ON THE ACCURACY OF ELECTROMETRIC AND COLORIMETRIC METHODS FOR DETERMINING P_H VALUES OF SOILS

BY

W. A. J. OOSTING

AGRICULTURAL ENGINEER.

ASSISTANT GEOLOGICAL LABORATORY, AGRICULTURAL
UNIVERSITY, WAGENINGEN (HOLLAND).

444678

On the accuracy of electrometric and colorimetric methods for determining P_h values of soils, by W. A. J. Oosting

Agricultural Engineer, Assistant Geological Laboratory, Agricultural University Wageningen (Holland).

As the knowledge of the P_h value became of interest for geologists, studying the formation of soils, some years ago I determined the value of a number of Indian limestone-soils. A monograph on the genesis of these soils has been published by Prof. J. VAN BAREN, who also collected most of the samples examined, during his agrogeological journey in 1916 and 1917 (12, **Landbouw** 4, 4, 1928, 200).

The determination of the hydrogen ion concentration of soils being still attended with many difficulties, and moreover the merits of the methods in use not being well known, I found it necessary not only to use the standard hydrogen electrode, but to try other methods as well.

In this way, it was possible to get an idea of the merits of those methods, *applied to this type of soil*. For though many investigators are convinced of the efficiency of the colorimetrical methods, or of the quinhydrone method, there is not always a sufficient basis for this conviction.

The P_h values obtained for Indian limestone-soils will show that many variations may occur between the results of the different methods, even when one works with one type of soil.

SOILS.

The following soils were examined:

91*b*. Dark-brown soil with a little fragments of limestone. Railway-station Tagok Apu at the railway Bandung—Tjiandjur (West-Java).

101*b*. Brown loam with fragments of limestone. Gunung Tjibodas, N.W. of Buitenzorg. (West-Java).

102. The same loam as 101*b*, but removed by pluvial erosion and accumulated at the foot of the hill.

105*a*. Light-brown soil, with iron-concretions, sub-soil. N.E. of Buitenzorg, in the neighbourhood of Tjiteureup (West-Java).

105*b*. Yellow soil, surface-soil. Locality = 105*a*.

108*b.* Grey soil. Parakan terus, N.W. of Purwakarta (West-Java).

145*b.* Brown-yellow loam, Foot of the Gunung Kromong in the neighbourhood of Cheribon (West-Java).

244*b.* Grey soil with a great many small fragments of the rock, with concretion. Christmas-Island, in the neighbourhood of Dolly Beach.

245. Grey soil, Christmas-Island, Giants Well.

246. Grey soil with many concretions. Christmas-Island, in the neighbourhood of Dolly Beach.

320*a.* Grey, sandy limestone-soil, sub-soil. Forest-division Manggar, Residency Semarang. (Central-Java).

320*b.* Black-grey loamy soil, surface-soil. Locality = 320*a.*

321*a.* Grey soil with brown spots, sub-soil. Locality = 320*a.*

321*b.* Grey-black soil, surface-soil. Locality = 320*a.*

322*b.* Light-grey, loamy soil. W. of Gundih, S.W. of Purwodadi. (Central-Java).

323. Black-grey clay. Locality = N°. 322*b.*

324. Loam, surface-soil, burnt, because the vegetation was often destroyed by fire. Locality = N°. 322*b.*

335*b.* Grey-black soil, sub-soil, with some fragments of the limestone. Redjoso, W. of Djokja. (Central-Java).

335*c.* Black-grey soil, surface-soil, with fragments of the limestone. Locality = 335*b.*

535*a.* Yellow-brown soil with many fragments of limestone, sub-soil. Bunder, along the road from Piungan te Wonosari. (Central-Java).

535*b.* Brown soil with a crumble structure. Locality = 535*a.*

535*c.* Black soil, with a quantity of humic matter. Locality = 535*a.*

538. Brown-yellow loam, 9 K.M. W. of Grobogan, N. of Purwodadi, (Central-Java).

539. Brown-yellow loam. Locallity = 538.

546*a.* Grey loam, sub-soil. S. of the little village Ngliron, N.E. of Randu-Blatung. (Central-Java).

546*b.* Black-grey loam with a crumble structure, surface-soil. Locality = 546*a.*

548*b.* Light-yellow soil with many fragments of limestone, sub-soil. In the neighbourhood of Tjabak. (Central-Java).

549. Grey and hard clay with calcareous concretions. Locality = 548*b.*

550. Grey clay. Nglebur, S.E. of Blora. (Central-Java).

551*b*. Brown-red sandy loam. Locality = 548*b*.

552. Red, sandy soil. Locality = 548*b*.

553. Brown-red, sandy loam. Forest-division Ledok, S.E. of Blora. (Central-Java).

557. Brown-red, fine-sandy loam. Gg. Lasem, E. of Rembang. (Central-Java).

566. Darkbrown clay. In the neighbourhood of Suroh-djolok, E. of Kreteg. (Central-Java).

567. Brown-yellow clay. Locality = 566.

568. Brown-red clay. Locality = 566.

569. Brown-black, stiff clay. In the neighbourhood of Wonosari, (Central-Java).

707*b*. Black soil with many fragments of coral-limestone. Pulu Pandjang, coral-island, W. of Djapara. Res. Semarang. (Central-Java).

728*a*. Grey-yellow clay, sub-soil. Along the road Pamekasan—Tamberu, N. of Pamekasan, Isle of Madura.

728*b*. Grey soil, with plant-remains, surface-soil. Locality = 728*a*.

729*a*. Yellow clay, sub-soil. N. of Bulang, along the road Sampang—Ketapang, Isle of Madura.

729*b*. Crumble clay, surface-soil. Locality = 729*a*.

730. Brown-red, sandy loam. In the neighbourhood of Ketapang, N. coast of the isle of Madura.

744*b*. Red clay with some fragments of limestone. Bitoni, near bivouac Oilolok, Isle of Timor.

745*b*. Red clay with grey spots. Fatu-Ino, in the neighbourhood of Niki-Niki, Isle of Timor.

746*b*. Dark-grey clay, sub-soil. Baun (Baoen), district Amarassi, Isle of Timor.

746*c*. Grey-black soil, surface-soil. Locality = 746*b*.

747. Grey-black soil. Niki-Niki, Isle of Timor.

The numbers are those of the Geological Museum at Wageningen (director Prof. J. VAN BAREN).

METHODS.

The methods used are:

1. Electrometric measurement of the suspensions with the hydrogen electrode.

2. Electrometric measurement of the suspensions with the quinhydrone electrode.

3. Electrometric measurement of the suspensions with the antimony electrode (**37, 59, 75.**)

4.   Colorimetric measurement of the filtrates.

5.   Colorimetric measurement of the centrifugates.

6.   Colorimetric measurement of the dialysed liquid.

7.   The Comber method as modified by HISSINK (**35, 46, 47**).

The suspensions were prepared by electrically stirring during twenty minutes one part of soil (passed through a 2 m.m. mesh sieve) and two parts of distilled water.

Then the suspensions were allowed to stand for twenty-four hours, after which they were stirred again during twenty minutes.

One part of the suspension was used for the hydrogen electrode, another part for the quinhydrone electrode, a third part for the preparation of the filtrate, the remainder being centrifuged.

For the antimony electrode new suspensions were prepared.

As a hydrogen electrode I used a platinized piece of Pt wire.

The electrode vessel consisted of a U-shaped tube having a wide leg and a small one.

In the wide tube the suspension was poured, the hydrogen entered, and left this part of the apparatus through very small tubes, the Pt electrode being dipped in the liquid in the wide tube.

The narrow part of the U-tube was used for establishing the connection with the calomel-half cell by means of an agar-gelatine-potassiumchloride tube, which dipped in a vessel which contained saturated K Cl solution.

I used streaming hydrogen, generated from sulfuric acid and zinc.

Special care was taken that hydrogen always flowed at a sufficient rate.

The hydrogen stirred the suspension, and was purified by washing it by means of solutions of basic leadacetate, $AgNO_3$, $KMnO_4$ + H_2SO_4, and alkaline pyrogallic solution.

Many determinations could be made before replatinizing the hydrogen electrode was necessary, and abrasion by sandy soils proved of little importance.

The quinhydrone electrode consisted of a simple Jena beaker in which a peace of platinum wire was dipped, a glass screw, electrically driven, being used for stirring.

The antimony electrode consisted of a rod 6 m.M. in diameter, obtained by pouring molten Kahlbaum antimony into a pyrex tube.

The electrode was polished, and took on a very bright finish, but gradually tarnished during use.

The same apparatus was used as for the quinhydrone electrode, but another KCl-agar-gelatine tube was used.

KOLTHOFF and HARTONG report, that between P_h 5.0 and 9.0 no equation can be given for this electrode (59). I made my calculations after a great number of determinations on buffer mixtures.

The P_h values of the buffer mixtures were checked with the hydrogen-electrode, and the antimony readings were gathered in a table. When using this electrode I worked at 14° C. Readings were made during agitation.

From the Millivoltreadings on biphtalate NaOH, bifosfate NaOH, and boric-acid KCl NaOH mixtures I calculated the following equations:

$$\text{From } 4.0 - 4.7 \; P_h = \frac{E + 0,0416}{0,0629}$$

$$4.7 - 5.5 \; P_h = \frac{E - 0,0236}{0,0488}$$

$$5.5 - 7.4 \; P_h = \frac{E - 0,0467}{0,0447}$$

$$8.0 - 9.5 \; P_h = \frac{E + 0,0967}{0,0607}$$

Between 7.4 and 8.0 the function is not stable and it is not allowed to calculate a formula for this range.

The formula's do not agree with those given by KOLTHOFF, nor with the formula of FRANKE and WILLAMAN. The latter authors however worked at 25°, whereas KOLTHOFF worked also at a room of 14° C.

A special study will be necessary to investigate the causes of these discrepancies. As to other phenomena concerning the use of the antimony electrode, I point to a paper on this subject which I intend to publish within short.

The saturated calomel half-cell was used, and gave constant values when checked from time to time against a hydrogen electrode in standard solutions.

In the beginning I made my readings with a capillary electrometer, later on I used a flip-flop galvanometer of Leeds and Northrup.

I employed the Poggendorf compensation method, and used a „Walzenbrücke nach Kohlrausch" as potentiometer.

The quinhydrone was prepared by turning a solution of ferric ammonium alum into a warm solution of hydroquinone in water, after

which the fine needles were washed many times with cold distilled water.

When using the hydrogen electrode, readings were made every five minutes, and the potential was considered constant, when the same reading was obtained three times. Usually these determinations asked half an hour, with acid soils, and at least 45 minutes with alcaline ones. When using the quinhydrone electrode readings were made every minute, and constancy was practically obtained, when three equal readings were made in succeeding minutes. Nearly always this electrode required less than 10 minutes for constancy.

On general the antimony electrode gave constant potentials after 30 secunds, the P_h values are taken from readings after two minutes.

The Standard buffer solutions were prepared according to CLARK and LUBS. I used mixtures of Kbiphtalate and HCl, Kbiphtalate and NaOH, Kbiphosphate and NaOH, boric acid KCl and NaOH.

The standard mixtures were checked electrometrically by the hydrogen-electrode.

I made use of the following indicators: phenol red, bromphenol blue, cresol red, bromcresol purple, methyl red, thymol blue, bromthymol blue.

The solutions of the CLARK and LUBS indicators were prepared by dissolving 0,100 gram of indicator in 20 c.c. of hot alcohol, diluting the solution with distilled water to 100 c.c.

0,2 gram of methylred was dissolved in 6 c.c. of alcohol and diluted with water to 100 c.c. (57).

The filtrates were obtained by filtering the suspensions through Swedish paper (63).

The centrifugates were prepared by centrifuging for one hour at the rate of 3500 revolutions p. minute.

The dialysis was executed according to the specifications of I. M. KOLTHOFF (56).

20 grams of soil were mixed with 15 c.c. of distilled water, in a pleated „filter" of parchment paper. This mixture was placed in a cup-shaped glass, containing 7 c.c. of distilled water.

After leaving this alone for 24 hours the P_h value of the diffusate was determined colorimetrically.

Concerning this method I beg to observe that neither the determinations published by KOLTHOFF, nor those communicated in this paper were executed by means of old parchment membranes. The bad correlation between the three methods, in the paper of KOLTHOFF

cannot be due to the second reason, suggested by PIERRE and PARKER (67 p. 402).

When working colorimetrically always two drops of indicator were added to 5 c.c. of soil solution.

When two indicators were used, and a small difference was found, I always noted that value which was in nearest conformity with the P_h of the electrometric measurement.

The Comber-Hissink liquids were obtained from Dr. HISSINK'S laboratory.

RESULTS.

Table I gives the results of the determinations.

Most of the soils were alcaline. As an exception, soils which were acid, contained some $CaCO_3$.

I calculated for each P_h value, found electrometrically, the deviations which occurred, when I used other methods.

Of course the number of determinations for each P_h value is very small. Yet some conclusions may be drawn.

The deviations are reported in table II.

Table III reports the frequency of the different deviations.

In the alcaline range the quinhydrone method gave lower results than the hydrogen one. Yet also positive deviations occurred in the alcaline soils.

The antimony electrode has given rather good results, differing however less or more from the standard electrode.

If the P_h values of the antimony electrode are calculated from potentiometer readings after two minutes, without stirring, a much better agreement is obtained with the values indicated by the hydrogen electrode. Remarkably the P_h values determinated during stirring are in general in a rather good agreement with those found colorimetrically.

I calculated my P_h values from a table obtained with stirred buffer mixtures. Perhape it were better to use for unstirred soilwater mixtures a special table obtained on unstirred buffer mixtures. The millivolt readings of this table may be lower than those of the table used, so that the P_h values are still higher than those mentioned in table III.

The values obtained by the colorimetric methods gave, especially when the P_h of the hydrogen electrode was above 6.6, much greater deviations than those obtained by the quinhydrone method.

According to table V the great deviations are found in the colorimetric determinations, the small ones in the quinhydrone values. Practically the deviations of the different colorimetric methods were of the same order.

Only once the colorimetric method gave a positive deviation, while the quinhydrone method produced 14 positive deviations.

With acid soils good results were obtained as well by the quinhydrone method as by the colorimetric methods.

P_h values above 7.6 are seldom found colorimetrically.

Later on it will be discussed whether the higher P_h values of alcaline soils, as indicated by the hydrogen electrode are due to errors of the hydrogen method or to errors of other methods.

Table I, which gives also the results of the hydrogenion determinations by means of the Comber-Hissink method proves that this method may be used for an approximate taxation.

Perhaps it would be better to replace 5.5—6 by 6.0—7.5 when using this method.

From tables II and III one may conclude that after two days the equilibrium has not always been attained.

The cause of this phenomenon is perhaps to be found in the changes in consequence of the long time the soils have been kept dry.

Also alcaline Dutch clay soils („polder"soils) reacted more slowly after having been kept dry.

As to the different indicators used, it was observed that cresol red usually gave results which were 0.1—0.3 lower in P_h thans those found with phenol red. For this reason phenol red must be preferred to cresol red. When studying the salt error, KOLTHOFF found better results with cresol red (58).

The determinations with the quinhydrone electrode gave only little differences between first reading (after two minutes) and latest reading.

When neglecting the little differences between these two readings (table VI), which may be allowed for the purpose of practical soil work, the efficiency of the quinhydrone method has proved to be higher and no other method could give so good results in such an easy manner.

As to the colorimetric methods it must be said that while the deviations of the dialysis-method were practically the same as those of the other colorimetric methods, the former elegant method must be preferred, which requires much less work and garantees a clear liquid in all cases.

That the possibility of obtaining a clear extract is of great importance, may be concluded from the experience of Mr. BRENNER, who could not work colorimetrically with Finnish loam soils, as neither filtring, nor sedimentation could give a sufficient clear liquid (29, p. 125). *)

CONCLUSIONS.

If we start from the supposition that the hydrogen electrode gives the true values, we may conclude that the quinhydrone method was of some use, especially in the acid range, whereas the colorimetric method failed more than the quinhydrone method, especially in the most alkaline parts.

The Comber-Hissink method could be used for a rough taxation of soil acidity. For this type of soil it may be proposed to use the hydrogen electrode, when a qualitative test indicates alcalinity, and to use another method when soils are acid.

For acid lime-soils one may prefer the quinhydrone method, as being munch easier in use, and requiring less time than colorimetric methods. When using the colorimetric method, dialysis may be recommended.

In the following chapter I will discuss whether there is agreement between my results and those of other investigators.

SOME OBSERVATIONS ABOUT THE EFFICIENCY OF DIFFERENT METHODS, AS RELATED BY LITERATURE.

KOLTHOFF showed the possibility of applying the quinhydrone method to soil-work in 1923 (55), and in the same year this investigator published some preleminary researches concerning the colorimetric determination of the P_h values of soils (56).

In 1924 BILLMANN published a paper on the use of the quinhydrone electrode for soils (17), drawing the conclusion (p. 233) that in soil-suspensions up to P_h 8,5 this method may be used. Deviations from 0,1—0,2 are allowed and this author did not find great differences between quinhydrone and hydrogen electrode.

---

*) Using the Komplex indicator and the Reaktiometer of KÜHN, I recently obtained good results with alkaline soils, as shown in table VIII.

The soil is shaken with boiled distilled water in a small tube, seven drops of indicator and some BaSO4 are added and the tube is closed.

After shaking the soil sinks to the bottom, and in the clear liquid the color can be compared with a color-scale. I used buffer mixtures for comparing.

BILLMANN asked CHRISTENSEN to make a prolonged investigation. This paper appeared in 1923 in the Danish language (30) and in 1924 the same investigations were published in „Internationale Mitteilungen für Bodenkunde" (31).

CHRISTENSEN and TOVBORG—JENSEN examined a great number of Danish soils, and came to conclusions, from which I give an extract.

For Danish soils the quinhydrone electrode was, as regards accuracy quite equal to the hydrogen electrode, but the quinhydrone electrode failed for lateritic soils from Africa.

The electrometric determination gives more reliable information than the colorimetric determination, *which in the case of neutral or alcaline reacting soils shows too low, — in certain cases very much too low — results.*

The bad results of the colorimetric determinations seem to be due to the very slight buffer content of clear soil extracts.

As the quinhydrone method permits of as quick a reaction test as the colorimetric method, it should be preferred in mass investigations to the latter method.

Important also is that CHRISTENSEN and TOVBORG—JENSEN found *only very seldom colorimetrically* a P_h value being higher than 7.6.

With 5000 determinations, 10 times P_h 7.6 was found, 3 times 7.8, and only once 8.0 (p. 17).

In the same manner as for my own values, I calculated the average deviations found by CHRISTENSEN and JENSEN, for each P_h value.

Table VIII reports the results of my calculations and shows that the quinhydrone method usually gave small deviations when soils were alcaline, whereas the colorimetric methods gave much lower values for alcaline soils.

When examining African lateritic coffee-soils, they found with the quinhydrone electrode values were much too high.

This proves again that the efficiency of a method is best jugded for *types* of *soil* only, and that generalising is very dangerous in this respect.

As a rule the deviations of the colorimetric methods were negative in the alcaline range, and positive in the acid range.

The differences between filtrate and centrifugate were not important. As to the Comber-Hissink method also CHRISTENSEN and JENSEN observed that liquid II is only seldom red, above P_h 7.5, and that

under P_h 6.6 liquid I — which is always red when the P_h is 5.5.— becomes red.

In 1923 GAINEY (38) published a comparison between the hydrogen-electrode values and the values obtained colorimetrically.

This author examined nearly 400 soils, but his conclusion was rather dangerous: „In general the electrometric and the colorimetric determinations of the hydrogen ion concentration agreed".

The average difference as 0.28, which is not so low that it may be neglected.

Moreover one must not consider the average deviation of a large number of determinations, for the soils which gave good conformity lower the value of the average deviation, — when some soils give large deviations. — One must look how the deviations are divided among the different types of soil.

The first classification is shown in table IX, which I calculated from the values of GAINEY.

It appears that below P_h 4.3 and above P_h 7.6 great and very great deviations occurred.

Table X shows another classification of the deviations, from which we may conclude, *that in nearly half the cases the deviation was more than 0.2.*

Table IX also shows that in the **alcaline range negative deviations are the rule,** while we must look for positive deviations in the acid range.

NIKLAS and' KOCK (61, 62, p. 91) conclude that the colorimetric method may be used, but they give only 16 determinations.

The number of the determinations is too small, to allow of a conclusion. Moreover their soils were all acid, and the writers consider as well the quinhydrone method as a standard as the hydrogen method.

EVERETT CARLETON (27) examined 31 soils and found only small differences between the values obtained electrometrically with the hydrogen-electrode, and the values obtained colorimetrically.

But the soils of CARLETON too were nearly all acid (except two). **I also calculated deviation tables from the values of CARLETON** (table XI and XII).

From these investigations it may only be concluded that the colorimetric method has given good results between P_h 4.8 and P_h 7.0.

BARNETTE, HISSINK and VAN DER SPEK (13, 14) used 32 soils, and determined hydrogen ion concentrations electrometrically with the

hydrogen electrode, and colorimetrically in the centrifugated suspension.

These authors found rather small deviations, they cite GAINEY (38), CARLETON (27) and GÖRBING (42) and come to the following conclusions, which I translate from Dutch:

„From the results of our researches and from those of other investigators, we think we may conclude that the colorimetric determination of the P_h value of the soil, if one works with well centrifugated suspensions, as compared with the electrometric methods, gives sufficiently exact results". (14 p. 147, see also 13 p. 35).

This conclusion seems to me rather risky, for the soils which are mentioned in BARNETTE, HISSINK and VAN DER SPEK's paper *were all acid*, so that their own results only allow of a conclusion concerning a group of soils.

These authors too have neglected the alcaline range. The papers by GAINEY and CARLETON, they cite, have already been discussed.

As to the communication of GÖRBING that in the Hamburg Laboratory the exact measurements (die genauen Messungen) of the hydrogen-ion concentration are performed by means of the colorimetric methods, this may not, as BARNETTE, HISSINK and VAN DER SPEK do, be considered as sustaining the thesis that the results obtained by the colorimetric method as compared with those of the electrometric method, are sufficiently exact.

Apparently GÖRBING supposes that colorimetric measurements are exact, also for soils, but he does not give any basis for this supposition.

In 1923 OLSEN published a study on P_h and vegetation (63) using the colorimetric method (filtrate). Page 22 shows a comparison between colorimetric and electrometric (hydrogen) methods, practically there is no difference. Only two soils out of 18 are somewhat alcaline.

In OLSEN's paper one seldom meets with P_h values above 7.7. The same can be said of the publications by other plantgeographers. The very important study by BIJHOUWER (21) usually gives 7.6 as highest Ph value, but many soils contain much $CaCO_3$ and would have shown a P_h value of $\pm$ 8.5, when examined electrometrically with the hydrogen electrode.

Also CHODAT (28) and SAGER (70) practically give P_h 7.6 as the lowest acidity.

As long as the hydrogen electrode is considered as a standard, the P_h values of alcaline soils found colorimetrically must be considered as too low. Only when it will be proved that the values obtained by

the hydrogen electrode are erroneous, and can be corrected, it will be allowed to use the colorimetric values, supposed also that the International Society of Soil Science accepts this correction as a standard.

In 1927 OLSEN published, together with LINDERSTRÖM—LANG, a paper on the merits of the different methods for determining the hydrogen ion concentration of soils (64).

They examined 93 Danish soils of different type, and a number of these soils were alcaline.

Many times the quinhydrone method gave results which were too high, the colorimetric method gave too high values as well as too low values, the deviations ranging from $+$ 0.3 to $-$ 0.4.

For P_h values under 5.0 and above 8.0 their results are usually 0.3 too low and between P_h 5.5 and 7.7 they are on an average 0.15 too high.

According to OLSEN and LANG, there must be two causes for these phenomena.

Filtrates with a P_h value 8.0 lose carbonic acid to the air, and the colloidal humic substances influence the color of the indicator.

The indicator-error does not depend on the indicator used, nor on the P_h value of the soil; the error is always $-$ 0.35.

The authors have calculated a correction curve for suspensions 1 : 1 of undried soils which have been filtered after 24 hours.

When the correctiongraph given is used, the accuracy of $\pm$ 0.15 P_h is said to be attained, and OLSEN and LANG prefer the colorimetric method, moreover they write that the colorimetric method may be used, for all soils, with the exeption perhabs of the alkali soils.

OLSEN and LANG do not accept the values obtained by the hydrogen electrode as a standard. They have got a new standard by correcting the values of the hydrogen electrode. According to these investigators the hydrogen has driven out carbonic acid from the soil-suspensions, causing changes in the reaction.

They have determined the P_h of a suspension in three ways:

1°. by means of the quinhydrone electrode;

2°. by means of the quinhydrone electrode after leading carbonic-acid-free air through the suspension during 24 hours;

3°. with the hydrogen electrode after leading through air, as under 2°.

Subtracting the difference between the two quinhydrone measurements from the result obtained by the hydrogen-electrode, they get the standard value.

From their determinations OLSEN and LANG have constructed the correcting-graph, which is said to be valid for any soil.

This cannot be accepted. As there are different factors causing the hydrogen-ion concentration of soils, the effect upon the soil reaction of driving away the carbonic acid must vary too.

Moreover the investigators have not proved that the values which they get when correcting may really be called: *standard values.*

Nor can the conclusion that with the aid of the correcting-graph, the colorimetric method has become valid for all soils, be right.

These authors have generalised too much, for it is not allowed to draw conclusions concerning the soils of our earth globe from 93 Danish soils.

Many times I filtered the suspension which had been used for the hydrogenelectrode, and determined the P_h value of the filtrate by means of the colorimetric method. However I did not find the differences mentioned by OLSEN. The results were:

91*b*	7.3	335*c*	7.2	728*b*	6.8
102	5.6	535*b*	5.4	729*a*	7.5
105*a*	4.6	536	6.9	729*b*	7.3
105*b*	4.6	552	6.3	730	5.9
320*b*	7.2	567	7.5	744*b*	7.2
321*a*	6.9	568	6.1	745*b*	7.5
321*b*	7.5	569	7.1	746*b*	7.4
335*b*	7.3	728*a*	7.2		

Contrary to OLSEN and LANG, ARND and SIEMERS (3) came to the conclusion that CO_2 must always be driven out in order to get the right P_h values.

BRIOUX and PIEN (24) examined 37 French soils by means of the hydrogen-electrode and the quinhydrone one. Sometimes they got large deviations when using suspensions, but better results when using centrifugates.

It may be that the error caused by centrifuging is compensated by other errors.

SNYDER (74) determined P_h of 56 soils. He used the hydrogen

electrode, the quinhydrone electrode and sometimes also GILLESPIE's colorimetric method.

The values obtained by the quinhydrone method usually tallied well with the values of the hydrogen electrode, when soils were acid, but in alcaline soils larger deviations occurred.

As SNYDER reports in his summary that, when using the hydrogen electrode equilibrium was in general established in 5—10 minutes, it may be that this author has not waited long enough and therefore found too low values with the hydrogen electrode, which causes smaller deviations.

Only alcaline soils were examined colorimetrically by SNYDER. The deviations of the colorimetric method were mostly negative, and as a rule rather great. Many times SNYDER colorimetrically found values above 7.6.

Working with 26 Kentucky soils HEALY (44) finds good accordance between electrometric and colorimetric methods. His deviations range from 0.03—0.35, the average deviation being 0.17. Only two soils were alcaline, and no more than P_h 7.3.

According to CHRISTENSEN centrifuging is better than filtering, when one works colorimetrically, but the colorimetric method takes too much time for mass work, and this author recommends the quinhydrone method, which is said to be as accurate as the hydrogen method, up to a P_h value 8.4 (32, p. 512).

Also BILLMANN recommends the quinhydrone method, which is a very *fast* one.

When using the colorimetric method on alcaline soils, I found many erroneous results in the Geological Laboratory at Wageningen.

In general the quinhydrone electrode gave results tallying well with the results obtained by the hydrogen electrode, also in the alcaline range.

Only as an exception results obtained by quinhydrone showed great deviations. For instance a series of 15 samples obtained when a well was bored in the Wageningsche Berg (Holland) and consisting of loamy sand, have given P_h values by the hydrogen electrode, ranging from 8.1—8.8, the results obtained by the quinhydrone electrode being on an average 0.7 P_h lower.

A loamy sand from the Wolkenburg (Siebengebirge, Germany) gave P_h 7.8 with the hydrogen electrode, and with the quinhydrone electrode P_h 6.7, but a loamy sand from Römlinghoven (Siebengebirge, Germany)

gave P_h 5.7 by the hydrogen electrode and P_h 7.1 by the quinhydrone method.

A grey weathering-soil of sandstone from Spitsbergen gave P_h 8.3" by the hydrogen electrode, and 7.2 by the quinhydrone electrode.

A red soil from cape Boheman (Spitsbergen) gave P_h 8.7 by the hydrogen electrode and by the quinhydrone method 7.3.

The possibility of deviations always exists, but this bad chance is not equal to the large advantages of the quinhydrone method.

NOVAK (82, p. 54) has found lower values colorimetrically than when using the quinhydrone method, especially when working with alcaline soils.

KAPPEN and BELING (53, p. 25) consider the quinhydrone method a „für bodenkundliche Zwecke durchaus brauchbare und wegen ihrer schnellen Einstellung vor allem für Massenuntersuchungen geeignete Methode".

HUDIG has introduced the quinhydrone method in the Dutch Experiment Stations. The energetical manner in which HUDIG has applied the quinhydrone electrode for determining the lime status of sandy soils gave rise the creation of a special laboratory, and nowadays in farming on Dutch sandy soils it has become a rule to consult „HUDIG's laboratory".

HETTERSCHY and HUDIG (45) have found good accordance between the results obtained by hydrogen method and quinhydrone one, but do not communicate their values.

In general we may say that different investigators are satisfied with the results obtained by the quinhydrone method.

ARRHENIUS wrongly states that colorimetric methods and electrometric methods are of equal value (7). ARRHENIUS proposes the use of the colorimetric method, saying: „der Unterschied zwischen den auf kolorimetrischem und elektrometrischem Wege gefundenen Werten ist ja auch sehr gering", and „eine gut ausgeführte kolorimetrische Messung mit einem zuverlässigen Indikator hat den gleichen Wert wie eine gewissenhaft ausgeführte elektrometrische Bestimmung". (6, p. 134, 8, p. 84).

That the differences between colorimetric and electrometric values are not always very small, is proved by the determinations of N°. 746*b*, 746*c*, 747, 745 and 744, which correspond to the numbers 697, 698, 699, 700 and 701 of a paper of ARRHENIUS (9).

The statement of ARRHENIUS is very dangerous, as also appears from the papers by other investigators.

PIERRE (66, p. 292) has made the experience that differences between the colorimetric method and the electrometric one are not due to errors of the colorimetric method, but to so-called poisoned hydrogen electrode.

When repeating the electrometric determination, the result was often found to be erroneous.

PIERRE made a comparison between the electrometric method and the colorimetric one applied to 20 soils, and found no differences higher than 0.1 in P_h. Of these soils 9 were alkaline, but always less than P_h 7.8. This investigator states that: „The colorimetric method therefore can be used as a check on the electrometric method, if the procedure described is followed." This statement however must be wrong.

HISSINK and VAN DER SPEK (48, p. 32) have determined P_h in a number of acid soils, using centrifugates and suspensions with quinhydrone, and determining colorimetrically when using centrifugates.

They found large deviations between quinhydrone values and those obtained colorimetrically, whereas the values of the suspension were in nearest conformity with the values found colorimetrically.

It is a pity that they have not also used the hydrogen electrode too, which still must be considered as a standard.

Recently Mc. GEORGE has shown that the quinhydrone electrode can give too high results in manganiferous soils (39).

SUMMARY.

It may be stated that for the present the colorimetric method is not accurate enough for alkaline soils, the quinhydrone methods giving better results, which are not always the same however as those obtained by the hydrogen electrode.

It is not yet possible to obtain standard values by correcting the values obtained by the hydrogen-electrode.

The quinhydrone method has proved to be cheap, easy in use, for many soils also accurate, asking only a short time, and it seems to be the method for *masswork*.

However it is necessary to codify the use of this method, for there are different factors affecting the results. The discussions on this subject show how difficult it is, to come to an agreement.

QUESTIONS CONCERNING THE CODIFICATION OF THE USE OF THE QUINHYDRONE METHOD.

The first question is: which soil water ratio must be considered the best?

SHARP and HOAGLAND found hardly any change of the reaction when diluting suspensions from 1 : 2 as far as 1 : 500 (72).

KOLTHOFF and the author observed in 1923 only a very small influence of diluting. A soil-water ration 1 : 1½ gave the same result as a ration 1 : 3. (56, p. 676).

In the same year SALTER and MORGAN (71) came to a soil-water ratio 1 : 5 as a norm.

CHRISTENSEN found hardly any influence, when diluting from 1 : 1 up to 1 : 20 (29, p. 129).

OLSEN found no difference between ratios 1 : 1 and 1 : 2 (63, p. 20).

ATKINS proposed a soil-water ratio 1 : 2 for faintly buffering soils, and 1 : 5 for other soils (10).

In 1924 the German Experiment Stations adopted diluting 1 : 2½. To this recommendation the prescription was added that only filtrates should be used when working with electrometrical methods (52, p. 248). The use of filtered extract was based on an observation by KAPPEN, who found that a filtrate showing a P_h value 6.1, gave a P_h value 4.8, after adding some soil, the P_h of the suspension being 4.6 (51, p. 78).

In my opinion, however, this experience rather points to the use of suspensions.

As to colorimetric determinations, the same ratio was recommended but the use of 1 m.KCl instead of water was adopted.

This is a consequence of the German preference for determining „Austausch Azidität".

It must be stated that when using KCl, we do not determine the P_h value of the soil, as a physical constant.

The result of the determination may be of value, but when one wishes to determine the P_h with KCl, one should use the P_h value in water as well, and consider the differences between these figures.

TRUOG and PIERRE came to the conclusion that diluting the suspension only influences the P_h value, when the soil contains soluble salts and acids (80).

PIERRE observed hardly any influence between 1 : 1 and 1 : 100 (66).

HISSINK and VAN DER SPEK observed in few cases that on increasing the concentration the P_h value rose, at first, and then it fell.

They think that perhaps as concentrated a suspension as possible may be the best (48, p. 34).

In another paper they propose always to take the suspension as thick as possible (49, p. 245).

BILLMANN thinks systematic researches necessary to find the best soil-water ratio (19, p. 195).

BILLMANN and TOVBORG—JENSEN have given some directions for the right use of the quinhydrone method.

According tot these investigators it is an advantage of the quinhydrone method that it allows of using a very concentrated suspension, but the best soil-water ratio varies with the soil used.

In the Geological Laboratory at Wageningen, Holland, where the most divergent types of soil, from all parts of the earth have been examined, I observed many times that some heavy soils must be diluted very much; humic soils also ask much water, as they absorb a great volume of this liquid.

BILLMANN and JENSEN have given the standard-ratio 1 : 1 (20, p. 258).

Also CLARK and COLLINS used this soil-water ratio (33).

BAVER used a ratio 1 : 1 for the quinhydrone electrode and for the hydrogen electrode 1 : 5 (16).

KAPPEN and BELING gave the ratio 1 : 2½ for the quinhydrone electrode (53, p. 3), OLSEN and L. LANG a volume ratio 1 : 1 (64, p. 6).

TERLIKOWSKI wishes a suspension as concentrated as possible (79).

At first LEMMERMAN wanted „das Verhältniss so eng wie möglich gewählt", later on 1 : 2½.

GEHRING was of opinion that the water holding capacity was of influence and that the water should be 1 m.m. above the soil-water mixture (82, p. 62).

CHRISTENSEN denies the influence of the waterholding capacity, and states little influence of the soil-water ratio for Danish soils. He gives a ratio 1 : 2 as a norm (82, p. 62).

KAPPEN wishes a ratio 1 : 2 (82, p. 63).

The second Commission of the International Society for Soil Science has preferred a soil-water ratio 1 : 2½ (82, p. 64), but later on the report of BILLMANN and JENSEN was accepted, and a ratio of 1 : 1 adopted (36, p. 226).

Recently McGEORGE has given a table showing the influence of diluting from 1 : 1 up to 1 : 5, on 22 Hawaiian soils as measured by

hydrogen and quinhydrone electrodes. In most cases the P_h becomes somewhat higher on diluting the suspensions (39, p. 85).

The soil water ratio 1 : 2½ may do very well in most cases, but strongly *humic* and *very heavy* soils require more water.

ARND and HOFFMANN come to the conclusion that 10 grams of peat soil (on a dry basis) must be treated with 100 c.c. water (4, p. 231).

I suppose that the ratio 1 : 1 will prove to be too dry, when more types of soil are used than BILLMANN and JENSEN could have at their disposal, especially when suspensions are stirred during the readings and soils contain much clay and fine silt, a ration of at least 1 : 2½ is necessary.

It may be proposed to make comparative investigations for every country in order to find the most preferable soil-water ratio for every existing type of soil.

Another question is: How long must the soil be in contact with the water?

From investigations by KOLTHOFF and the author that have been mentioned above, it appears that the soils of 1923 were usually in equilibrium with water after half an hour already, and at any rate after two hours (56, p. 676).

I usually wait 24 hours in order to be sure that equilibrium is attained. Especially for soils which have been kept dry during a long time, this seems necessary.

HISSINK and VAN DER SPEK intended to wait 20 hours (48, p. 33).

CHRISTENSEN proposed to prepare the suspensions in the afternoon and to measure them the next morning (82, p. 63).

BILLMANN and TOVBORG—JENSEN observed only small differences between the reactions after a quarter and those after 24 hours, but they say that in a concentrated suspension the equilibrium is attained more quickly than in more diluted suspensions.

Using the quinhydrone electrode the platinum electrode can be dipped in the thick „paste" as far as the bottom of the vesel, in which case the equilibrium is attained after few secunds (20, p. 259).

According to BRIOUX and PIEN 24 hours are necessary, when applying electrometric methods (25, p. 5,6).

OLSEN and L. LANG came to the same conclusion (64, p. 6).

ARND and HOFFMAN found that peat soils must be shaken during 15 minutes and that the P_h value can be determined after half an

hour. If shaking produces difficulties, the soil water mixture must stand 24 hours (4).

A third question is whether it is necessary to use ordinary distilled water, or carbonic-acid-free distilled water, for preparing suspensions.

Of course carbonic acid has some influence. If carbonic acid is driven out, as it may be observed, when the hydrogen electrode is used, dissection of bicarbonates can change the reaction, which has been observed by HUDIG and STURM (50), BILLMANN (19, p. 196). OLSEN and LINDERSTRÖM—LANG (64, p. 13).

Also BAVER observed wrong results of the hydrogen electrode when working on alcaline soils (16, p. 173).

SHARP and HOAGLAND (73) did not find much influence of carbonic acid, when blowing hydrogen containing 10 % CO_2 into a suspension.

PIERRE (66) observed some influence, when leading CO_2 through the soil liquid, but hardly any influence of CO_2 when preparing the suspensions.

TRUOG and PIERRE (80) state that the influence of carbonic acid is very slight.

KAPPEN and BELING (53, p. 3) advise the use of boiled distilled water, but report only little influence of carbonic acid.

According to ARND and SIEMERS (3) the carbonic acid must be driven out, in using the quinhydrone electrode above P_h 5 carbonic acid must be driven off, for which carbonic-acid-free air can be used up to P_h 8.5.

This elimination can be effected by means of carbonic-acid-free air up to a P_h value of 8.5.

According to TERLIKOWSKY (79, p. 135) the soils buffering most are least affected by carbonic acid.

CHRISTENSEN and TOVBORG—JENSEN (31, 18—21) have proposed to free boiled distilled water from CO_2 by leading carbonic acid free air through it. In this way water is obtained, which contains 1 mgr. CO_2 a L.

BILLMANN and TOVBORG—JENSEN also (20, p. 263) proposed the use of boiled water or water that has been treated with carbonic-acid-free air.

According to these authors, water containing carbonic acid brings the suspension nearer to the natural state, this natural state being indefinable however.

OLSEN and L. LANG used carbonic acid free distilled water. (64).

According tot BJERRUM (22) in soils, in which $CaCO_3$ causes alcaline reaction, the influence of carbonic acid on P_h is determined by the equation:

$$P_h = 5.05 - \tfrac{1}{2} \log (Ca) - \tfrac{1}{2} \log PCO_2.$$

The Second Commission of the International Pedologic Society proposed to work with distilled water, which must be in equilibrium with the pressure of the carbonic acid in the atmospherical air.

This proposal of the Second Commission seems very logical. When the suspension is exposed to the air during some time, the carbonic acid will also act upon the suspension.

Trying to keep the suspension absolutely free from the air will render the determination needlessly complicate. After all the suspensions do buffer, and usually the influence of carbonic acid is very slight.

Moreover from the interspaces of the soil, air containing carbonic acid is sure to come into the suspension, from the spaces in the soil.

Another question is: May air-dried soil be used for determining P_h values?

Practice frequently necessitates the use of air-dried soil samples, so that this question is very important.

ARRHENIUS (5, p. 223) observed that the drying of soil samples was of little influence upon the P_h values.

HEALY and KARRAKER (43) found that drying rendered soils somewhat more acid, ROST and FIEGER (68, 69) came to the same conclusion BURGESS (26) examined 14 soils, their P_h ranging between 4.36 and 7.78 and observed some effect of drying upon the acidity of soils; especially when working on alcaline soils.

SAGER (70) found but a small deviation in P_h (0.1).

In 1924 the Commission of the German Experiment Stations recommanded drying the samples and to execute determinations as soon as possible after drying. (52).

AARNIO and SALMINEN (1) observed a great difference, which they attributed to air-drying, but as they compare aproximate colorimetric determinations with electrometric laboratory determinations this conclusion cannot be accepted.

Erich KNICKMAN (54) reports that the titration-acidity is changed by drying the soil.

BAVER (15) mentions some influence of drying, some times 0.3 —0.6 in P_h.

LEMMERMANN (**83**, p. 146) proposed to examine air-dried soil, as soon as possible after taking the samples.

TERLIKOWSKY has reported (**79**, pp. 153—156) irregular changes owing to drying, and proposed not to dry soil samples and not to keep them dry.

Of course this proposal cannot be accepted, as it is impossible to keep moist soil samples for a long time without any change.

BILLMANN and TOVBORG-JENSEN did not observe that drying (**20**, p. 261) had any effect.

ARND and HOFFMANN (**4**, p. 231) did not observe great changes by drying peat soils. In the Geological Laboratory of the Agricultural University at Wageningen influence of air-drying was sometimes observed, alcaline soils were rendered less alcaline, and the general tendency was to become more acid.

The deviations however were very small, and were not caused by *drying, but by keeping dry during a long period.*

The best method for all soil work is to make determinations on the spot, but this is not always possible. Whenever possible I place my apparatus in the neighbourhoud of the field the soil of which must be examined, and take the samples in moist state to the „laboratory" for immediate determination of the P_h value.

Approximate determinations are made in the field, the further ones being made in the laboratory.

We do not use TRENEL's field apparatus (**77**, **78**), as it is too expensive and moreover in using it, KCl reacts with the soil suspension, which may give a lower P_h value (**69**, p. 30, **42**, p. 35).

A great advantage of using dry soil is that the soil-water ratio can be regulated. Also BILLMANN and TOVBORG-JENSEN draw attention to this point. (**20**, p. 261).

AARNIO reports important changes of the reaction caused by storing some Finish soil samples (Ton) in a thermostate at 25° C. (**2**).

BRENNER, however, who had examined 2000 Finish soil samples at the time stated that he only seldom observed changes in reaction of soil samples, caused by storing them dry. The soils which changed their reaction were as a rule „Tonböden". (**23**, p. 4).

After all the tendency of soil to become more acid upon air-drying gives deviations remaining in general within the limits of practical accuracy.

In 1927 Dr. COMBER recommended the use of air-dried soils, as soon as possible after taking the sample (**36**).

The fourth question concerning the use of the quinhydrone electrode is, whether direct readings of the potentiometer give exact results or whether it is advisable to wait till constancy is obtained.

CHRISTENSEN and TOVBORG-JENSEN made readings some minutes after adding quinhydrone (31, p. 5).

According to HISSINK and VAN DER SPEK (48, p. 37) the reaction becomes a little more acid, immediately after adding quinhydrone, after ten minutes a constant potential being obtained in a soil suspension. For the time being these investigators could only draw the conclusion that there must be an equilibrum which was not immediately attained.

BILLMANN (17, p. 197; 18, p. 178) makes the funny remark, that the best reading can be obtained immediately after adding quinhydrone, because doing so bad influences have no time enough to react.

OLSEN and LINDENSTRÖM-LANG (64, p. 8) report inconstant potentials as well for acid as for alcaline soils. They always took the first reading.

BAVER (16, p. 173) mentions a difference of 0.3 in P_h with an alcaline soil between the first reading and that when constancy was attained. After two minutes the potential of this soil appeared to be constant. Soils having a P_h value below 8.0 were speedily constant.

BILLMANN and TOVBORG-JENSEN (20, p. 248) observed only small deviations ($\pm$ 0.1) between readings after ¼ hour, and those after 4 hours, and conclude that the exact potential is attained immediately. The changes in their potentials were not in one direction. The soils used were loams, clays and soils containing much humus.

Also OOSTING and STAF (65) found only small differences when studying acid Dutch forest-soils.

As to the examination of the Indian limestone-soils, I usually observed good conformity between the first reading and that when the potential was constant.

Also small deviations occurred, and only seldom larger deviations, up to 0.4 in P_h were observed. As well positive as negative deviations, were found. As a rule the readings were constant after 10 minutes. Table VI shows differences obtained on some of the limestone soils.

Similar results were obtained on other soils. Sometimes readings rose to a maximum, but I also met with minima. I always stirred the suspensions, and generally after 10 or 15 minutes constancy was attained.

Some soils showed very curious fenomena.

The interjacent layer between violet and yellow weathered tuff from an acid volcanic rock, a sample taken near the new road from Siantar to the Lake Toba, near Aik Na Oelei (Sumatra, Dutch-Indian Archipelago) has given three times the same value P_h 5.7, when using the hydrogen electrode in suspensions.

Using the quinhydrone electrode suspension I gave: first reading 7.2 the reading became constant as 7.3; suspension II gave; 1st reading 6.5, became constant at 5.6⁵, then drifted during some time between 5.7 and 5.1 and showed a P_h value 5.1 after 4 hours; suspension III gave: 1st reading 7.25, was constant at 7.35; suspension IV on first 7.35, when constant 7.5; suspension V first reading 6.4, when constant 7.6; suspension VI 7.3, during some time 6.4 and became constant at 7.0.

Filtrate and diffusate gave P_h 5.5 with methyl red.

Another volcanic soil (yellow weathering soil from liparitic pumice stone tuff, Pabatoe near Tebing Tinggi, Sumatra) gave P_h 7.0 on first reading and was constant after 15 minutes at P_h 5.35.

Both colorimetric determination and electrometric with hydrogen electrode gave a P_h value 5.3.

These cases show that the first reading not always gives the exact value. In the second case surely equilibrium was not immediately attained.

Samples of tropical peat-soils, collected by Prof. J. VAN BAREN in Java and Sumatra, possessed a P_h from 2.3 to 4.8, and always the first reading was the same as the following readings.

An alcaline soil (P_h hydrogen electrode 8.8) from a kaolin quarry (Römlinghoven, Siebengebirge, Germany) gave a drifting potential, whereas another sample taken not far from the place of the first sample (P_h hydrogen electrode 8.5) did not show this phenomenon.

The B_2 layer from a Fennish podsol-profile, which was kindly sent to our laboratory by Prof. Dr. B. AARNIO, gave 5.8 on first reading, became constant after 7 minutes at 4.8. The hydrogen electrode indicated a P_h value 5.05.

A calcareous loam, kindly sent to our laboratory by Dr. H. RASZKOWSKY, from the neighbourhood of Gaza (Palestina) gave readings which varied between 7.4 and 9.2.

These examples of drifting potentials and rather great differences might be increased by a great number of similar cases.

However they are exceptions, which need not go together with

great differences between the quinhydrone electrode and the hydrogen one.

With regard to the great saving of time for masswork, I think it advisable to make only one reading some minutes after adding quinhydrone.

Also stirring the suspensions can be omitted, for considering the first reading is taken as the correct one, stirring is of little influence.

For mass work in our laboratory I put one part of soil together with two parts of distilled water in a Pyrex tube and from time to time this is shaken. After 24 hours quinhydrone is added to the tubes and readings are made. While readings are made, meantime other suspensions reach equilibrium with quinhydrone.

From the literature which has been discussed and from the experience in our laboratory, I think I may conclude that if the cost of an electrometric apparatus is no objection the quinhydrone electrode must be preferred to the colorimetric method.

A determination with the quinhydrone method takes less time, and danger of bad results through color-blindness or bad light need not to be feared.

Moreover the apparatus can always easily be controlled, which is not the case with the much used colorimetric method of GILLESPIE (41).

If an indicator has not been prepared well, bad results with this method may be obtained, without being observed.

A skilled staff is less necessary for the quinhydrone method than for the colorimetric one.

Filtering suspensions is always a work that asks much care, the filtering paper must be neutral, centrifuging requires a centrifuge; dialysis is cheap and simple, but simplest is a simple suspension which may be used for the quinhydrone method.

Also BRENNER thinks centrifuging a way more round about than working electrometrically (2, p. 6).

Consequently there are many reasons for using the quinhydrone method. Of course for scientific detail-work and for controlling the results obtained by the quinhydrone electrode, the hydrogen electrode must be used.

At the end of this discussion concerning the quinhydrone method, I draw attention to the fact that KOLTHOFF and BOSCH have proved that ill-prepared quinhydrone may give too low P_h values (60).

When working with soil suspensions KOLTHOFF and BOSCH's sug-

gestion to redress this error by continuously decantating after adding quinhydrone cannot be practically acted upon.

Therefore working with a well prepared quinhydrone must be advised.

ACKNOWLEDGEMENT.

Wageningen, April '29.

SAMENVATTING.

Sinds een zestal jaren werden in het Geologisch Laboratorium der Landbouwhoogeschool een aantal gronden op zuurgraad onderzocht, teneinde na te gaan, welk verband er bestond tusschen dezen factor, den geologischen ouderdom, het klimaat en de petrografische samenstelling van den moedergrond. Een dusdanig onderzoek, destijds nog nieuw, vond en vindt in Wageningen een rijk materiaal, daar het Geologisch Museum bodemprofielen bevat van Nederland, België, Frankrijk, Spanje, Italië, Istrië, Dalmatië, Zwitserland, Hongarije, Duitschland, Zweden, Noorwegen, Spitsbergen, Engeland, Spaansch-Marokko, Algerië, Tunis, Palestina, Amerika, Ned. Oost-Indië en West-Indië. Deze mededeeling, die later gevolgd zal worden door meerdere, bericht alleen over gebruikte methoden.

De veelsoortigheid van dit materiaal bracht n.l. verschillende technische moeilijkheden naar voren. Omtrent de Indische kalkgronden werden door Prof. VAN BAREN zeer vele onderzoekingen gedaan en gegevens medegedeeld, welke te vinden zijn in diens studie: Microscopical, physical and chemical studies of limestones and limestone-soils from the East Indian Archipelago. (Mededeelingen van de Landbouwhoogeschool, Deel XXXII, N°. 7, Wageningen, 1928). Het is daarom in verband met de studie van de methodiek der zuurgraadsbepaling van belang thans uitvoerig bijzonderheden mede te deelen, over de resultaten van verschillende methoden, toegepast op gronden waarvan vele eigenschappen bekend zijn.

Alle beschreven bepalingen werden door mijzelf verricht.

De volgende methoden werden toegepast:

1. Electrometrische methoden:
   a. waterstofelectrode;
   b. chinhydronelectrode;
   c. antimoonelectrode.

2. Colorimetrische methoden:
   a. met Amerikaansche indicatoren en buffermengsels;
   b. onderzoek van centrifugaat;
   c. onderzoek van exarisaat, verkregen door eenvoudige dialyse door perkamentpapier;

d. onderzoek van filtraat, verkregen met behulp van Zweedsch filtreerpapier;

e. de methode Comber-Hissink.

De electrometrische methoden werden toegepast op suspensies. Wat betreft de chinhydronelectrode, deze heb ik in 1923 in gebruik genomen voor het onderzoek dezer gronden. De antimoonelectrode werd vóór mij slechts door SNIJDER toegepast op enkele Amerikaansche gronden. Binnenkort zal omtrent deze electrode een uitvoerige mededeeling gedaan worden.

De resultaten der bepalingen zijn te vinden in tabel I tot en met VI. Voor iedere P_h werd de gemiddelde afwijking bepaald. Door deze berekening kan men nagaan of een bepaalde methode voor een bepaald P_h traject wel, en voor een ander traject niet bruikbaar is.

Het bleek, dat de colorimetrische methode voor alcalische gronden zeer verkeerde waarden opleveren kan.

De door de chinhydronelectrode aangegeven waarden waren in het alcalische gebied niet geheel juist, maar practisch bruikbaar.

De resultaten met de antimoonelectrode zijn dusdanig, dat de mogelijkheid niet ontkend kan worden, dat deze electrode na nauwkeurige bestudeering der eigenschappen een belangrijke aanwinst kan worden voor de P_h bepaling in gronden. De methode Comber-Hissink bleek voor een schatting van den zuurgraad zeer wel bruikbaar.

Bij het toepassen dezer methode is het echter raadzaam minstens 2 etmalen te wachten alvorens af te lezen.

De resultaten van verschillende onderzoekers heb ik omgerekend en de berekening leerde, dat in bepaalde gevallen bij het vellen van een gunstig oordeel over de colorimetrische methode, òf dit oordeel niet gewettigd was, omdat de gronden nagenoeg alle zuur waren, òf omdat verzuimd was bij de beschouwing de resultaten te classificeeren naar den P_h. Terwijl de colorimetrische methode voor zure gronden zeer goede resultaten kan geven, geeft zij in den regel voor alcalische gronden veel te lage waarden. Vooral met het oog op de colorimetrische P_h bepalingen der plantengeografen is deze opmerking van belang.

Over het geheel genomen zijn de resultaten met de chinhydronelectrode bereikt, zeer bevredigend.

Een uitvoerige beschouwing is gewijd aan de codificatie van het gebruik der chinhydronelectrode. Hierbij dient men niet te veel te generaliseeren, en rekening te houden met het grondtype.

Over het algemeen verdient het aanbeveling, te werken met luchtdrogen grond, die zoo spoedig mogelijk na de monsterneming gesuspen-

deerd wordt met twee gewichtsdeelen gedistilleerd water, hetwelk niet uitgekookt behoeft te zijn. Veengronden en zeer zware gronden eischen meer water.

De aflezing kan geschieden enkele minuten na het toevoegen van chinhydron. Voor nauwkeurig onderzoek is het gewenscht te roeren, en herhaaldelijk af te lezen, totdat een constante aflezing bereikt is.

Voor wetenschappelijk detailwerk blijft de waterstofelectrode als standaard echter steeds noodzakelijk.

TABLE I.

Determinations of P_h values.

| | Electrometric | | | Colorimetric | | | Comber-Hissink | | | |
| | Hydrogen electrode | Quinhydrone electrode | Antimony electrode | Filtrate | Centrifugate | Diffusate | Red reagent | | Colorless reagent | |
							24 hours	48 hours	24 hours	48 hours
91b	8.5	7.8	7.5	7.3	6.9	7.4	pink	pink	> 6.5	> 6.5
101b	7.6	7.7	7.1	7.0	6.9	6.8	red	light red	> 6.5	> 6.5
102	6.0	6.1	5.7	5.7	5.9	5.5	red	red	> 6.5	6.5-6
105a	4.6	4.8		4.6	4.6	4.6	red	red	5.5-5	5.5-5
105b	4.7	4.5		4.6	4.5	4.6	red	red	5	5
108b	8.2	8.0	7.4	7.1	7.1	7.1	light red	light red	> 6.5	> 6.5
145b	7.4	7.0	6.6	6.8	6.8	6.8	red	red	6.5-6	6.5-6
958	7.8	7.3		6.4	6.5	6.4	red	red	> 6.5	> 6.5
244b	8.3	8.0	7.2	7.1	7.0	7.0	colorless	green	> 6.5	> 6.5
245	8.3	8.0		7.1	7.1	6.9	colorless	colorless	> 6.5	> 6.5
246	8.5	8.0	6.6	6.5	6.7	6.5	colorless	colorless	> 6.5	> 6.5
320a	8.2	7.8		7.6	7.3	7.3	red	pink	> 6.5	> 6.5
320b	8.6	7.8	7.5	7.2	7.2	7.3	pink	pink	> 6.5	> 6.5
321a	8.5	8.1		7.4	7.4	7.5	very light red	colorless	> 6.5	> 6.5
321b	8.3	7.4		6.9	8.1	6.9	pink	pink	> 6.5	> 6.5
322b	8.3	7.3	7.4	7.2	7.1	7.2	very light pink	colorless	> 6.5	> 6.5
323	8.5	7.5	7.45	7.3	6.8	7.3	red	red	> 6.5	> 6.5
324	8.5	8.0	7.4	7.3	7.5	7.4	colorless	colorless	> 6.5	> 6.5
335b	8.1	8.3		7.3	7.4	7.4	very light red	colorless	> 6.5	> 6.5
335c	8.2	8.1	7.5	7.3	7.4	7.4	light red	pink	> 6.5	> 6.5
535a	8.0	7.3	6.0	7.1	7.3	7.3	light red	pink	> 6.5	> 6.5
535b	5.8	5.8	5.4	5.4	5.8	5.5	red	red	6.5-6	6.5-6
535c	6.5	6.7	6.3	6.7	6.8	6.3	red	red	> 6.5	> 6.5
538	7.3	6.8	6.0	6.6	6.7	6.6	red	red	6.5-6	6.5-6
539	8.1	8.1	7.7	7.1	7.1	7.1	pink	colorless	> 6.5	> 6.5
546a	8.6	8.7	8.1	7.6	7.6	7.6	colorless	colorless	> 6.5	> 6.5
546b	6.6	6.8	6.4	6.4	6.3	6.6	red	red	6.5-6	6.5-6
548b	8.3	8.1	7.8	7.3	7.1	7.4	light red	pink	> 6.5	> 6.5
549	8.5	7.9	7.9	7.9	7.1	7.3	colorless	colorless	> 6.5	> 6.5
550	8.0	8.2		7.0	7.5	7.0	red	red	> 6.5	> 6.5
551b	6.6	6.7	6.45	6.1	6.1	6.1	light red	very light red	6.5-6	6.5-6
552	7.3	6.3		6.3	6.2	6.2	red	red	6.5-6	6.5-6
556	6.0	6.5		5.8	5.9	5.9	red	red	6.5-6	6.5-6
557	6.1	5.8			5.7		red	red	6.5-6	6.5-6
566	7.6	7.6		6.8	6.8	6.9	red	red	6.5-6	6.5-6
567	8.2	8.1	8.0	7.3	7.3	7.3	light red	pink	> 6.5	> 6.5
568	6.6	6.0	6.6	5.9	6.3	6.2	red	red	> 6.5	6.5-6
569	8.2	8.4	8.0	7.1	7.5	7.5	red	red	> 6.5	> 6.5
707b	8.5	8.0	7.6	7.2	7.4	7.3	colorless	colorless	> 6.5	> 6.5
728a	8.3	8.0	7.6	7.3	7.3	7.2	light red	colorless	> 6.5	> 6.5
728b	8.0	7.5	7.1	6.8	6.9	6.6	very light pink	colorless	> 6.5	> 6.5
729a	8.4	7.8	7.95	7.5	7.5	7.5	light red	very light red	> 6.5	> 6.5
729b	7.8	8.1	7.3	7.2	7.4	7.3	very light red	colorless	> 6.5	> 6.5
730	7.2	6.4	6.35	6.2	6.2	6.1	red	red	> 6.5	> 6.5
744b	8.2	7.9	7.5	7.5	7.6	7.4	red	red	> 6.5	> 6.5
745b	8.5	8.1	7.95	7.3	7.7	7.5	red	very light red	> 6.5	> 6.5
746b	8.3	8.5	7.6	7.4	7.6	7.3	very light pink	colorless	> 6.5	> 6.5
746c	8.2	8.3	7.95	7.5	7.3	7.5	light red	pink	> 6.5	> 6.5
747b	8.3	7.8	8.0	7.5	7.5	7.3	very light red	very light pink	> 6.5	> 6.5

3

TABLE II.

Deviations of different P_h values.

P_h	Number of determinations	Quinhydrone	filtrate	centrifugate	diffusate
8.6	2	— 0.8^5 (0.9^5)	— 1.2	— 1.2	— 1.1^5
8.5	8	— 0.6	— 1.3	— 1.2	— 1.2
8.4	1	— 0.6	— 0.9	— 0.9	— 0.9
8.3	8	— 0.4	— 1.1	— 0.9^5	— 1.1
8.2	7	— 0.1 (0.2)	— 0.9	— 0.8	— 0.8
8.1	2	+ 0.1	— 0.9	— 0.8^5	— 0.8^5
8.0	3	— 0.3^5 (0.5)	— 1.0	— 0.8	— 1.0
7.8	2	— 0.1^5 (0.4)	— 1.0	— 0.8^5	— 0.8^5
7.6	2	+ 0.5	— 0.7	— 1.2^5	— 0.7^5
7.4	1	— 0.4	— 0.6	— 0.6	— 0.6
7.3	2	— 0.7^5	— 0.8^5	— 0.8	— 0.9
7.2	1	— 0.8	— 1.0	— 1.0	— 1.1
6.6	3	— 0.1 (0.3)	— 0.5	— 0.4	— 0.3
6.1	1	— 0.3	—	— 0.4	—
6.0	2	— 0.1^5 (0.3)	— 0.2^5	— 0.1	— 0.3
5.8	1	— 0.0	— 0.4	— 0.0	— 0.3
4.7	1	— 0.2	— 0.1	— 0.2	— 0.1
4.6	1	+ 0.2	— 0.0	— 0.0	— 0.0

The values between ( ) are the average of the absolute values of the deviations.

TABLE III.

Value and number of deviations.

Dev.	quinh.	F.	C.	D.	Dev.	quinh.	F.	C.	E.
0.0	3	1	2	2	0.9	1	5	4	4
0.1	7	1	2	2	1.0	3	7	6	7
0.2	10	3	2	1	1.1	—	4	4	7
0.3	5	1	3	1	1.2	—	8	3	3
0.4	4	1	1	1	1.3	—	1	2	3
0.5	8	1	2	3	1.4	—	3	2	3
0.6	3	4	3	1	1.6	—	—	1	—
0.7	2	4	4	6	1.8	—	—	1	—
0.8	2	3	4	3	2.0	—	1	—	—

One colorimetric deviation was positive (0.2),

the quinhydrone method gave 5 deviations 0.1, 7 0.2, 1 0.3, and

1 0.5 which were positive.

N°. 557 is omitted in this table.

TABLE IV.

Comber — Hissink, Red Reagent.

Days.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
No.										
101b	r.	l.r.	l.r.	l.r.	p.	p.	p.	p.	p.	p.
102	r.	r.	r.	r.	r.	r.	r.	cl.		
108b	l.r.	l.r.	v.l.r.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
145b	r.	r.	r.	r.	r.	r.	p.	p.	p.	p.
958	r.	r.	r.	r.	l.r.	l.r.	l.r.	p.	p.	p.
320a	r.	p.	v.l.r.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
321a	v.l.r.	cl.	cl.	cl.	cl.	cl.	cl.	cl.		
322b	v.l.p.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
323	r.	r.	p.	l.p.	cl.	cl.	cl.	cl.	cl.	cl.
333b	l.p.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
335c	l.r.	p.	cl.	cl.	v.l.p.	v.l.p.	v.l.p.	cl.	cl.	cl.
535a	l.r.	p.	v.l.r.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
535c	r.	r.	l.r.	l.p.	v.l.p.	v.l.p.	cl.	cl.	cl.	cl.
538	r.	r.				l.r.				
539	p.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
546a	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
546b	r.	r.	r.	r.	r.	r.	r.	r.	r.	r.
548b	l.r.	p.	v.l.p.	cl.	cl.	cl.	cl.	cl.	cl.	cl.
550	r.	r.	r.			cl.				
531b	l.r.	v.l.r.	v.l.r.	p.	l.p.	v.l.p.	cl.	cl.	cl.	r.
553	r.	r.	r.	r.	r.	r.	r.	r.	r.	r.
568	r.	r.	r.	r.	r.	r.	r.	r.	r.	r.
569	r.	r.				cl.				
728a	l.r.	cl.	cl.	cl.	cl.	cl.	cl.	cl.		
728b	l.p.	cl.	cl.	cl.	cl.	cl.	cl.	cl.		
729b	v.l.r.	cl.			cl.	cl.	cl.	cl.		
730	r.	cl.	r.	r.	r.	r.	r.	r.		
747b	v.l.r.	v.l.p.			cl.	cl.	cl.	cl.		

r. = red.
l.r. = light red.
p. = pink.
v.l.r. = very light red.
cl. = colorless.
l.p. = light pink.
v.l.p. = very light pink.

TABLE V.

Comber — Hissink, Colorless Reagent.

Days.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	30.
No.											
102	cl.	v.l.p.	v.l.p.	orange	orange	r.	r.	r.	r.	r.	r.
145b	v.l.p.	v.l.p.	v.l.p.	cl.	cl.	cl.	green	green			green
320a	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.			cl.
321a		—					cl.				cl.
323	cl.	cl.	cl.	cl.	green	green	green	green			green
335b								cl.			cl.
335c								cl.			cl.
535c	cl.	cl.	cl.	cl.	green	green	green	green			green
553	v.l.p.	v.l.p.	p.	p.	p.	p.	p.	p.			p.
568	cl.	v.l.p.	v.l.p.	v.l.p.	v.l.p.	v.l.p.	v.l.p.	v.l.p.			v.l.p.
728a	cl.		cl.	cl.	cl.	cl.	cl.	cl.			cl.
729b							cl.				cl.
730	cl.	cl.	cl.	cl.	cl.	cl.	cl.	cl.			cl.
747b							cl.				cl.

cl. = colorless.
v.l.p. = very light pink.
r. = red.
p. = pink.

TABLE VI.

Differences between first reading of P_h value with quinhydrone electrode, and reading when constant.

No.	Differences.	No.	Differences.
101b	+ 0,1	539	+ 0,5
102	— 0,3	546a	0,0
105a	+ 0,3⁵	546b	— 0,3⁵
105b	0,0	549	0,0
108b	+ 0,1	551b	+ 0,5
244a	0,0	557	0,0
246	0,0	566	+ 0,1
255	0,0	567	— 0,0⁵
322b	— 0,2⁵	568	+ 0,2
335b	+ 0,2	728a	+ 0,0⁵
335c	0,0	728b	— 0,2
535a	0,0	730	+ 0,1
535c	0,0	746c	0,0
538	0,0	747b	+ 0,3

TABLE VII.

Antimony electrode.

Soil No.	Stirred after 2 minutes.	Not stirred after 2 minutes.	col. filter.	hydrogen electrode.
91b	7.5	8.2⁵	7.3	8.5
101b	7.1	7.9	7.0	7.6
102	5.7	6.2⁵	5.7	6.0
108b	7.4	7.5⁵	7.1	8.2
145b	6.5	7.0	6.8	7.4
244b	7.2	7.2	7.1	8.3
246	6.6	6.9	6.5	8.5
320b	7.5	8.5	7.2	8.6
322b	7.4	8.3	7.2	8.3
323	7.4⁵	7.6	7.3	8.5
324	7.4	7.7	7.3	8.5
335c	7.5	8.4	7.3	8.2
535a	6.0	6.4	7.1	8.0
535b	5.4	6.0	5.4	5.8
535c	6.3	7.1⁵	6.7	6.5
538	6.0	6.7	6.6	7.3
539	7.7	8.0⁵	7.1	8.1
546a	8.1	8.5⁵	7.6	8.6
546b	6.4	6.6	6.4	6.6
548b	7.8⁵	8.0	7.3	8.3
549	7.9	8.1	7.9	8.5
551b	6.4⁵	7.1⁵	6.1	6.6
567	8.0	8.2⁵	7.3	8.2
568	6.6	6.8	5.9	6.6
569	8.0	8.5⁵	7.1	8.2
707b	7.6	8.4	7.2	8.5
728a	7.6	8.1	7.8	8.3
728b	7.1	7.3	6.8	8.0
729a	7.9⁵	8.1	7.5	8.4
729b	7.3	7.8	7.2	7.8
730	6.3⁵	7.3	6.2	7.2
744b	7.5	7.8⁵	7.5	8.2
745b	7.9⁵	8.1	7.3	8.5
746b	7.5	8.2	7.4	8.3
746c	7.9⁵	8.2	7.5	8.2
747b	8.0	9.0	7.5	8.3

TABLE VIII.

Deviations and P_h Christensen and Jensen.

P_h	Number	Quin-hydrone	Colori-metric
a. Deviations of loamsoils.			
8.2	1	+ 0,06	— 0,39
8.1	2	+ 0,03	— 0,47
8.0	2	+ 0,02	— 0,43
7.9	1	+ 0,05	— 0,46
7.8	3	+ 0,07	— 0,61
7.7	3		— 0,57
7.5	3	+ 0,03	— 0,24
7.4	4	+ 0,16	— 0,51
7.3	2	+ 0,09	— 0,28
7.2	3	+ 0,06	— 0,43
7.1	6	+ 0,00	— 0,36
7.0	3		— 0,42
6.9	2	+ 0,16	— 0,14
6.8	3	+ 0,02	— 0,32
6.7	2	+ 0,05	— 0,24
6.6	4	+ 0,14	+ 0,02
6.5	4	+ 0,07	— 0,10
6.4	4	+ 0,08	+ 0,04
6.3	4	+ 0,01	— 0,02
6.2	2	+ 0,03	+ 0,05
6.1	3	+ 0,05	+ 0,05
6.0	1	+ 0,10	+ 0,10
5.9	2	+ 0,08	+ 0,08
5.8	1	+ 0,02	+ 0,14
5.7	1	+ 0,00	— 0,16
5.6	2	+ 0,08	+ 0,08
5.4	2	+ 0,05	+ 0,09
5.3	2	+ 0,11	+ 0,23
5.2	1	+ 0,18	+ 0,25
5.1	2	+ 0,26	+ 0,27
b. sands.			
8.4	2	+ 0,04	— 0,87
8.3	1	— 0,04	— 0,74
8.2	2	+ 0,09	— 0,63
8.0	2	+ 0,13	— 0,68
7.9	4	+ 0,07	— 0,36
7.8	1	+ 0,06	— 0,64
7.6	2	— 0,01	— 0,64
7.5	2	— 0,02	— 0,44
7.4	3	+ 0,11	— 0,26
7.3	1	+ 0,08	— 0,42
7.1	4	+ 0,04	— 0,29
7.0	3	+ 0,20	— 0,18
6.8	6	+ 0,06	— 0,10
6.7	4	— 0,04	— 0,11
6.6	4	+ 0,10	— 0,09
6.5	3	+ 0,12	— 0,02
6.4	3	+ 0,05	+ 0,02
6.3	5	+ 0,03	+ 0,05

P_h	Number	Quin-hydrone	Colori-metric
6.2	2	+ 0,03	+ 0,05
6.1	5	+ 0,02	— 0,05
6.0	5	+ 0,01	— 0,03
5.9	1	+ 0,12	+ 0,21
5.8	2	+ 0,05	+ 0,15
5.5	1	+ 0,12	
5.3	1	+ 0.08	+ 0.09
c. clays.			
8.6	1	— 0,10	— 0,65
8.3	1	— 0,06	— 0,79
8.2	2	+ 0,01	— 0,54
8.0	1	— 0,12	— 0,50
7.8	2	+ 0,05	
7.7	2	+ 0,07	— 0,58
7.6	1	+ 0,32	— 0,57
7.5	1	+ 0,08	— 0,31
7.2	2	+ 0,20	
7.1	1	+ 0,04	— 0,37
7.0	1	0,00	
6.8	2	+ 0,06	— 0,14
6.6	1	+ 0,08	
6.5	1	+ 0,08	
d. humic soils.			
6.9	1	— 0,10	
6.6	1	+ 0,14	
6 0	1	+ 0,08	
5.7	1	— 0,08	— 0,08
5.6	1	+ 0,08	+ 0,03
5.5	1	— 0,02	+ 0,06
5.2	1	— 0,02	+ 0,25
5.1	2	+ 0,01	+ 0,33
4.8	1	— 0,06	
4.7	1	+ 0,08	
4.2	1	— 0,01	
4.1	2	+ 0,14	
3.6	1	— 0,10	
e. African coffee soils (laterite).			
7.2	1	+ 0,21	— 0,22
7.1	1	+ 0,51	— 0,43
6.9	1	+ 1,44	— 0,33
6.7	1	+ 1,42	— 0,19
6.6	1	+ 1,65	— 0,27
6.4	1	+ 1,58	— 0,17
6.3	1	+ 1,63	— 0,17
6.1	1	+ 1,92	— 0,07
5.9	1	+ 1,88	— 0,04
5.8	1	+ 2,20	+ 0,13

TABLE IX.

GAINEY

P_h values and deviations.

P_h	Number of determinations	deviation	P_h	Number of determinations	deviation
3.7	1	+ 0,67	6.4	5	+ 0,15
3.8	2	+ 0,81	6.5	9	— 0.30
4.0	3	+ 0,59	6.6	4	— 0,02
4.1	2	+ 0.40	6.7	11	— 0,09
4.2	4	+ 0,48	6.8	12	— 0,21
4.3	1	+ 0,29	6.9	5	— 0,16
4.4	1	+ 0,25	7.0	10	— 0,21
4.5	3	+ 0,23	7.1	9	— 0,19
4.6	4	+ 0,23	7.2	12	— 0,28
4.7	9	+ 0,21	7.3	12	— 0,13
4.8	8	+ 0,09	7.4	7	— 0,19
4.9	13	+ 0,08	7.5	13	— 0,20
5.0	17	+ 0,13	7.6	12	— 0,21
5.1	15	+ 0.22	7.7	10	— 0,34
5.2	12	+ 0,25	7.8	6	— 0,42
5.3	16	+ 0.21	7.9	2	— 0,79
5.4	13	+ 0,16	8.0	2	— 0,63
5.5	20	+ 0,17	8.1	4	— 0,57
5.6	12	+ 0,04	8.2	3	— 0,56
5.7	11	— 0,001	8.3	3	— 0,70
5.8	11	+ 0,07	8.4	1	— 1,01
5.9	14	+ 0,06	8.5	1	— 1,02
6.0	14	— 0,05	8.6	—	—
6.1	13	— 0,08	8.7	1	— 1,05
6.2	12	— 0,06	8.8	1	— 0,67
6.3	9	— 0,02			

TABLE X.

GAINEY.
Value and number of deviations.

Differences.	Number.	Differences.	Number.
0,0	45 ×	0,7	16 ×
0,1	92	0,8	6
0,2	75	0,9	3
0,3	67	1,0	3
0,4	41	1,1	2
0,5	28	1,2	1
0,6	19		

TABLE XI.

CARLETON.
P_h values and deviations.

P_h	Number	Deviation	P_h	Number	Deviation
4.8	2	+ 0,20	5.9	1	+ 0,15
4.9	3	— 0,28	6.0	3	— 0,07
5.0	2	+ 0,15	6.1	1	+ 0,15
5.1	6	— 0,09	6.2	1	— 0,11
5.2	3	— 0,01	6.3	1	— 0,06
5.3	3	— 0,08	6.4	2	— 0,02
5.4	7	0,00	6.6	4	+ 0,03
5.5	1	+ 0,03	6.7	1	+ 0,06
5.6	3	+ 0,22	7.0	3	0,00
5.7	1	+ 0,10	7.3	1	+ 0,07
5.8	1	+ 0,07	7.6	1	+ 0,01

TABLE XII.

CARLETON.

Value and number of deviations.

Deviation	Number	Deviation	Number
0,0	20	0,3	5
0,1	21	0,4	1
0,2	2	0,5	2

TABLE XIII.

„REAKTIOMETER" OF KÜHN.

Number	P_h	Number	P_h
91b	8.1	707b	8.3
101b	8.1	728b	8.0
108b	8.2	729a	8.5
322b	8.3	729b	8.1
323	8.3	744b	8.3
324	8.5	745b	8.4
569	8.2	747b	8.3

LITERATURE CITED.

1. AARNIO, B., SALMINEN, A., Die Aenderung der Reaktion durch Altern der Bodenproben. (Comptes Rendus de la Deuxième Commission de l'Association internationale de la Science du sol. Vol. **B**, pp. 30—33, Groningen 1927).

2. AARNIO, B., Die Veränderung des Azidilätsgrades durch Trocknen der Bodenproben. (Bulletin of the Agrogeological Institution of Finland, N°. **26**, Helsinki 1928).

3. ARND, Th., SIEMERS, W., Zur Methodik der pH-Bestimmung mit der Chinhydron-Methode. (Zeitschrift für Pflanzenernährung und Düngung, Bd. **7** A. 1926, pp. 191 etc.).

4. ARND, Th., HOFFMANN, W., Die Bestimmung des Reaktionszustandes von Moorböden. (Zeitschr. f. Pflanzenernährung, Düngung und Bodenkunde, Bd. **X**, 1928, Heft 4, pp. 219—231).

5. ARRHENIUS, O., The potential Acidity of Soils. (Soil Science **14**, 1922, pp. 223—232).

6. —— , Der Kalkbedarf des Bodens vom pflanzenphysiogischem Standpunkte. (Zeitschrift für Pflanzenernährung und Düngung, 1924, **A**, pp. 129, etc.).

7. —— , Soil Acidity, Statements. (Comptes Rendus de la Deuxième Commission de l'Association internationale de la Science du sol. Vol. **A**. Groningen 1926, pp. 41—42).

8. —— , Kalkfrage, Bodenreaktion und Pflanzenwachstum. Leipzig 1926.

9. —— , VAN HARREVELD—LAKO, C. H., Grondonderzoekingen van de Buitenbezittingen. (Archief voor de Suikerindustrie in Nederlandsch Indië, **III**, 1927, N°. 18).

10. ATKINS, W. R. G., Notes on the filtration and other errors in the determination of the Hydrogen-ion concentration of Soils. (Royal Dublin Society of Science, Proceedings, new series, **17**, 1924, (44), pp. 341—347).

11. BAREN, J. VAN., Catalogus der Geologische en Agrogeologische verzamelingen van de Landbouwhoogeschool. (Mededeelingen van de Landbouwhoogeschool, **XXVII** 1924, verh. 8. (Wageningen).

12. BAREN, J. VAN., Microscopical, physical and chemical studies of limestones and limestone-soils from the East Indian Archipelago. (Communications of the Agricultural University, Wageningen Holland, 32, 7, 1928).

13. BARNETTE, R. M., HISSINK, D. J., VAN DER SPEK, J., Some remarks on the determination of the hydrogen-ion concentration of the Soil. (Recueil des Travaux chimiques des Pays-Bas (4), 5 May 1924).

14. —— , —— , —— , De colorimetrische bepaling van den zuurgraad van den grond. (Chemisch Weekblad, Jrg. 21, 1924 (12), pp. 147, etc.).

15. BAVER, L. D., Factors affecting the Hydrogen-ion Concentration of soils. (Soil Science, 23, 1927, pp. 399—414).

16. —— , The use of the Quinhydron-electrode for Measuring the Hydrogen-ion Concentration of Soils. (Soil Science, 22, 1926, pp. 167—179).

17. BILLMANN, E., On the Measurement of Hydrogen-ion Concentration in Soil by means of the Quinhydrone electrode. (Journal of Agricultural Science, XIV, 1924, pp. 233, etc.).

18. —— , Some Remarks on the Application of the Quinhydrone electrode for Soil Researches. (Compt. Rend. Deux. Comm. de l'Assoc. intern. de la Science du Sol, Vol; B, Groningen 1927, pp. 175—178).

19. —— , Bemerkungen über die Anwendung des Chinhydrons bei Bodenuntersuchungen. (Ibid., Vol. B, Groningen, 1927, pp. 194—198).

20. BILLMANN, E., TOVBORG-JENSEN, S., On the Determination of the Reaction of Soils by means of the Quinhydrone electrode. (Ibid., Vol. B., Groningen 1927, p. 236 etc.).

21. BIJHOUWER, J. T. P., Geobotanische studie van de Berger Duinen. Deventer 1926.

22. BJERRUM, NIELS, GJALDBACK, J., Undersoegelser over de Faktorer Som bestemmer Jordbundens Reaktion. I. Om Bestemmelse af en Jords sure eller basische Egenskaber. II. Om Reaktion af Vaedsker som er maettet med Kalziumkarbonat. (Meddelelse fra kemisk Lab. Kgl. Veterin og Landbohoegskole. Kopenhagen. Aarskrift 1919).

See also: Internationale Mitteilungen für Bodenkunde 1919, pp. 95—98.

23. BRENNER, Widar, Ueber die Reaction Finnländischer Böden. (Agrogeologska Meddelanden, N°. **19**, Helsingfors 1924).

24. BRIOUX, CH., PIEN, J., Emploi de l'électrode a quinhydrone pour la détermination du P_h des sols. (Compt. Rend. Deux. Comm. de l'Assoc. intern. de la Science du sol. Vol. **A.**, Groningen 1926, pp. 22—24).

25. —— , —— , Recherches complémentaires sur l'électrode à quinhydrone appliqué à la détermination du pH des Sols. (Ibid., Vol. **B**, Groningen 1927, pp. 5—7).

26. BURGESS, P. S., The Hydrogen-ion Concentration of Soils as affected by drying. (Science, new series, **55**, 1922, pp. 647—648).

27. CARLETON, Everett, A., A comparison of the Jones Calcium-Acetate Method for Lime Requirement with the Hydrogen-ion Concentration of some Quebec Soils. (Soil Science, **14**, 1923, pp. 79—93).

28. CHODAT, F., La Concentration en ions Hydrogène du Sol et son importance pour la constitution des formations végétables. Genève 1924.

29. CHRISTENSEN, Harold, R., Untersuchungen über einige neuere Methoden zur Bestimmung der Reaktion und des Kalkbedürfnisses des Erdbodens. (Int. Mitt. für Bodenkunde, **13**, 1923(pp. 116—147).

30. CHRISTENSEN, H. R., TOVBORG-JENSEN, S., Undersoegelser ver-drörende elektrometriske metoder til bestemmelse af jord-reak-tionen. (Tidskrift for planteavl. **29**, 1923).

31. —— , —— , Untersuchungen bezüglich der zur Bestimmung der Bodenreaktion benutzten electrometrischen Methoden. (Int. Mitteilungen für Bodenkunde, **XIV**, 1924.

32. —— , The acidity of Soils. (Actes de la IVème Conférence Internationale de Pédologie, vol. **II**, pp. 509—515, Rome 1926).

33. CLARK, Norman Ashwell, EMERSON, COLLINS, R., The Quinhydrone electrode and the Soil-Reaction. (Soil Science, **24**, 1927, pp. 453—465).

34. CLARK, W. M., The determination of hydrogen ions. 2nd ed.. Baltimore 1925.

35. COMBER, Norman M., A qualitative test for sour soils. (Journal of Agricultural Science, **XX**, 1920, pp. 420—424).

36. —— , The Determination of Soil Acidity. (Report of the Proceedings of the Second Commission, Groningen 1926, Washington 1927, Vol. I, pp. 224—230).

37. FRANKE, K. W., WILLAMAN, J. J., Measurement of Hydrogen Ion Concentration in the mole of pulp and paper manufacture. (Journ. Ind. Eng. Chemistry, 1928, **20**, pp. 87—95).

38. GAINEY, P. L., Influence of the absolute reaction of a Soil upon its Azotobacter flora and nitrogen fixing ability. (Journal of Agricultural Research, **24**, 1923, pp. 907—938).

39. McGEORGE, W. T., The influence of Manganiferous Soils on the accuracy of the quinhydrone electrode. (Soil Science, **27**, 1928, pp. 83—89).

40. GERRETSEN, F. C., Over den invloed van de waterstofionen-concentratie op bacteriologische processen. (Verslagen van de landbouwkundige Onderzoekingen der Rijkslandbouw-Proefstations, **XXX**, 1925, p. 1—45).

41. GILLESPIE, L. J., Colorimetric Determination of Hydrogen-ion Concentration without Buffer Mixtures, with especial Reference to Soils. (Soil Science, **9**, 1920, pp. 115—136).

42. GÖRBING, J., Säureschäden bei Getreidearten (Deutsche Landwirtschaftliche Presse, **50**, 1923, (42), p. 352).

43. HEALY, D. J., KARRAKER, P. E., The Clark hydrogen-electrode vessel and soil measurements. (Soil Science, **13**, 1922, pp. 323—328).

44. —— , Colorimetric measurements of the reaction of air-dried soils. Proceedings and Papers of the First International Congress of Soil Science, Washington 1928, Vol. II, pp. 107—110).
Kolorimetrische Messung der Reaktion in Luftgetrockneten Böden. (Abstracts of the Proceedings etc., Washington 1928, p. 19).

45. HETTERSCHY, C. W. G., HUDIG, J., De bepaling van de waterstofionen concentratie in vloeistoffen en suspensies. Toepassing van de chinhydronmethode van Emar BILLMANN in de praktijk. (Chemisch Weekblad, **23**, 1926, pp. 2—3).

46. HISSINK, D. J., Een eenvoudige en snelle methode, die ons in staat stelt een indruk van den zuurgraad van den grond te krijgen. (Chemisch Weekblad, **19**, 1922, pp. 281—283).

47. ——, De methode COMBER voor het schatten van den zuurgraad van den grond. (Verslagen van de Landbouwkundige Onderzoekingen der Rijkslandbouwproefstations, **XXXI**, 1926, p. 250).

48. ——, VAN DER SPEK, J., Die pH Bestimmung des Bodens nach der BILLMANN'schen Chinhydron-Methode. (Compt. Rend. Deux. Comm. de l'Assoc. intern. de la Science du Sol. Vol. **A**., Groningen 1926, pp. 29—40).

49. ——, ——, De potentiometrische methode ter bepaling van den zuurgraad van den grond (pH). (Verslagen van de Landbouwkundige Onderzoekingen der Rijkslandbouw-proefstations, **XXXI**, 1926, pp. 241—250).

50. HUDIG, J., STURM, W., Het meten van waterstofionen-concentraties in bodemextracten en bodemsuspensies. (Verslagen Landbouwkundige Onderzoekingen der Rijkslandbouwproefstations, **XXIII**, 1919, pp. 85—128).
See also: Chemisch Weekblad, **16**, 1919, p. 472.

51. KAPPEN, H., Studien an sauren Mineralböden aus der Nähe von Jena. (Die Landwirtschaftlichen Versuchsstationen, **88**, 1916, p. 78).

52. ——, etc., Wesen, Bedeutung, und Bestimmung der sogenannten Bodenazidität. (Zeitschrift für Pflanzenernährung und Düngung, 1924, **A**., Wiss. Teil, pp. 209—257).

53. ——, BELING, R. W., Ueber die Chinhydron-electrode und über die Beziehungen ihrer Resultate zu den Aziditätsformen der Böden. (Ibid., **A**, II, 1926, pp. 1—26).

54. KNICKMANN, Erich., Untersuchungen zur Frage der Bodenazidität. (Zeitschrift für Pflanzenernährung und Düngung, A., **5**, 1925, pp. 1—90).

55. KOLTHOFF, I. M., Die Verwendung der Chinhydron statt der Wasserstoffelectrode bei potentiometrischen Aziditätsbestimmungen. (Recueil des travaux chimiques des Pays-Bas, **42**, 1923, pp. 186—199).

56. ——, De colorimetrische bepaling van den waterstof-exponent van den grond. (Chemisch Weekblad, **20**, 1923, pp. 675, etc.).

57. KOLTHOFF, I. M., Der Gebrauch von Farbenindicatoren, 2nd. Edition, Berlin 1923, 3rd Edition, Berlin 1926.

58. —— , Der Salzfehler von Indicatoren in Electrolytarmen Lösungen. (Recueil des travaux chimiques des Pays-Bas, 44, 1925, pp. 275—278).

59. —— , HARTONG, B. D., The Antimony Electrode as an Indicator for Hydrogen Ion Concentration. (Ibid., 44, 1925, pp. 113—120).

60. —— , BOSCH, W., De toepassing der chinhydronelectrode in vloeistoffen met een geringe buffercapaciteit. (Chemisch Weekblad, 24, 1927, p. 79).

61. NIKLAS, H., HOCK, A., Bestimmung der Wasserstoffionenkonzentration von Böden auf colorimetrischem Wege. (Zeitschrift für Angewandte Chemie, 38, 1925, p. 150).

62. —— , —— , Vergleichung der Methoden zur Bestimmung der Wasserstoffionenkonzentration von Böden. (Die Landwirtschaftlichen Versuchsstationen, C, IV, 1925, pp. 86—91).

63. OLSEN, Carsten, Studies on the Hydrogen-ion Concentration of the soil and its Significance to the Vegetation especially to the Natural Distribution of Plants. (Comptes-Rendus des Travaux du Laboratoire Carlsberg, 15me Volume I, Copenhaque 1923).

64. —— , LINDERSTRÖM LANG, On the Accuracy of the various methods of measuring concentration of Hydrogen-ions in Soil. (Ibid., 17me Volume, I, Copenhague 1927).

65. OOSTING, W. A. J., STAF, C., Over het zuurgraadprofiel van eenige Nederlandsche boschgronden. (Nederlandsch Boschbouw Tijdschrift, I, 1928, p. 64).

66. PIERRE, W. H., The Hydrogen-ion Concentration of Soils as affected by Carbonic Acid and the Soil-water Ratio and the Nature of Soil Acidity as Revealed by these Studies. (Soil Science, 20, 1925, pp. 285—307).

67. —— , PARKER, F. W., The use of Collodion sacks in soil Investigations. (Proceedings and Papers of the First Int. Congress of Soil Science, Vol. II, pp. 396—413, Washington 1928).

68. ROST, C. O., FIEGER, E. A., Effect of drying and storage upon the hydrogen-ion concentration of soil samples. Soil Science, 16, 1924, pp. 145—170).

69. —— , —— , The Effect of drying upon the acidity of soil samples. (Science, 60, 1924, p. 297).

70. SAGER, J. L., Studies in Soil acidity. Cambridge 1923.

71. SALTER, R. M., MORGAN, M. T., Factors effecting soil reaction. (Journal of Physical Chemistry, 27, 1923, pp. 117—140).
72. SHARP, L. T., HOAGLAND, D. R., Acidity and Adsorption in Soils as measured by the Hydrogen-electrode. (Journal of Agricultural Research, 7, 1916, pp. 123—145).
73. ——, ——, Relation of CO_2 to soil reaction as measured by the Hydrogen electrode. (Journal of Agricultural Research, 12, 1918, p. 139).
74. SNIJDER, E. F., A comparative study of the Quinhydrone and Hydrogen Electrodes for determining the Hydrogen-ion Concentration of Soils. (Journal of Agricultural Research, 35, 1927, pp. 825—835).
75. ——, The application of the Antimony electrode to the Determination of the P_h value of Soils. (Soil Science, 26, 1928, pp. 107, etc.).
76. SWANSON, C. O., GAINEY, P. L., LATSHAW, W. L., The Calcium content of Soil in relation to absolute reaction. (Soil Science, 17, 1924, pp. 181—191).
77. TRENEL, M., Azidimeter. Siemens und Halske A.G., Berlin—Siemensstadt, w.y.
78. ——, Ein tragbares Gerät zur electrischen Bestimmung der Bodenazidität. (Internationale Mitteilungen für Bodenkunde, 1924, p. 27).
See also: Actes de la IVème Conf. Intern. de Pédologie, II, 1926, p. 451; Zeitschrift für Pflanzenernährung und Düngung, A., 1925, p. 239).
79. TERLIKOWSKI, F., Zur Methodik der potentiometrischen pH-Bestimmung des Bodens. (Compt. Rend. Deux. Comm. de l'Assoc. intern. de la Science du sol). Groningen 1927, Vol. B., pp. 151—155).
80. TRUOG, A., PIERRE, W. H., Determining H-ion concentration of Soils. (Wisconsin Station Bulletin 388, 1926; Experiment Station Record, 56, 1927, pp. 715).
81. Die Natur der Bodenazidität. (Compt. Rend. Deux. Comm. de l'Assoc. intern. de la Science du sol. Groningen 1927, Vol. B, pp. 40—44).
82. Die Bestimmung der Bodenazidität. (Ibid., Groningen 1927, Vol. B, pp. 52—64).
83. Zur Bestimmung und Beurteilung der Bodenazidität. (Ibid., Groningen 1927, Vol. B., pp. 77—79).