p. 7-13 (see § 4, p. 11-12).
- 8. Because of the negative adsorption less Cl is found by greater dilution (0,073 grCl by a concentration of 1200 cc H<sub>2</sub>O per 100 gr soil against 0,079 gr Cl by a concentration of 34,2 cc H<sub>2</sub>O per 100 gr soil). For SO<sub>3</sub> was, however, found 0,142 against 0,116. This latter figure cannot be correct. Probably not all the SO<sub>3</sub> (CaSO<sub>4</sub>, MgSO<sub>4</sub>) has gone into solution by the concentration of 34,2 cc H<sub>2</sub>O per 100 gr soil.
- 9. See further my paper in Soil Research, Volume I (1928), No. 1, p. 33-34.
- 10. Soil Research, Volume I (1928), No. 1. The figure (170) given on p. 25-26 is not calculated correctly, viz. without taking the adsorption of the clay substance into account; the correct figure is 193 (100000: 193 = 519).
- 11. This figure is taken from table IV, p. 50-51 of Soil Research Volume V (1936), No. 1: Der mineralische Bodenkomplex.
- 12. It would be interesting to know the reason of the differences in the base binding capacity (T values) of fraction I per 100 gr fraction I. Is this only a question of the base binding surface, or do the chemical and mineralogical composition of this surface play a role also? For this reason it would be instructive to determine the surface of the particles of fraction I of the six soil samples. If the soil particles were massive spheres, it would be possible to estimate this surface accurately. The soil particles are, however, of more or less fantastic shapes, and presumably also have hollows and cracks and fissures, so that the surface can be determined only approximately. For a few Dutch soils we have tried to do this; see Soil Research, Volume V (1936), p- 30-32. Furthermore Dr. S.B. Hooghoudt, Verslagen van Landbouwk. Onderzoekingen, No. 41, B, (1935), p. 589--615.