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

I. Determination of pH in the Paddy-field Soil.

By

Arao Itano and Yasuhiko Tsuji.

[February 19, 1935.]

Previously the senior author (ITANO[1),2)]) devised a portable form of potentiometric apparatus for determination of hydrogen ion concentration by using quinhydrone so that the determination can be carried out in the field or at any convenient place in a laboratory. Eversince the apparatus has been used quite extensively in various fields in this country as well as in other countries. This method however can not be used directly to the soil under the natural condition since the soil sample should be removed from the field and placed in an electrode vessel before the determination is made. Consequently the author has been seeking for a direct method for several years. Meantime, VERWELL[4)] reported a method by which P_H in soil can be determined potentiometrically in its natural state so that its applicability was tested under the field condition, 180 determinations within 720 square meters in the experimental plot at this institute, by using VERWELL's electrode in combination with ITANO's portable apparatus, and the results are given in this paper.

Experimental:

Method of Procedure :

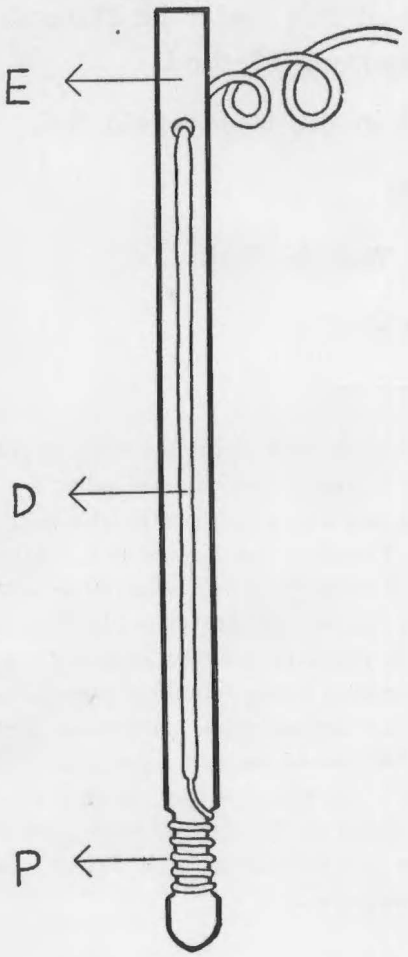
I. Apparatus used :

a.) *Electrode :* — The electrode is shown in Figure I.

(See Figure I on the next page.)

b.) *Connection to the saturated calomel electrode :* — The electrode box of ITANO's apparatus is taken off from the potentiometer as shown in Plate XXXIII and the connection to the calomel electrode is made through Sat. KCl vessel (K) as usual; rubber tube (G) is attached to the end of glass tube coming from the vessel, and a tip of a glass tube at the end of (G) is widened and has a special arrangement as shown in Figure II.

Figure I.
Platinum Electrode.

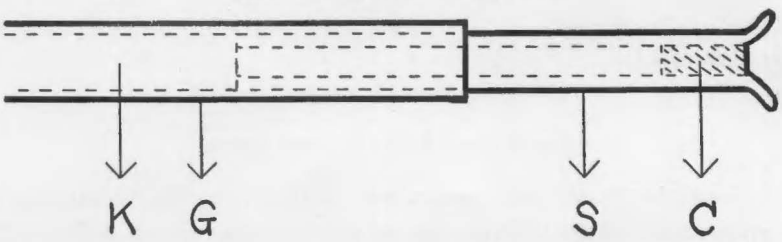


E.= Ebonite (5×5×50 mm.) of which the end is pointed and the neck portion is depressed slightly where platinum wire is wound.

D.= Covered wire lead.

P.= Platinum wire (40 mm. long and 1 mm. diameter.)

Figure II.
End of Rubber Tube (G).



C.= Wooden cork, previously boiled in saturated KCl solution.
S.= Glass tube, of which end is widened like a funnel.
G.= Rubber tube.
K.= Saturated KCl, the entire system is filled with Sat. KCl solution, excluding all the air bubble.

c.) *Connection to the potentiometer :—* The platinum electrode and the calomel electrode are connected to the posts P_2 and P_1 respectively as shown in Plate XXXIII, and each post is connected to the potentiometer by means of rubber coated wire of least resistance which is 100 meters long so that the measurements are made at any distance within the reach.

II. Determination of pH :

1.) Remove 2—4 cm. of the surface soil with spatula so that large particles of organic debries and other materials are eliminated.

2.) Smear the platinum electrode (Plate XXXIII, E) with quinhydrone paste (quinhydrone crystal is mixed with a small amount of distilled water and made into paste) and insert the electrode into the soil as far as the platinum part is imbeded. If the soil is too hard, make a hole with a stick as large as the electrode previously so that the electrode can be inserted readily.

3.) Connection between the electrode and calomel electrode is made by the rubber tube (Plate XXXIII, G) of which the end is immersed in Sat. KCl solution and carrying an excess of St. KCl, pressed against the soil surface close-by the electrode viz. ± 1 cm. distance. If the soil is too dry, add a sufficient amount of Sat. KCl to the soil so that good connection is made in the chain.

4.) After the chain is completed, the potentiometric readings are taken as usual at any convenient distance and place. Meantime the temperature of soil near-by the electrode and a necessary correction is made.

Results :

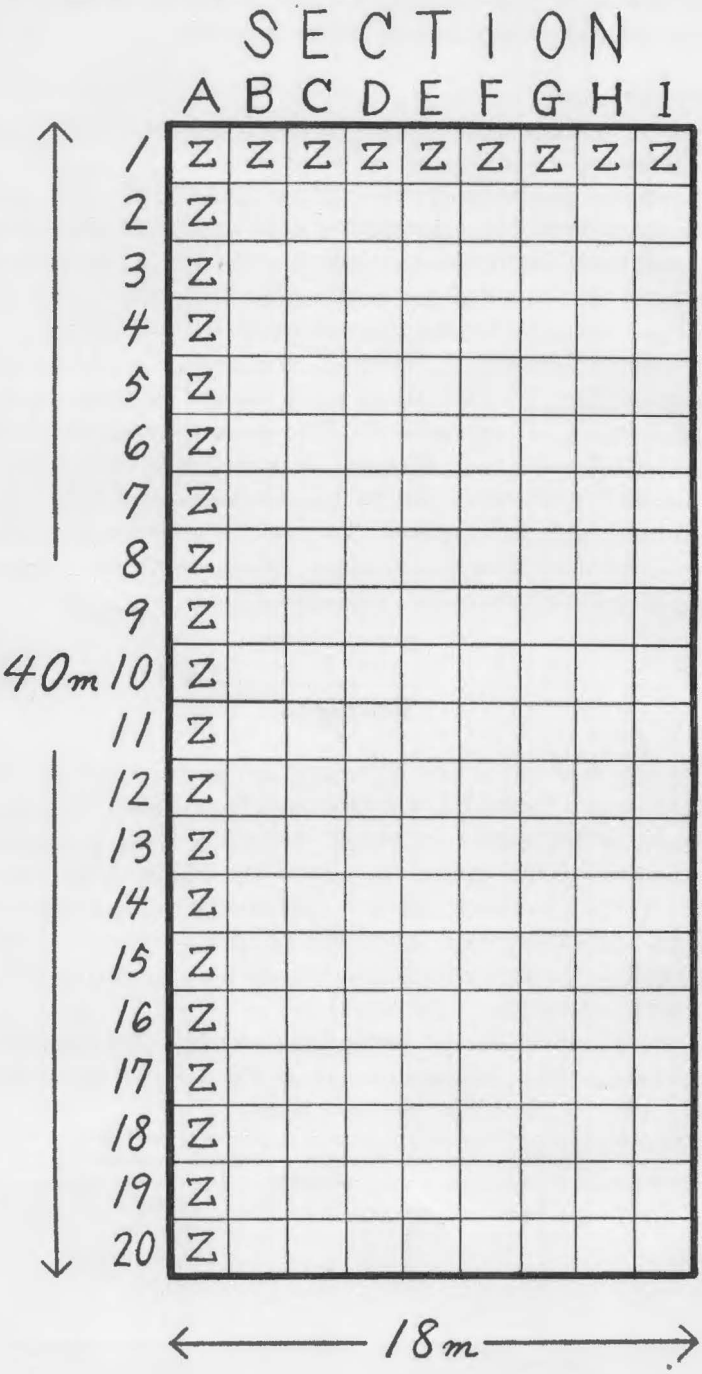
For this investigation, a plot (720 sq. m.) in the experimental field at our institute, as shown in Figure III, was taken and the P_H measurement was made in each 2 sq. m., or 180 spots were tested. In each 2 sq. m., two measurements were made, one at the center of four rice plant stubs, and the other, close right by a stub so that 360 such measurements were made in all besides others which will be noted later. At the sametime, the similar determinations were made in those squares, marked Z, by the methods which have been employed formerly viz. air-dried or fresh soil samples in the laboratory.

The nature of soil is alluvial, sandy loam of which the composition[3] was reported previously. The moisture content at the time of determination was as follows : (See Figure III on the next page.)

Samples.	Moisture content.
1.	33.3%
2.	33.0
3.	33.9
4.	34.5
5.	31.4
Average.	33.22

Figure III.

Sections where the Determinations were Made.



The results for each two sq. m. will be presented in the following tables (Tables I—IX, inclusive) as to E.M.F. with temperature correction as p_H, average p_H, the deviation from the mean p_H and the standard deviation which are noted as follows:

Z = A center of four stubs,
R = Close by the stub,
E = E. M. F. in millivolts at 18°C.,
D = Deviation of p_H from the mean,
D^2 = Square of deviation,
Σ = Sum of p_H values,
Mean = Average of p_H values,
σ = Standard deviation.

σ was calculated by the following equation:

$$\sigma = \sqrt{\frac{\Sigma D^2 f}{n}}$$

in which

Σ = Sum of p_H values,
D^2 = Square of deviation,
f = Frequency,
n = Number of variants.

Table I. (Section A.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	119.3	5.80	+0.27	0.0729	115.8	5.86	−0.15	0.0225
2	146.0	5.34	−0.19	0.0361	78.5	6.51	+0.50	0.2500
3	129.8	5.61	+0.08	0.0064	104.4	6.06	+0.05	0.0025
4	142.4	5.40	−0.13	0.0169	128.4	5.64	−0.37	0.1369
5	132.4	5.57	+0.04	0.0016	120.3	5.79	−0.22	0.0484
6	130.4	5.61	+0.08	0.0064	111.3	5.94	−0.07	0.0049
7	128.9	5.63	+0.10	0.0100	96.7	6.18	+0.17	0.0289
8	106.7	6.01	+0.48	0.2304	91.6	6.28	+0.27	0.0729
9	129.9	5.61	+0.08	0.0064	105.7	6.03	+0.02	0.0004
10	122.3	5.75	+0.22	0.0484	113.2	5.91	−0.10	0.0100
11	138.5	5.46	−0.07	0.0049	97.0	6.18	+0.17	0.0289
12	143.0	5.39	−0.14	0.0196	94.7	6.22	+0.21	0.0441
13	136.2	5.51	−0.02	0.0004	111.4	5.93	−0.08	0.0064
14	143.4	5.38	−0.15	0.0225	81.5	6.45	+0.44	0.1936
15	139.9	5.44	−0.09	0.0081	101.9	6.10	+0.09	0.0081
16	154.8	5.18	−0.35	0.1225	124.0	5.72	−0.29	0.0841
17	137.9	5.47	−0.06	0.0036	111.1	5.94	−0.07	0.0049
18	125.0	5.70	+0.17	0.0289	118.9	5.80	−0.21	0.0441
19	149.7	5.27	−0.26	0.0676	117.9	5.82	−0.19	0.0361
20	138.9	5.46	−0.07	0.0049	119.7	5.79	−0.22	0.0484
Σ		110.59				120.15		
Mean		5.53				6.01		
σ		0.1895				0.2320		

Table II. (Section B.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	123.9	5.72	+0.21	0.0441	115.8	5.86	+0.16	0.0256
2	132.4	5.57	+0.06	0.0036	120.3	5.79	+0.09	0.0081
3	146.6	5.33	−0.18	0.0324	120.3	5.79	+0.09	0.0081
4	150.6	5.26	−0.25	0.0625	136.5	5.50	−0.20	0.0400
5	131.9	5.58	+0.07	0.0049	127.9	5.65	−0.05	0.0025
6	145.4	5.35	−0.16	0.0256	135.4	5.52	−0.18	0.0324
7	142.0	5.41	−0.10	0.0100	131.9	5.58	−0.12	0.0144
8	121.8	5.75	+0.24	0.0576	96.7	6.18	+0.48	0.2304
9	125.9	5.68	+0.17	0.0289	121.8	5.75	+0.05	0.0025
10	122.3	5.75	+0.24	0.0576	122.3	5.75	+0.05	0.0025
11	122.3	5.75	+0.24	0.0576	130.7	5.61	−0.09	0.0081
12	149.6	5.27	−0.24	0.0576	118.7	5.80	+0.10	0.0100
13	157.9	5.13	−0.38	0.1444	124.9	5.70	0.00	0.0000
14	134.8	5.53	+0.02	0.0004	132.7	5.56	−0.14	0.0196
15	126.6	5.67	+0.16	0.0256	155.4	5.17	−0.33	0.1089
16	140.4	5.43	−0.08	0.0064	128.1	5.65	−0.05	0.0025
17	134.3	5.54	+0.03	0.0009	110.7	5.94	+0.24	0.0576
18	136.3	5.51	0.00	0.0000	134.3	5.54	−0.16	0.0256
19	133.8	5.54	+0.03	0.0009	128.6	5.63	−0.07	0.0049
20	145.6	5.34	−0.17	0.0289	106.9	6.01	+0.31	0.0961
Σ		110.11				113.98		
Mean		5.51				5.70		
σ		0.1803				0.1871		

Table III. (Section C.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	130.4	5.61	+0.11	0.0121	110.2	5.96	+0.21	0.0441
2	90.0	6.31	+0.81	0.6561	120.3	5.79	+0.02	0.0004
3	120.3	5.79	+0.29	0.0841	129.4	5.62	−0.15	0.0225
4	151.0	5.25	−0.25	0.0625	95.7	6.20	+0.43	0.1849
5	141.4	5.42	−0.08	0.0064	151.4	5.24	−0.53	0.2809
6	146.0	5.34	−0.16	0.0256	101.7	6.10	+0.33	0.1089
7	146.0	5.34	−0.16	0.0256	121.8	5.75	−0.02	0.0004
8	122.3	5.75	+0.25	0.0625	83.9	6.41	+0.64	0.4096
9	140.5	5.43	−0.07	0.0049	84.9	6.39	+0.62	0.3844
10	126.9	5.67	+0.17	0.0289	109.8	5.96	+0.19	0.0361

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
11	139.0	5.46	−0.04	0.0016	107.7	5.99	+0.22	0.0484
12	145.5	5.34	−0.16	0.0256	133.1	5.56	−0.21	0.0441
13	139.3	5.46	−0.04	0.0016	143.4	5.38	−0.39	0.1521
14	142.4	5.40	−0.10	0.0100	139.3	5.46	−0.31	0.0961
15	141.0	5.42	−0.08	0.0064	139.9	5.44	−0.33	0.1089
16	151.7	5.23	−0.27	0.0729	135.3	5.53	−0.24	0.0576
17	134.3	5.54	+0.04	0.0016	142.5	5.40	−0.37	0.1369
18	161.3	5.08	−0.42	0.1764	91.9	6.27	+0.50	0.2500
19	136.8	5.49	−0.01	0.0001	122.5	5.74	−0.03	0.0009
20	124.7	5.70	+0.20	0.0400	150.0	5.27	−0.50	0.2500
Σ		110.03				115.46		
Mean		5.50				5.77		
σ		0.2554				0.3615		

Table IV. (Section D.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	105.7	6.03	+0.38	0.1444	91.6	6.28	+0.35	0.1225
2	115.8	5.86	+0.21	0.0441	105.7	6.03	+0.10	0.0100
3	104.1	6.06	+0.41	0.1681	127.4	5.66	−0.27	0.0729
4	128.4	5.64	−0.01	0.0001	127.4	5.66	−0.27	0.0729
5	128.9	5.63	−0.02	0.0004	122.9	5.73	−0.20	0.0400
6	126.4	5.68	+0.03	0.0009	122.4	5.74	−0.19	0.0361
7	131.4	5.60	−0.05	0.0025	89.0	6.32	+0.39	0.1521
8	114.8	5.87	+0.22	0.0484	102.7	6.08	+0.15	0.0225
9	113.8	5.89	+0.24	0.0576	92.6	6.25	+0.32	0.1024
10	130.4	5.61	−0.04	0.0220	108.2	5.99	+0.06	0.0036
11	114.2	5.89	+0.24	0.0576	89.0	6.32	+0.39	0.1521
12	124.9	5.70	+0.15	0.0225	124.9	5.70	−0.23	0.0529
13	135.2	5.53	−0.12	0.0144	120.7	5.77	−0.16	0.0256
14	136.2	5.51	−0.14	0.0196	147.6	5.30	−0.63	0.3969
15	153.3	5.22	−0.43	0.1849	112.2	5.92	−0.01	0.0001
16	142.5	5.40	−0.15	0.0225	124.0	5.72	−0.21	0.0441
17	136.3	5.51	−0.14	0.0196	122.0	5.75	−0.18	0.0324
18	144.5	5.36	−0.29	0.0841	91.0	6.29	+0.36	0.1296
19	133.3	5.56	+0.09	0.0081	114.0	5.89	−0.04	0.0016
20	136.5	5.50	−0.15	0.0225	92.0	6.27	+0.34	0.1156
Σ		113.05				118.67		
Mean		5.65				5.93		
σ		0.2149				0.2816		

Table V. (Section E.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	105.7	6.03	+0.54	0.2916	103.7	6.06	+0.18	0.0324
2	131.4	5.60	+0.11	0.0121	98.3	6.17	+0.29	0.0841
3	117.3	5.84	+0.35	0.1225	101.1	6.12	+0.24	0.0576
4	139.4	5.45	−0.04	0.0016	89.3	6.32	+0.44	0.1936
5	149.4	5.28	−0.21	0.0441	119.4	5.80	−0.08	0.0064
6	150.0	5.27	−0.22	0.0484	133.9	5.54	−0.34	0.1156
7	118.8	5.80	+0.31	0.0961	111.7	5.92	+0.04	0.0016
8	121.8	5.75	+0.26	0.0676	82.6	6.43	+0.55	0.3025
9	129.9	5.61	+0.12	0.0144	121.8	5.75	−0.13	0.0169
10	131.9	5.58	+0.09	0.0081	99.7	6.13	+0.25	0.0625
11	119.3	5.80	+0.31	0.0961	156.7	5.15	−0.73	0.5329
12	153.8	5.20	−0.29	0.0841	102.1	6.10	+0.22	0.0484
13	140.4	5.43	−0.06	0.0036	139.3	5.46	−0.42	0.1764
14	143.0	5.39	−0.10	0.0100	97.8	6.17	+0.29	0.0841
15	146.1	5.34	−0.15	0.0225	122.4	5.74	−0.14	0.0196
16	151.7	5.23	−0.26	0.0676	132.2	5.58	−0.30	0.0900
17	161.3	5.08	−0.41	0.1681	95.0	6.22	+0.34	0.1156
18	144.0	5.37	−0.12	0.0144	134.8	5.53	−0.35	0.1225
19	150.1	5.27	−0.22	0.0484	133.8	5.54	−0.34	0.1156
20	140.5	5.42	−0.07	0.0049	113.2	5.91	+0.03	0.0009
Σ		109.74				117.64		
Mean		5.49				5.88		
σ		0.2476				0.3301		

Table VI. (Section F.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	112.8	5.91	+0.41	0.1600	82.6	6.43	+0.69	0.4761
2	120.7	5.77	+0.26	0.0676	112.6	5.91	+0.17	0.0289
3	132.9	5.56	+0.05	0.0025	110.8	5.94	+0.20	0.0400
4	135.9	5.51	0.00	0.0000	108.8	5.98	+0.24	0.0576
5	152.5	5.22	−0.29	0.0841	160.5	5.08	−0.66	0.4356
6	146.0	5.34	−0.17	0.0289	152.0	5.23	−0.51	0.2601
7	129.9	5.61	+0.10	0.0100	119.8	5.79	+0.05	0.0025
8	121.8	5.75	+0.24	0.0576	88.6	6.32	+0.58	0.3364
9	129.9	5.61	+0.10	0.0100	113.8	5.89	+0.15	0.0225
10	121.8	5.75	+0.24	0.0576	113.8	5.89	+0.15	0.0225

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
11	132.9	5.56	+0.05	0.0025	138.9	5.46	−0.31	0.0961
12	155.8	5.16	−0.35	0.1225	90.8	6.29	+0.55	0.3025
13	135.2	5.53	+0.02	0.0004	146.5	5.33	−0.41	0.1681
14	140.9	5.42	−0.09	0.0081	135.8	5.51	−0.23	0.0529
15	131.7	5.58	+0.07	0.0049	128.6	5.64	−0.10	0.0100
16	146.1	5.34	−0.17	0.0289	135.8	5.51	−0.23	0.0529
17	145.6	5.34	−0.17	0.0289	114.8	5.87	+0.13	0.0169
18	144.0	5.37	−0.14	0.0196	135.8	5.51	−0.23	0.0529
19	140.9	5.42	−0.09	0.0081	120.7	5.77	+0.03	0.0009
20	136.9	5.49	−0.02	0.0004	140.9	5.42	−0.32	0.1024
Σ		110.24				114.77		
Mean		5.51				5.74		
σ		0.1874				0.3562		

Table VII. (Section G.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	128.9	5.63	+0.16	0.0256	112.8	5.91	+0.11	0.0121
2	135.5	5.52	+0.05	0.0025	129.4	5.62	−0.18	0.0324
3	119.8	5.79	+0.32	0.1024	103.7	6.06	+0.26	0.0676
4	123.4	5.73	+0.26	0.0676	139.4	5.45	−0.35	0.1225
5	150.0	5.27	−0.20	0.0400	135.9	5.51	−0.39	0.1521
6	142.0	5.41	−0.06	0.0036	115.8	5.86	+0.06	0.0036
7	132.9	5.56	+0.09	0.0081	113.8	5.89	+0.09	0.0081
8	131.9	5.58	+0.11	0.0121	99.7	6.13	+0.33	0.1089
9	118.8	5.80	+0.33	0.1089	107.7	5.99	+0.19	0.0361
10	133.5	5.55	+0.08	0.0064	72.8	6.60	+0.80	0.6400
11	139.0	5.46	−0.01	0.0001	121.8	5.75	−0.05	0.0025
12	167.2	4.97	−0.50	0.2500	86.7	6.36	+0.56	0.3136
13	152.7	5.22	−0.25	0.0625	139.3	5.46	−0.34	0.1156
14	155.4	5.17	−0.30	0.0900	120.4	5.84	+0.04	0.0016
15	145.6	5.34	−0.13	0.0169	144.5	5.36	−0.44	0.1936
16	154.8	5.18	−0.29	0.0841	132.2	5.58	−0.22	0.0484
17	134.3	5.54	+0.07	0.0049	141.5	5.41	−0.39	0.1521
18	133.8	5.54	+0.07	0.0049	148.0	5.30	−0.50	0.2500
19	119.7	5.79	+0.32	0.1024	129.8	5.61	−0.19	0.0361
20	143.6	5.37	−0.10	0.0100	90.0	6.31	+0.51	0.1601
Σ		109.42				116.00		
Mean		5.47				5.80		
σ		0.2238				0.3505		

Table VIII. (Section H.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	P_H	D	D^2	E (m.v.)	P_H	D	D^2
1	119.8	5.79	+0.38	0.1444	98.7	6.15	+0.36	0.1296
2	146.6	5.32	−0.09	0.0081	117.3	5.84	+0.05	0.0025
3	142.6	5.40	−0.01	0.0001	123.3	5.73	+0.06	0.0036
4	149.6	5.27	−0.14	0.0196	133.5	5.55	−0.24	0.0576
5	135.4	5.52	+0.11	0.0121	128.4	5.64	−0.15	0.0225
6	146.0	5.34	−0.07	0.0049	92.6	6.25	+0.46	0.2116
7	129.9	5.61	+0.20	0.0400	92.6	6.25	+0.46	0.2116
8	119.3	5.80	+0.39	0.1521	111.2	5.94	+0.15	0.0255
9	125.9	5.68	+0.27	0.0729	132.9	5.56	−0.23	0.0529
10	132.9	5.56	+0.15	0.0255	107.7	5.99	−0.24	0.0576
11	144.0	5 37	−0.04	0.0016	132.9	5.56	−0.23	0.0529
12	173.3	4.87	−0.54	0.2916	95.0	6.22	+0.43	0.1849
13	152.7	5.22	−0.19	0.0361	147.6	5.31	−0.48	0.2304
14	146.5	5.33	−0.08	0.0064	143.9	5.37	−0.42	0.1766
15	153.3	5.22	−0.19	0.0361	142.0	5.41	−0.38	0.1444
16	142.5	5.40	−0.01	0.0001	139.4	5.45	−0.34	0.1156
17	145.6	5.34	−0.07	0.0049	110.7	5.94	+0.15	0.0225
18	161.9	5.06	−0.35	0.1225	157.8	5.13	−0.66	0.4356
19	138.9	5.46	+0.05	0.0025	113.6	5.90	+0.11	0.0121
20	132.4	5.57	+0.16	0.0256	68.7	6.67	+0.88	0.7744
Σ		108.13			115.86			
Mean		5.41			5.79			
σ		0.2244			0.3822			

Table IX. (Section I.)

Determinations were Made under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	P_H	D	D^2	E (m.v.)	P_H	D	D^2
1	122.9	5.73	+0.18	0.0324	123.9	5.72	−0.11	0.0121
2	152.0	5.23	−0.32	0.1024	103.7	6.06	+0.23	0.0529
3	86.2	6.37	+0.82	0.6724	116.6	5.85	+0.02	0.0004
4	139.5	5.45	−0.10	0.0100	142.6	5.40	−0.43	0.1849
5	139.5	5.45	−0.10	0.0100	90.0	6.31	+0.48	0.2304
6	133.5	5.55	0.00	0.0000	120.3	5.79	−0.04	0.0016
7	126.4	5.67	+0.12	0.0144	104.1	6.06	+0.23	0.0529
8	129.9	5.61	+0.06	0.0036	110.8	5.94	+0.11	0.0121
9	132.9	5.56	+0.01	0.0001	118.8	5.80	−0.03	0.0009
10	139.0	5.46	−0.09	0.0081	124.9	5.70	−0.13	0.0169

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
11	152.0	5.23	−0.32	0.1024	131.9	5.58	−0.25	0.0625
12	132.0	5.58	+0.03	0.0009	136.2	5.51	−0.32	0.1024
13	138.9	5.46	−0.09	0.0081	131.7	5.58	−0.25	0.0625
14	141.0	5.42	−0.13	0.0169	115.2	5.87	+0.04	0.0016
15	144.5	5.36	−0.19	0.0361	130.2	5.61	−0.22	0.0484
16	141.5	5.41	−0.14	0.0196	135.3	5.53	−0.30	0.0900
17	141.9	5.41	−0.14	0.0196	114.4	5.88	+0.05	0.0025
18	140.5	5.43	−0.12	0.0144	121.1	5.77	−0.06	0.0036
19	129.8	5.61	+0.06	0.0036	93.3	6.25	+0.42	0.1766
20	110.5	5.95	+0.40	0.1600	80.1	6.48	+0.65	0.4225
Σ		110.94				116.69		
Mean		5.55				5.83		
σ		0.2485				0.2773		

Table I indicates that even among those spots lie very elose each other, somewhat big differences are noted in their p_H values, and in a marked case, the difference of about p_H 0.5 was found ; the smallest p_H was 5.18 and the largest, 6.01 giving the difference of 0.8. For both X and R spots, a similar tendency was observed, from which it may be stated that p_H values for the soil in the same field vary by the spots where the measurements are taken. No marked difference was found among the mean p_H values for different spots vis. p_H 5.5 for X and p_H 5.7 for R spots. It is noteworthy that the p_H values for the R spots are always larger than those of the X spots which means the concentration of hydrogen ions around the roots is less than that of the spots away from the roots. It remains to be questioned however that this condition prevails through a year or not. It may be different during the growing season of the plant, and again the different plant may vary in this regard. This question will be investigated later. The largest standard deviation for all the sections, 360 in all was 0.38 which means 0.80 in terms of p_H.

Determination of pH in Laboratory by the Methods used formerly :

In order to ascertain the comparative merits of this method with those existing hitherto, the following tests were carried out.

The soil samples were collected from the same spots in those sections marked (Z) in Fig. III and p_H was determined by quinhydrone electrode with K-type potentiometer under the following conditions :

1.) *The fresh soil mixed with distilled water (1 : 1).*

2.) *The air-dried soil, treated as above :* The results of these tests are given in Table X, XI, XII and XIII.

Table X.

Results obtained on Fresh Soil in the Laboratory.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
A_1	96.1	6.20	−0.15	0.0225	114.3	5.89	−0.70	0.4900
B_1	100.2	6.13	−0.22	0.0484	80.1	6.48	−0.11	0.0121
C_1	81.8	6.46	+0.11	0.0121	66.8	6.70	+0.11	0.0121
D_1	82.1	6.44	+0.09	0.0081	87.9	6.34	−0.25	0.0625
E_1	85.1	6.39	+0.04	0.0016	72.3	6.62	+0.03	0.0009
F_1	100.1	6.13	−0.22	0.0484	58.2	6.68	+0.27	0.0729
G_1	78.6	6.50	+0.15	0.0225	59.9	6.82	+0.23	0.0529
H_1	93.4	6.24	−0.11	0.0121	60.4	6.81	+0.22	0.0484
I_1	71.0	6.63	+0.28	0.0784	59.4	6.83	+0.24	0.0576
Σ		57.12				59.35		
Mean		6.35				6.59		
σ		0.1680				0.2999		

Table XI.

Results obtained on Air-dried Soil in the Laboratory.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
A_1	135.2	5.53	−0.43	0.1849	110.8	5.94	−0.36	0.1296
B_1	105.5	6.04	+0.08	0.0064	99.7	6.14	−0.16	0.0256
C_1	105.4	6.04	+0.08	0.0064	96.9	6.18	−0.12	0.0144
D_1	109.1	5.98	+0.02	0.0004	96.0	6.20	−0.10	0.0100
E_1	105.6	6.04	+0.08	0.0064	87.4	6.35	+0.05	0.0025
F_1	121.2	5.77	−0.19	0.0361	81.5	6.45	+0.15	0.0225
G_1	98.6	6.16	+0.20	0.0400	73.9	6.58	+0.28	0.0784
H_1	117.4	5.83	−0.13	0.0169	79.5	6.47	+0.19	0.0361
I_1	95.1	6.22	+0.29	0.0676	75.3	6.39	+0.09	0.0081
Σ		53.61				56.72		
Mean		5.96				6.30		
σ		0.2014				0.1907		

Table XII. (Section A.)

Results obtained on Fresh Soil in the Laboratory.

No.	Spot X				Spot R			
	E (m.v.)	P_H	D	D^2	E (m.v.)	P_H	D	D^2
A_1	97.1	6.18	+0.28	0.0784	115.5	5.86	−0.36	0.1296
A_2	127.6	5.66	−0.34	0.1156	98.5	6.16	−0.06	0.0036
A_3	95.3	6.22	+0.32	0.1024	88.8	6.33	+0.11	0.0121
A_4	109.2	5.98	+0.08	0.0064	104.0	6.06	−0.16	0.0256
A_5	94.6	6.23	+0.33	0.1089	79.6	6.49	+0.27	0.0729
A_6	103.3	6.08	+0.18	0.0324	90.0	6.31	+0.09	0.0081
A_7	109.9	5.96	+0.06	0.0036	95.8	6.21	−0.01	0.0001
A_8	105.4	6.04	+0.14	0.0196	88.4	6.33	+0.11	0.0121
A_9	106.5	6.02	+0.12	0.0144	62.2	6.79	+0.57	0.3249
A_{10}	116.9	5.84	−0.06	0.0036	98.9	6.15	−0.07	0.0049
A_{11}	123.6	5.72	−0.18	0.0324	77.9	6.51	+0.29	0.0841
A_{12}	101.9	6.10	+0.20	0.0400	105.9	6.03	−0.19	0.0361
A_{13}	114.0	5.89	−0.01	0.0001	87.6	6.35	+0.13	0.0169
A_{14}	109.7	5.97	+0.07	0.0049	83.5	6.42	+0.20	0.0400
A_{15}	115.2	5.87	−0.03	0.0009	90.4	6.30	+0.08	0.0064
A_{16}	110.0	5.96	+0.06	0.0036	96.2	6.20	−0.02	0.0004
A_{17}	129.4	5.62	−0.28	0.0784	107.4	6.00	−0.22	0.0484
A_{18}	136.5	5.50	−0.40	0.1600	126.9	5.67	−0.55	0.3025
A_{19}	130.0	5.61	−0.29	0.0841	99.1	6.15	−0.07	0.0049
A_{20}	132.0	5.58	−0.32	0.1024	107.3	6.01	−0.21	0.0441
Σ		118.03				124.33		
Mean		5.90				6.22		
σ		0.2227				0.2094		

Table XIII. (Section A.)

Results obtained on Air-dried Soil in the Laboratory.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
A_1	135.2	5.53	−0.25	0.0625	110.8	5.94	−0.10	0.0100
A_2	610.6	6.02	+0.24	0.0576	103.6	6.07	+0.03	0.0009
A_3	96.6	6.19	+0.41	0.1681	84.6	6.40	+0.36	0.1296
A_4	116.6	5.85	+0.07	0.0049	107.2	6.01	−0.03	0.0009
A_5	100.0	6.13	+0.35	0.1225	89.7	6.31	+0.27	0.0729
A_6	119.0	5.80	+0.02	0.0004	104.4	6.06	+0.02	0.0004
A_7	110.1	5.96	+0.18	0.0324	108.7	5.98	−0.06	0.0036
A_8	116.5	5.85	+0.07	0.0049	89.6	6.31	+0.27	0.0729
A_9	119.5	5.79	+0.01	0.0001	76.8	6.53	+0.49	0.2401
A_{10}	120.4	5.78	0.00	0.0000	116.8	5.84	−0.20	0.0400
A_{11}	130.9	5.61	−0.17	0.0289	91.2	6.29	+0.25	0.0625
A_{12}	110.4	5.95	+0.17	0.0289	117.5	5.83	−0.21	0.0441
A_{13}	126.0	5.68	−0.10	0.0100	95.1	6.22	+0.18	0.0324
A_{14}	116.1	5.86	+0.08	0.0064	100.0	6.13	+0.09	0.0081
A_{15}	117.6	5.83	+0.05	0.0025	112.4	5.92	−0.12	0.0144
A_{16}	120.8	5.77	−0.01	0.0001	106.6	6.02	−0.02	0.0004
A_{17}	127.1	5.67	−0.11	0.0121	124.5	5.71	−0.33	0.1089
A_{18}	133.1	5.56	−0.22	0.0484	131.0	5.61	−0.43	0.1849
A_{19}	138.4	5.47	−0.31	0.0961	118.2	5.82	−0.22	0.0484
A_{20}	145.5	5.34	−0.44	0.1936	122.6	5.74	−0.30	0.0900
Σ		115.64				120.74		
Mean		5.78				6.04		
σ		0.2098				0.2414		

For the sake of comparison, E, p_H, D and D^2 values obtained under the natural condition for the sections A., B., C., D., E., F., G., H. and I., are given collectively in Table XIV.

Table XIV. (Section A_1—I_1)

Results obtained under Natural Conditions in the Field.

No.	Spot X				Spot R			
	E (m.v.)	P_H	D	D^2	E (m.v.)	P_H	D	D^2
A_1	119.3	5.80	−0.01	0.0001	115.8	5.86	−0.17	0.0289
B_1	123.9	5.72	−0.09	0.0081	115.8	5.86	−0.17	0.0289
C_1	130.4	5.61	−0.20	0.0400	110.2	5.96	−0.07	0.0049
D_1	105.7	6.03	+0.22	0.0484	91.6	6.28	+0.25	0.0625
E_1	105.7	6.03	+0.22	0.0484	103.7	6.06	+0.03	0.0009
F_1	112.8	5.91	+0.10	0.0100	82.6	6.43	+0.04	0.1600
G_1	128.9	5.63	−0.18	0.0324	112.8	5.91	−0.12	0.0144
H_1	119.8	5.79	−0.02	0.0004	98.7	6.15	+0.12	0.0144
I_1	122.9	5.73	−0.08	0.0064	123.9	5.72	−0.31	0.0961
Σ		52.25				54.23		
Mean		5.81				6.03		
σ		0.1469				0.2137		

From the foregoing results, it is evident that the P_H values among the spots and sections vary when determined in the laboratory as noted under the natural condition. The maximum deviation and the standard deviation for different method, given in the preceding tables (Table I—XIII inclusive) are presented collectively in Table XV.

Table XV.

Maximum Deviations and the Standard Deviations.

		Section A			Section A_1-I_1		
		Methods.			Methods.		
		Natural.	Fresh.	Air-dried.	Natural.	Fresh.	Air-dried.
Maximum deviations.	Spot X	0.48	0.40	0.44	0.22	0.28	0.43
	Spot R	0.50	0.57	0.49	0.40	0.70	0.36
Standard deviations.	Spot X	0.19	0.22	0.21	0.15	0.17	0.20
	Spot R	0.23	0.21	0.24	0.21	0.30	0.19

Table XV indicates that no marked difference was noted among these different methods. But it is clearly shown that the concentration of hydrogen ions is less in R spot or a spot next to the stub.

3.) *Comparison of the results obtained by three different methods:* The results obtained by three different methods for the sections A_1–20 and A_1–I inclusive, are given in Tables XVI and XVII, in regard to P_H.

Table XVI.

Comparison of Results obtained by three Different Methods.

No.	Spot X			Spot R		
	Methods.			Methods.		
	Natural.	Fresh.	Air-dried.	Natural.	Fresh.	Air-dried.
	(P_H)	(P_H)	(P_H)	(P_H)	(P_H)	(P_H)
1	5.80	6.18	5.53	5.86	5.86	5.94
2	5.34	5.66	6.02	6.51	6.16	6.07
3	5.61	6.22	6.19	6.06	6.33	6.40
4	5.40	5.98	5.85	5.64	6.06	6.01
5	5.57	6.23	6.13	5.79	6.49	6.31
6	5.61	6.08	5.80	5.94	6.31	6.06
7	5.63	5.96	5.96	6.18	6.21	5.98
8	6.01	6.04	5.85	6.28	6.33	6.31
9	5.61	6.02	5.79	6.03	6.79	6.53
10	5.75	5.84	5.78	5.91	6.15	5.84
11	5.46	5.72	5.61	6.18	6.51	6.29
12	5.39	6.10	5.95	6.22	6.03	5.83
13	5.51	5.89	5.68	5.93	6.35	6.22
14	5.38	5.97	5.86	6.45	6.42	6.13
15	5.44	5.87	5.83	6.10	6.30	5.92
16	5.18	5.96	5.77	5.72	6.20	6.02
17	5.47	5.62	5.67	5.94	6.00	5.71
18	5.70	5.50	5.56	5.80	5.67	5.61
19	5.27	5.61	5.47	5.82	6.15	5.82
20	5.46	5.58	5.34	5.79	6.01	5.74
Σ	110.59	118.03	115.64	120.15	124.33	120.74
Mean	5.53	5.90	5.78	6.01	6.22	6.04

Table XVII.

Comparisons of Results obtained by three Different Methods.

No.	Spot X			Spot R		
	Methods.			Methods.		
	Natural.	Fresh.	Air-dried.	Natural.	Fresh.	Air-dried.
	(P_H)	(P_H)	(P_H)	(P_H)	(P_H)	(P_H)
A_1	5.80	6.20	5.53	5.86	5.89	5.94
B_1	5.72	6.13	6.04	5.86	6.48	6.14
C_1	5.61	6.46	6.04	5.96	6.70	6.18
D_1	6.03	6.44	5.98	6.28	6.34	6.20
E_1	6.03	6.39	6.04	6.06	6.62	6.35
F_1	5.91	6.13	5.77	6.43	6.86	6.45
G_1	5.83	6.50	6.16	5.91	6.82	6.58
H_1	5.79	6.24	5.83	6.15	6.81	6.49
I_1	5.73	6.63	6.22	5.72	6.83	6.39
Σ	52.25	57.12	53.61	54.23	59.35	56.42
Mean	5.81	6.35	5.96	6.03	6.59	6.30

As noted in these tables, the P_H values are smallest in all the cases than by two other methods, followed by the air-dried and the fresh soils showed the largest P_H values. However no definite difference in the results was found between the natural and other two methods which may be due to a fact that the soil samples were not exactly the same although came from very close spots. On the other hand, a similar tendency was found between the latter two methods, the air-dried soils showing less P_H as reported by Rost[5]. As to the causes of difference among the results obtained by three methods, several factors may be considered. But an addition of distilled water to the soil in the former methods may be the most important factor. Baver[6], Clark[7] and Perkins[8] reported that the soil-water ratio influence the P_H value, viz. less water gives less P_H. Consequently in this case, the dilution by adding distilled water might have brought the larger P_H values in the last two methods.

4.) *Variation of pH within 2 sq. m. of soil:* Further it was tested under the natural condition within a 2 sq. m. soil by determining at 9 spots, as shown in Figure IV, and the results are given in Table XVIII and XIX.

Figure IV.

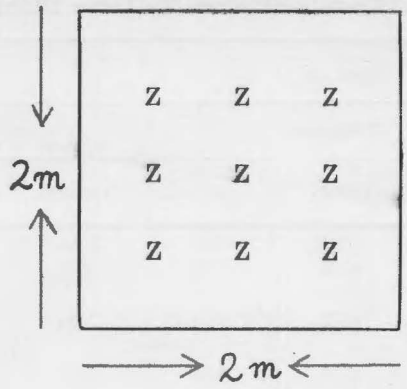


Table XVIII.

Results obtained within Two Square Meters under Natural Condition.

No.	Spot X				Spot R			
	E (m.v.)	p_H	D	D^2	E (m.v.)	p_H	D	D^2
1	143.6	5.38	−0.09	0.0081	99.1	6.15	+0.42	0.1766
2	140.9	5.42	−0.05	0.0025	124.7	5.70	−0.03	0.0009
3	118.6	5.81	+0.34	0.1156	155.1	5.18	−0.55	0.3025
4	140.5	5.43	−0.04	0.0016	147.6	5.31	−0.42	0.1766
5	140.9	5.42	−0.05	0.0025	106.5	6.02	+0.29	0.0841
6	124.7	5.70	+0.23	0.0529	120.7	5.77	+0.04	0.0016
7	140.5	5.43	−0.04	0.0016	92.0	6.27	+0.54	0.2916
8	140.9	5.42	−0.05	0.0025	136.9	5.49	−0.24	0.0576
9	151.1	5.25	−0.22	0.0484	124.7	5.71	−0.02	0.0004
Σ		49.26				51.60		
Mean		5.47				5.73		
σ		0.1618				0.3483		

Table XIX.

Results obtained within Two Square Meters by three Different Methods compared.

	Spot X			Spot R		
E (m.v.)	140.9	128.1	143.4	106.5	97.4	111.6
P_H	5.42	5.65	5.38	6.02	6.18	5.93

The results given in Table XVIII and XIX indicate that, as shown in the preceding experiments, the variation of P_H values was found in the soils close-by each other, 0.5 m. distance in this case.

Among the results obtained by different methods, no marked difference was noted.

Summary.

The concentration of hydrogen ions in the soil of paddy-field after the rice crop was harvested, was determined under the natural condition by using ITANO's modified, portable potentiometer in combination with quinhydrone electrode recommended by VERWELL, and the results were compared with those two methods, namely 1. the fresh soil; 2. the air-dried soil, formerly employed in the laboratory.

The results may be summarized as follows:

1.) The present method gave less P_H values, viz.: 0.21—0.56 less P_H against the fresh soil and 0.03—0.27, against the air-dried soil measured in the laboratory.

2.) The P_H values of the soils away from the rice plant stubs, were less than those next to the stubs, which means that the soils around the stubs were less acidic in all the cases examined.

3.) The special merits of the present method are noted below:

(a.) Under the natural field conditions, P_H of soil can be determined easily and quickly.

(b.) By carrying around only the electrode portion, the determinations can be made at any spots within the length of wire attached, viz.: 100 m. in this case.

(c.) P_H value at the root or under any other conditions such as the soil profile can conveniently be determined.

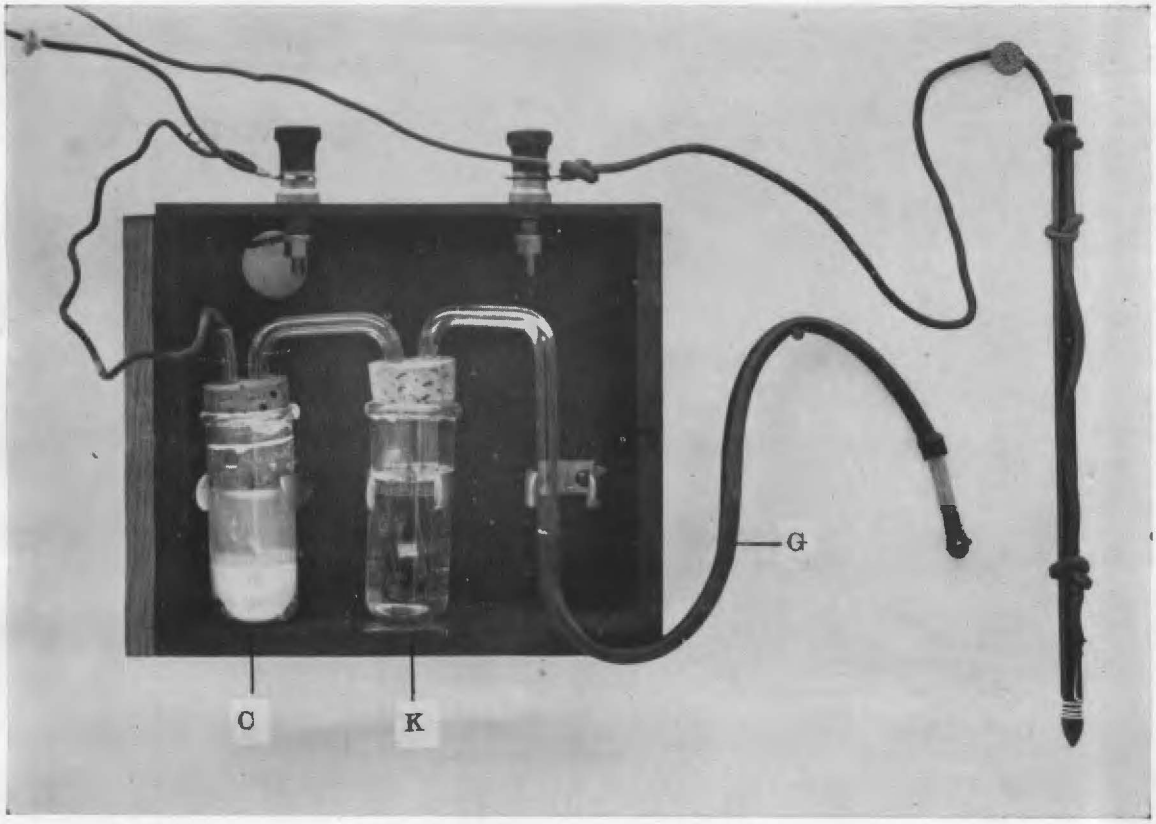
(d.) The method can be used for other purposes besides the soil.

Literature.

1.) ITANO, A., Berichte d. Ōhara Inst. f. landw. Forschungen, IV: 19—26, 1929.
2.) ————, Ibid, IV: 472—474, 1930.
3.) ITANO, A. and ARAKAWA, S., Berichte d. Ōhara Inst. etc., III: 331—332, 1927.
4.) VERWELL, H. J., Soil Research, IV: 67, 1934.
5.) ROST, C. O. and FIEGER, E. A., Soil Science, XVI: 121, 1923.
6.) BAVER, L. D., Soil Science, XXI: 167, 1926.
7.) CLARK, N. A. and COLLINS, E. R., Soil Science, XXIV: 453, 1927.
8.) PERKINS, A. T. and KING, H. H., Soil Science, XXXII: 1, 1931.

PLATE XXXIII.

Electrode Box.

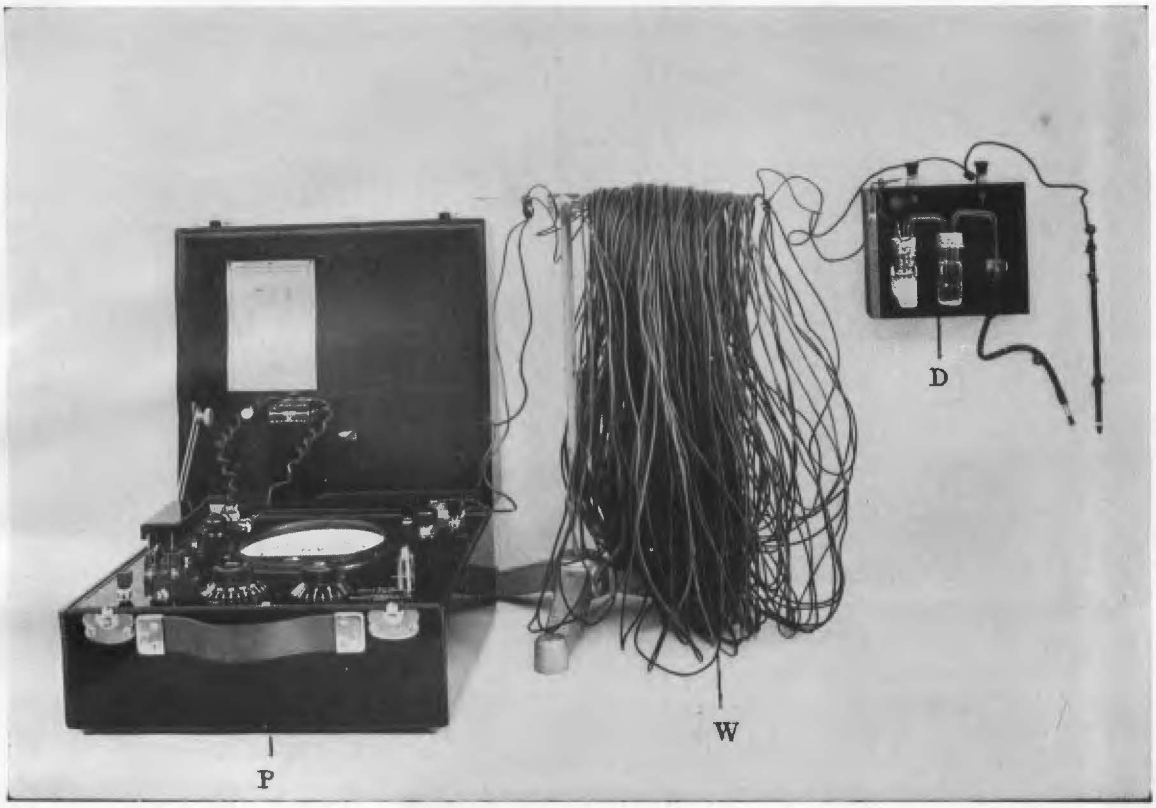


Explanation of Plate XXXIII : (Electrode box.)

C = saturated calomel electrode, K = a vessel with saturated KCl solution; G = a rubber tube with glass tube at the end which is plugged with a boiled cork; E = platinum electrode; P_1 & P_2 = posts which are connected to the potentiometer.

PLATE XXXIV.

Complete Outfit.



Explanations of Plate XXXIV: (Complete outfit.)

P = ITANO's portable potentiometer; W = double covered, compound copper wire of 100 meters long; D = electrode box.