

## Direct pH Determination of Soil under Its Natural State by Quinhydrone Method.

### III. Determination of pH of Soils in the Dry Farm.

By

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In the previous publications<sup>1,2)</sup>, the direct method as proposed by VERWELL<sup>3)</sup> and also a new modified electrode were presented, and the  $P_H$  determinations were made in the paddy-field. This paper presents the results obtained in the dry farm which is different from the paddy-field especially in regard to the moisture contents as well as the soil gradients so that it was necessary to test the efficiency of the method.

### Experimental.

Previous to the field tests, the following experiments were carried out :

#### *Part I. Preliminary Tests.*

- 1.) Influence of the moisture contents of the soil and its limit for the  $P_H$  measurements.
- 2.) Influence of the purity of quinhydrone.
- 3.) Influence of the distance between the platinum electrodes with the quinhydrone paste and the calomel electrode.
- 4.) The time required to reach the equilibrium.

#### *1.) Influence of the moisture contents of the soil and its limit for the pH measurements :*

Under the dry farm condition where the moisture contents is very low in general, it was first questioned if the sufficient dissociation of quinhydrone is possible and also the conductivity of the soil itself is sufficient to permit the accurate reading when the soil moisture is very low. In regard to this factor TROFIMOV<sup>4)</sup> experimented with well washed quartz sand with various quantity of buffer solutions added and found no difference whatsoever in the efficiency of quinhydrone electrode. To substantiate the foregoing report, KAHLBAUM quartz sand was taken and after repeated washing for several days, dried and various

amount of CLARK'S buffer solution (50 cc. M/5 phthalate + 2.63 cc. M/2 HCl + 147.37 cc. H<sub>2</sub>O) and SÖRENSEN'S (30 cc. M/15 secondary phosphate + 70 cc. M/15 primary phosphate) were added, as indicated in Table 1 and the  $P_H$  values were determined.

Table 1.  
Determination of  $P_H$  of standard Buffer Solutions in Quartz Sand.

Kinds. \ Moisture %.	2	5	10	20	Buffer solution alone.
SÖRENSEN.	$P_H$ 6.39	$P_H$ 6.39	$P_H$ 6.30	$P_H$ 6.37	$P_H$ 6.36
CLARK.	4.62	3.87	3.80	3.82	3.77

As noted in Table 1, very close results were obtained in case of SÖRENSEN'S buffer solution of which the  $P_H$  value was larger than that of CLARK'S where the results were larger especially so in low moisture content. Judging from these results, it seems that in case of higher acidity, hydrogen ions are absorbed by the sand particles as well as slight impurity might have remained in the sand caused the difference. In order to clarify this, both buffer solutions of higher concentration were tried as follows: Saturated potassium phthalate, and the mixture of M/1 primary and secondary phosphate solution, and tested as before. Table 2 gives the results obtained:

Table 2.  
Determination of  $P_H$  of concentrated Buffer Solutions in Quartz Sand.

Kinds. \ Moisture %.	2	5	10	15	20	30	Buffer solution alone.
M/1 KH <sub>2</sub> PO <sub>4</sub> .	$P_H$ 6.44	$P_H$ 6.46	$P_H$ 6.44	$P_H$ 6.46	$P_H$ 6.46	$P_H$ 6.46	$P_H$ 6.44
M/1 Na <sub>2</sub> HPO <sub>4</sub> .							
Sat. K-phthalate.	3.96	4.01	4.01	3.98	4.00	4.00	4.01

As Table 2 indicates, very close results were obtained which seem to indicate that the quantity of moisture has little influence on the results, and as low as two per cent moisture was sufficient to give good results. However it was questioned if the same results could be obtained in case of the soil which in general absorbs moisture much greater than the quartz sand so that the electric current may not be conducted in the soil with the least amount of moisture which allowed the passage in case of the quartz sand. The following experiment was carried out to ascertain the influence of different moisture content in the soil on the determination of  $P_H$ .

Determination of  $P_H$  in the soil of different moisture contents.

The air-dried soil was taken to which various amount of water was added to get 2–20 per cent moisture contents, left standing overnight and the  $P_H$  values were determined. At the sametime, the  $P_H$  determinations were made under the

natural, fresh and air-dried conditions and also the moisture contents were determined. The results are shown in Table 3.

Table 3.  
 $P_H$  Determination in the Soil of which the Soil-water Ratio was adjusted.

Moisture %.	2.4	8.6	12.9	15.5	18.3	19.2	
I. $P_H$ {	Natural.	—	6.05	6.39	6.70	6.77	6.58
	Fresh (1:1).	6.69	7.03	6.89	7.10	7.08	7.08
	Air-dried (1:2).	6.77	6.86	6.95	7.03	7.15	6.93
Moisture %.	4.9	8.3	8.8	11.0	11.2	14.9	
II. $P_H$ {	Natural.	6.70	6.67	6.89	7.07	7.05	7.15
	Fresh.	7.43	—	—	—	—	7.62
Moisture %.	6.7	8.8	9.2	11.7	11.9	16.8	
III. $P_H$ {	Natural.	6.63	6.90	6.95	7.12	7.14	7.17
	Fresh.	7.40	—	—	—	—	7.74

Table 3 indicates that it was impossible to determine  $P_H$  in the air-dried soil which contained 2.4 per cent moisture but with 4.9 and 6.7 per cent, the accurate determinations were made although it may differ by the different soils. The moisture content in the soil changes very rapidly by various factors but ordinarily under the natural state, it contains 16.0—17.0 per cent, as shown by ITANO and MATSUURA<sup>6</sup>). CAMERON<sup>1</sup>) determined the moisture contents in various kinds of soils in different season and reported that the sandy soil in June showed 4.0 per cent but in all other cases contained more than 7.0 per cent. Since the soil with 5.0 per cent moisture is very dry, it is reasonable to suppose that in a majority of the dry-farm soils, it is possible to determine the  $P_H$  values under the natural conditions, if a few centimeters of the top soil is removed.

The difference in the  $P_H$  values of the soils under natural conditions and the fresh soil samples (soil and water ratio 1:1) were as given in Table 4.

Table 4.  
Difference of  $P_H$  Values of the Soils with different Moisture Contents.

Moisture %.	(I)		(II)		(III)		
	8.6	18.3	4.9	14.9	6.7	16.8	
$P_H$ {	Natural. . . . .	6.05	6.77	6.70	7.15	6.63	7.17
	Fresh. . . . .	7.03	7.08	7.43	7.62	7.40	7.74
$P_H$ difference (Fresh-Natural).		0.98	0.31	0.73	0.47	0.77	0.57

As noted in Table 4, some discrepancies were obtained between the natural and fresh soil samples viz:  $P_H$  0.77—0.98 difference for 4.9—8.6 per cent moisture contents, and  $P_H$  0.31—0.57 for 14.9—18.3 per cent moisture. The difference was larger when the moisture contents was low.

It has been reported that the addition of different amount of water to the soil makes difference in  $P_H$  value of the same soil. PIERRE<sup>2)</sup> took five kinds of soils and determined their  $P_H$  values by using the hydrogen electrode and varying the amount of water added from 1:2 to 1:50, and found the increase of  $P_H$  values of 0.2—1.15 as the amount of water increased. BAVER<sup>3)</sup> used the quinhydrone electrode in determining the  $P_H$  values of twelve kinds of soils varying the soil water ratio, from 2:1 to 2:5 and found that the  $P_H$  values increased by 0.2—0.3 as the ratio increased. Further TROFIMOW<sup>5)</sup> tested with twelve kinds of soils, changing their water contents from 10—100 per cent, and found the increase in  $P_H$  values as the water contents increased, from  $P_H$  0.48 to 1.83, and noted that the change was greater in the soil of less than 50 per cent moisture of which the moisture contents was changed.

Considering the results obtained in this investigation in the light of these reports noted above, the difference found between the natural and fresh samples seems to be due to the difference of water content while the method is correct and the results obtained under the natural condition should be considered as the actual  $P_H$  values which have the direct influence on the growth of plants.

## 2.) Influence of the Purity of Quinhydrone :

ARND and SIEMERS<sup>4)</sup> reported that the use of impure quinhydrone gives smaller  $P_H$  values when the sample is weakly buffered. Since the buffer capacity of dry-farm soil is rather weak and contains small amount of water, the influence of quinhydrone was tested as follows: the quinhydrone prepared after BILLMANN washed thoroughly with cold water, and on the other hand, the quinhydrone precipitate was crystallized twice in warm water of 70°C. and washed thoroughly with cold water, were used. According to ARND and SIEMERS<sup>4)</sup>, recrystallized quin-

Table 5.  
Influence of Purity of Quinhydrone and Moisture Contents  
on  $P_H$  Values in Quartz Sand.

Moisture %.	5	10	$P_H$ of solution.
(SØRENSEN'S solution.)	( $P_H$ )	( $P_H$ )	
Quinhydrone I.	6.22	6.37	6.39
„ II.	6.39	6.39	„
(CLARK'S solution)			
Quinhydrone I.	3.80	3.85	3.77
„ II.	3.87	3.80	„

Note: Quinhydrone I=washed only; II=twice recrystallized.

Table 6.  
 $P_H$  in Soil of Different Moisture  
Contents.

Moisture %.	5.9	13.4
Quinhydrone I.	( $P_H$ ) 6.24	( $P_H$ ) 7.05
" II.	6.27	7.07

Table 5 indicates that the results in all cases agree fairly well except in 5 per cent of SØRENSEN'S buffer solution. Again in Table 6, the soils of which the moisture contents were adjusted gave very close results. Judging from these results, it is satisfactory to use the quinhydrone, well washed with cold water in making the  $P_H$  measurements in the field.

3.) *Influence of the distance between the platinum electrode with the quinhydrone paste and the calomel electrode :*

When the moisture content of soil is very low, it is suspected that the distance between the platinum and the calomel electrodes may have some influence on the results. Consequently the  $P_H$  determinations of soils in which the moisture content is adjusted, were carried out by placing the electrodes at 1, 2 and 3 cm. apart, and the following results were obtained as shown in Table 7.

As Table 7 indicates, at one centimeter distance, the determinations were made in all the moisture contents while in 4.9 per cent moisture, no reading was taken at two centimeters apart or more, although the higher moisture content permitted the determination at all distance. From these results, one centimeter or less is the suitable distance for practical determination. The determination is made very accurately as far as three centimeters apart when the moisture content is high.

4.) *Time required to reach the equilibrium :*

TROFIMOW<sup>7)</sup> reported that the equilibrium is reached most quickly with 20 to 50 per cent moisture content, and it took longer time in less or more than these limits. VERWEEL<sup>7)</sup> noted marked variation of 10 to 60 seconds after quinhydrone is added to the soil under the natural conditions. In this investigation, the E.M.F. of soil of different moisture contents was determined at different intervals, and the results were obtained as shown in Table 8.

hydrone gives an accurate result even in water with carbonate alone. Using the quinhydrone thus prepared and  $P_H$  determinations were carried out in quartz sand with 5 and 10 per cent of either CLARK'S or SØRENSEN'S buffer solution was added, and also in the soil of different moisture contents. The results are given in Table 5 and 6.

Table 7.  
Influence of Moisture and the Distance  
between Electrodes.

Moisture Distance of electrodes.	4.9	8.3	11.0
Moisture %. (cm.)	(m.v.)	(m.v.)	(m.v.)
1.	71	71	47
2.	X	73	47
3.	X	70	48

Notes: X=impossible to determine.

Table 8.  
Influence of Moisture Contents on the Time required to reach  
the Equilibrium.

Moisture %. Min.	6.7	9.2	11.9	16.8
	(m.v.) 82	(m.v.) 67	(m.v.) 45	(m.v.) 45
1				
2	72	57	43	42
3	72	57	42	40
5	71	54	42	40
10	70	53	41	40

As noted above, the difference between 6.7 and 9.2 per cent moisture is very marked and it is inclined to increase with time while for above 11.9 per cent, very close results are obtained. In the same moisture content, the equilibrium is reached after two minutes.

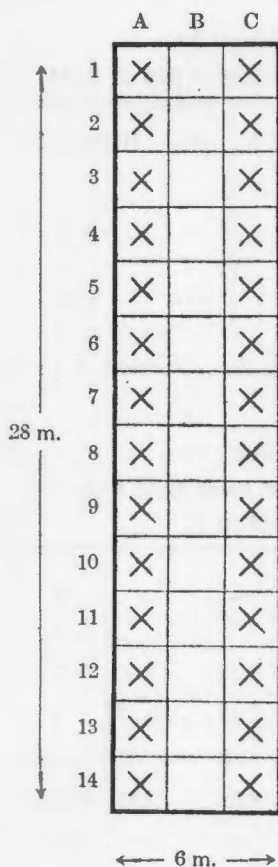
### Part II. Tests in the Dry-farm.

After the preliminary tests, the determinations were made under natural conditions in the dry-farm in order to test the accuracy of the method under dry condition.

The experimental plot has been under cultivation and wheat was growing at the time. At the centre of two meters square section, as shown in Fig. I, the determinations were made, and the soil sample was taken from the close spot at the sametime and subjected to the laboratory tests under the fresh and air-dried conditions with the soil-water ratio 1:1 and 1:2 respectively. The results of tests are given in the following tables:

Table 9.  
Section A under Natural Condition.

No.	E.M.F.	p <sub>H</sub>	D	D <sup>2</sup>	No.	E.M.F.	p <sub>H</sub>	D	D <sup>2</sup>
	(m.v.)					(m.v.)			
A 1	83	6.43	+0.71	0.5041	A 8	140	5.44	-0.28	0.0784
A 2	82	6.44	+0.72	0.5184	A 9	120	5.79	+0.07	0.0049
A 3	135	5.53	-0.19	0.0361	A 10	129	5.63	-0.09	0.0081
A 4	141	5.42	-0.30	0.0900	A 11	122	5.75	+0.03	0.0009
A 5	133	5.56	-0.16	0.0256	A 12	76	6.55	+0.83	0.6889
A 6	139	5.46	-0.28	0.0676	A 13	157	5.15	-0.57	0.3249
A 7	112	5.92	+0.30	0.0900	A 14	168	4.96	-0.76	0.5776
Σ					80.03				
Mean					5.72				
σ					0.4641				



No.	E.M.F.	P <sub>H</sub>	D	D <sup>2</sup>
B 1	(m.v.) 85	6.39	+0.74	0.5476
B 2	57	6.88	+1.13	1.2769
B 3	106	6.03	+0.38	0.1444
B 4	124	5.72	-0.03	0.0009
B 5	147	5.32	-0.43	0.1849
B 6	131	5.61	-0.14	0.0196
B 7	139	5.46	-0.29	0.0841
B 8	150	5.27	-0.48	0.2304
B 9	129	5.63	-0.12	0.0144
B 10	154	5.20	-0.55	0.3025
B 11	149	5.28	-0.47	0.2209
B 12	95	6.22	+0.47	0.2209
B 13	86	6.37	+0.62	0.3844
B 14	155	5.18	-0.57	0.3249
$\Sigma$		80.56		
Mean		5.75		
$\sigma$		0.5255		

No.	E.M.F.	$p_H$	D	D <sup>2</sup>	No.	E.M.F.	$p_H$	D	D <sup>2</sup>
C 1	(m.v.) 80	6.48	+0.75	0.5625	C 8	(m.v.) 162	5.06	-0.67	0.4489
C 2	82	6.44	+0.71	0.5041	C 9	169	4.94	-0.79	0.6241
C 3	99	6.15	+0.42	0.1764	C 10	119	5.80	+0.07	0.0049
C 4	129	5.63	-0.10	0.0100	C 11	119	5.80	+0.07	0.0049
C 5	150	5.27	-0.46	0.2116	C 12	151	5.25	-0.48	0.2304
C 6	143	5.39	-0.34	0.1156	C 13	121	5.77	+0.04	0.0016
C 7	133	5.56	-0.17	0.0289	C 14	69	6.67	+0.94	0.8836
$\Sigma$					80.21				
Mean					5.73				
$\sigma$					0.5215				



The foregoing tables indicate that the variation of  $P_H$  values among the spots tested is much more marked than that in the paddy-field. For instance, in Section A, an average of differences among the  $P_H$  values obtained was 0.411 while that of paddy-field was 0.219, and the biggest difference was 0.5 in the paddy-field and 1.4 in the dry-farm. Consequently the standard deviation in the dry-farm was 0.5 while that of the paddy-field was 0.2-0.3.

The moisture contents of the soils in the field are given in Table 12.

In Table 13, and 14 the results obtained with fresh soils from Sections A and C respectively making the soil-water ratio of 1:1, are given.

Table 13.

$P_H$  Values of Fresh Soils from  
Section A.

No.	E.M.F.	$P_H$	D	$D^2$
A 1	(m.v.) -5	7.95	+1.50	2.2500
A 2	9	7.71	+1.26	1.5876
A 3	64	6.76	+0.31	0.0961
A 4	87	6.36	-0.09	0.0081
A 5	114	5.89	-0.56	0.3136
A 6	105	6.05	-0.40	0.1600
A 7	91	6.29	-0.16	0.0256
A 8	81	6.46	+0.01	0.0001
A 9	73	6.60	+0.15	0.0225
A 10	78	6.51	+0.06	0.0036
A 11	81	6.46	+0.01	0.0001
A 12	64	6.67	+0.31	0.0900
A 13	138	5.46	-0.99	0.9801
A 14	162	5.06	-1.40	1.9600
$\Sigma$			90.32	
Mean			6.45	
$\sigma$			0.7318	

Table 12.

Moisture Contents of Soil in Field.

No.	Moisture %.	No.	Moisture %.
1	22.6	5	22.4
2	20.0	6	25.5
3	19.2	7	18.2
4	23.1	Ave.	21.6

Table 14.

$P_H$  Values of Fresh Soils from  
Section C.

No.	E.M.F.	$P_H$	D	$D^2$
C 1	(m.v.) 43	7.12	+0.50	0.2500
C 2	10	7.69	+1.07	1.1449
C 3	48	7.03	+0.41	0.1681
C 4	99	6.15	-0.47	0.2209
C 5	93	6.25	-0.37	0.1369
C 6	106	6.03	-0.59	0.3481
C 7	78	6.51	-0.11	0.0121
C 8	105	6.05	-0.57	0.3249
C 9	103	6.08	-0.54	0.2916
C 10	61	6.81	+0.19	0.0361
C 11	83	6.43	-0.19	0.0361
C 12	56	6.89	+0.27	0.0729
C 13	93	6.25	-0.37	0.1369
C 14	24	7.45	+0.83	0.6889
$\Sigma$			92.74	
Mean			6.62	
$\sigma$			0.5256	

Tables 15 and 16 show the results with the air-dried soils from Sections A and C respectively making the soil-water ratio of 1:2.



Table 15.  
 $p_H$  Values of Air-dried Soils from Section A.

No.	E.M.F.	$p_H$	D	$D^2$	No.	E.M.F.	$p_H$	D	$D^2$
A 1	(m.v.) 27	7.40	+1.18	1.3924	A 8	(m.v.) 107	6.01	-0.21	0.0441
A 2	27	7.40	+1.18	1.3924	A 9	100	6.13	-0.09	0.0081
A 3	81	6.46	+0.24	0.0576	A 10	110	5.96	-0.28	0.0676
A 4	96	6.20	-0.02	0.0004	A 11	97	6.18	-0.04	0.0016
A 5	125	5.70	-0.52	0.2704	A 12	77	6.53	+0.30	0.0900
A 6	112	5.92	-0.30	0.0900	A 13	143	5.39	-0.83	0.6889
A 7	94	6.24	+0.02	0.0004	A 14	134	5.54	-0.68	0.4624
$\Sigma$					87.06				
Mean					6.22				
$\sigma$					0.5711				

Table 16.  
 $p_H$  Values of Air-dried Soils from Section C.

No.	E.M.F.	$p_H$	D	$D^2$	No.	E.M.F.	$p_H$	D	$D^2$
C 1	(m.v.) 62	6.79	+0.46	0.2116	C 8	(m.v.) 124	5.72	-0.81	0.3721
C 2	25	7.43	+1.10	1.2100	C 9	109	5.98	-0.35	0.1225
C 3	71	6.63	+0.30	0.0900	C 10	87	6.36	+0.03	0.0009
C 4	108	5.99	-0.34	0.1156	C 11	98	6.17	-0.16	0.0256
C 5	113	5.91	-0.42	0.1764	C 12	81	6.46	+0.13	0.0169
C 6	118	5.82	-0.49	0.2401	C 13	103	6.08	-0.25	0.0625
C 7	92	6.27	-0.06	0.0036	C 14	48	7.03	+0.70	0.0490
$\Sigma$					88.64				
Mean					6.33				
$\sigma$					0.4389				

As the foregoing results indicate, the variations are marked in all these determinations, having the standard deviation of 0.73 largest and 0.43 smallest, which are much larger than that for the paddy-field soils.

*Part III. Comparison of Results obtained Under the Natural, Fresh and Air-dried Conditions.*

Tables 17 and 18 indicate the comparison of results obtained under the natural, fresh and air-dried conditions, on the soils from Section A and C respectively.

From these results, it is noted that  $p_H$  values obtained under the natural state were smallest, followed by the air-dried and largest in the fresh samples.

Table 17.  
Comparative Results on Section A.

No.	Natural.	Fresh-Natural.	Fresh.	Air-dried-Natural.	Air-dried.
A 1	6.43	1.52	7.95	0.97	7.40
A 2	6.44	1.27	7.71	0.96	7.40
A 3	5.53	1.23	6.76	0.93	6.46
A 4	5.42	0.94	6.36	0.78	6.20
A 5	5.56	0.33	5.89	0.14	5.70
A 6	5.46	0.59	6.05	0.46	5.92
A 7	5.92	0.37	6.29	0.32	6.24
A 8	5.44	1.02	6.46	0.57	6.01
A 9	5.79	0.81	6.60	0.34	6.13
A 10	5.63	0.88	6.51	0.33	5.96
A 11	5.75	0.71	6.46	0.43	6.18
A 12	6.55	0.21	6.76	0.02	6.53
A 13	5.15	0.31	5.46	0.24	5.39
A 14	4.96	0.10	5.06	0.58	5.54
$\Sigma$	80.03		90.32		80.06
Mean	5.72	0.73	6.45	0.51	6.22

Table 18.  
Comparative Results on Section C.

No.	Natural.	Fresh-Natural.	Fresh.	Air-dried-Natural.	Air-dried.
C 1	6.48	0.64	7.12	0.31	6.79
C 2	6.44	1.25	7.69	0.99	7.43
C 3	6.15	0.88	7.03	0.48	6.63
C 4	5.63	0.52	6.15	0.36	5.99
C 5	5.27	0.98	6.25	0.94	5.91
C 6	5.39	0.64	6.03	0.43	5.82
C 7	5.56	0.95	6.51	0.71	6.27
C 8	5.06	0.99	6.05	0.66	5.72
C 9	4.94	1.14	6.08	1.04	5.98
C 10	5.80	1.01	6.81	0.56	6.36
C 11	5.80	0.63	6.43	0.37	6.17
C 12	5.25	1.64	6.89	1.21	6.46
C 13	5.77	0.48	6.25	0.31	6.08
C 14	6.67	0.78	7.45	0.36	7.03
$\Sigma$	80.21		92.74		88.64
Mean	5.73	0.90	6.62	0.60	6.33

The largest and smallest differences and their average obtained by different methods, are presented in Table 19.

Table 19.  
Differences and their Average obtained by different Methods  
in Section A and C.

	Differences.	Maximum.	Minimum.	Average.
Section A.	Fresh-Natural.	1.52	0.10	0.73
	Air-dried-Natural.	0.97	0.02	0.51
Section C.	Fresh-Natural.	1.67	0.48	0.90
	Air-dried-Natural.	1.21	0.31	0.60

As noted in Table 19, the difference between the natural and aird-ried method is smaller than that between the natural and the fresh samples, and in all the cases it is apparent that the  $p_H$  values obtained under the natural condition are smaller than those found by other methods.

*Part IV. Determination of pH in the Paddy-field under  
Wheat Cultivation.*

The  $p_H$  values were determined in the soil within Section A of paddy-field which was surveyed in the previous investigation with wheat plants growing. The readings were taken around root and also between the stubs within two meters square. The results are noted in Table 20 and 21.

Table 20.  
 $p_H$  around Wheat Stubs in Paddy-field.

No.	E.M.F.	$p_H$	D	$D^2$	No.	E.M.F.	$p_H$	D	$D^2$
	(m.v.)					(m.v.)			
1	165	5.01	-0.07	0.0049	11	163	5.04	-0.04	0.0016
2	170	4.92	-0.16	0.0256	12	161	5.08	0	0
3	175	4.83	-0.25	0.0625	13	143	5.39	+0.31	0.0961
4	140	5.44	+0.36	0.1296	14	175	4.83	-0.25	0.0625
5	149	5.28	+0.20	0.0400	15	147	5.32	+0.24	0.0576
6	161	5.08	0	0	16	163	5.04	-0.01	0.0016
7	180	4.74	-0.31	0.1156	17	165	5.01	-0.07	0.0049
8	167	4.97	-0.11	0.0121	18	170	4.92	-0.16	0.0256
9	125	5.70	+0.62	0.3844	19	155	5.18	+0.10	0.0100
10	175	4.83	-0.25	0.0625	20	170	4.92	-0.16	0.0256
$\Sigma$					101.53				
Mean					5.08				
$\sigma$					0.2832				

Table 21.  
 $P_H$  of Soil between Wheat Stubs in Paddy-field.

No.	E.M.F.	$P_H$	D	$D^2$	No.	E.M.F.	$P_H$	D	$D^2$
1	(m.v.) 124	5.72	+0.05	0.0025	11	(m.v.) 138	5.47	-0.20	0.0400
2	127	5.67	0	0	12	134	5.54	-0.13	0.0169
3	128	5.65	-0.02	0.0004	13	131	5.61	-0.06	0.0036
4	149	5.28	-0.39	0.1521	14	124	5.72	+0.05	0.0025
5	121	5.77	+0.10	0.0100	15	143	5.30	-0.28	0.0784
6	129	5.63	-0.04	0.0016	16	134	5.54	-0.13	0.0169
7	115	5.87	+0.20	0.0400	17	141	5.42	-0.25	0.0625
8	139	5.46	-0.21	0.0441	18	143	5.39	-0.28	0.0784
9	130	5.61	-0.06	0.0036	19	140	5.44	-0.23	0.0552
10	134	5.54	-0.13	0.0169	20	121	5.77	+0.10	0.0100
$\Sigma$					2113.49				
Mean					5.67				
$\sigma$					0.2131				

As shown above,  $P_H$  values between the stubs were larger in all cases than those directly close round the stubs. On an average  $P_H$  between the stubs was 5.67 while that of around the stubs was 5.08 which means more acidic near the stubs and which is contrary to that of the rice stubs. This difference may be due to the physiological difference of rice and wheat.

The standard deviation was 0.23 and 0.21 for around and between the stubs respectively which are much smaller than those in the dry-farm. This may be attributed to the action of water in the paddy-field which equalizes the reaction in the field.

The moisture contents of the soils at the time of determination are given in Table 22.

Table 22.  
 Moisture Contents of Soils in  
 Paddy-field.

No.	Moisture %.	No.	Moisture %.
1	37.97	4	29.50
2	32.82	5	32.39
3	32.40	Average	33.02

### Summary.

In this investigation, the applicability of the quinhydrone electrode used under the natural field condition in the dry-farm which is different from the paddy-field in many respects together with some other factors, was tested and the results are reported as follows:

- 1.) The  $P_H$  determination can be carried out as low as 5 per cent moisture without trouble.

- 2.) Quinhydrone washed thoroughly with cold water gives satisfactory results.
- 3.) The good distance between the platinum and calomel electrodes is one centimeter.
- 4.) The equilibrium is reached after two minutes even in presence of small amount of moisture.
- 5.) Under the dry-farm condition, the difference in  $P_H$  values among the adjacent spots is much more marked than that in the paddy-field.
- 6.) The  $P_H$  values under the natural condition are lower than those obtained in the laboratory with the fresh or air-dried samples as usual, and more marked than in case of the paddy-field; on an average,  $P_H$  0.73—0.90 lower than the fresh and  $P_H$  0.51—0.60 lower than the air-dried samples.
- 7.) In the paddy-field where the wheat is cultivated,  $P_H$  values around the stubs are less than those found between the stubs which is contrary to the results obtained with the rice-plant stubs around which the  $P_H$  values were larger. This difference seems to be due to the difference of physiological function of these plants.

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