Investigation on the Biilmann's Quinhydrone Electrode. III.

(Further studies on the electrode and agar bridge.)

By

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Introduction:

In our previous publications, the description of the quinhydrone method[1] and the table for calculations of the electromotive force into the PH values[2] were published. In this paper, the results of the following investigations are reported:

1. To test the efficiency of the method in determination of PH and titration of different solution by using various arrangements.
2. On the uses of agar bridge and its study under different working conditions and treatment.

Experimental.

Experiment I. Determination of PH of the following six different solutions were carried out with different chain, and compared with the H_2-electrode as noted in the table:

Solution A. CLARK's buffer solution.[3]
„ B. Soil solution.[4]
„ C. Soil Filtrate.[5]
„ D. Nutrient broth.[6]
„ E. Medium for the cellulose fermenter.[7]
„ F. ASHBY's solution.[8]

1) ITANO, A. and K. HOSODA, J. Agr. Chem. Soc. of Japan, II, 2, 13, 1926.
2) Ibid III, 3, 23, 1926.
3) CLARK, M., The determination of Hydrogen Ions, 1923, 106.
4) Prepared by ISCHEREKOV's method: F. N. Parker, Soil Science XII, 214, 1926; described in detail later.
5) See p. 340 for the preparation.
6) The standard broth (Fred, Soil Bacteriology, 89, 1916).
7) Viljoen etc., J. Agr. Science XVI, part 1, 3, 1926.
8) ASHBY, S. F., ibid II, 35, 1907.

These solutions were chosen since they are used frequently in our laboratory, and may be of interest to those who are engaged in the similar work.

The determinations were carried out by the H_2-electrode and the quinhydrone electrode against the calomel and quinhydrone standard electrode. The results are given in the following table:

Table I.

Determination of PH in different Solutions.

Solutions	PH determined by		
	H_2-electrode*	Q−C+	Q−Qs++
A.	3.96	3.96	4.00
B.	6.71	7.01	7.04
C.	6.29	6.45	6.43
D.	7.55	7.22	7.19
E.	6.96	6.70	6.71
F.	7.85	7.64	7.70

Table I. indicates that the quinhydrone electrode gives slightly lower PH except in B and C. However the quinhydrone electrode may be used satifactorily in all these solutions for general purpose.

Experiment II. Titration of the Solutions used in Experiment I.

The titration was carried out in those solutions which were used in Experiment I to ascertain the efficiency of the electrode as well as the buffer property of these solutions.

Solution A. Buffer Solution.

50 cc. of the buffer solution was taken and titrated with N/10 NaOH. The results are given in Table II. and Graph I.

Table II.

Titration of the Buffer Solution. 12°C.

cc. N/10 NaOH	Q−Ci		Q−Qs ii	
	π	PH	π	PH
0.	0.1355	3.96	0.1106	4.00
3.	0.1162	4.30	0.1296	4.33
6.	0.1014	4.54	0.1450	4.59
9.	0.0895	4.78	0.1564	4.81
12.	0.0757	5.02	0.1701	5.04
15.	0.0585	5.33	0.1871	5.33
18.	0.0330	5.76	0.2119	5.78
21.	−0.1174	8.43	0.3637	8.45

* Hydrogen gas electrode against the calomel electrode. (See Figure II.)

\+ Quinhydrone against the calomel standard electrode. (See Figure III.)

++ " " " quinhydrone " " " " " "

i & ii For an arrangement of apparatus, see Figure V. The arrangement shown in Figure IV is used when the titration is carried out by H_2-electrode.

Graph I.

Titration of the Buffer Solution.

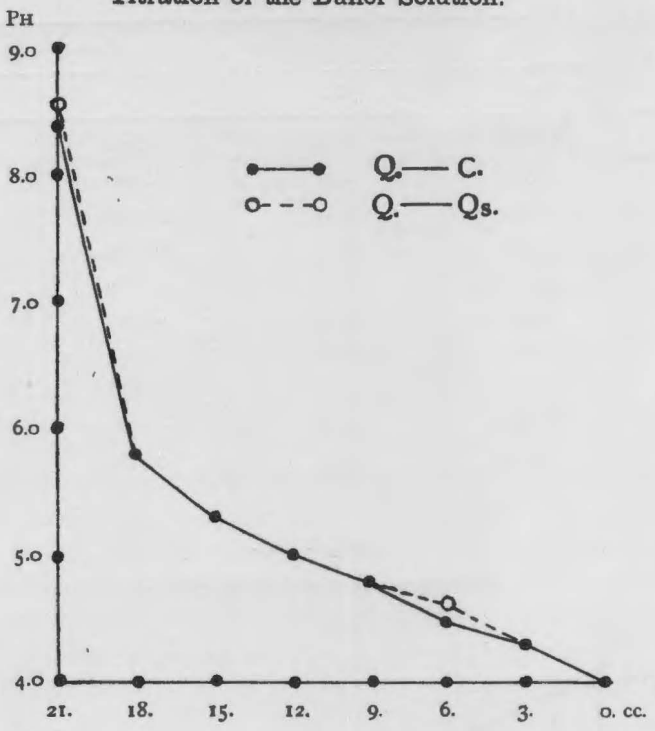


Table II. and Graph I. indicate that the buffer solution has the strong buffer action as expected. After each addition of the alkali, an equilibrium was established very quickly and the electrode responded accurately. So far as the chains are concerned, they gave very close results.

Solution B. Soil Solution.

As it was indicated previously, this solution was prepared according to ISCHEREKOV's method: 500 grams of the air dried soil from our experimental plot (rice-field) was packed in a glass tube of which diameter is about one and one half inch. The soil was saturated with the distilled water for about twelve hours. The water holding capacity of the soil was found to be 20%. After the saturation, the water was displaced by means of the absolute alcohol. About 80 cc. of the solution was obtained by this process in ten hours, and 50 cc. of it was taken in our experiment.

The solution thus prepared was found to be PH 7.01. First enough N/10 NaOH was added to bring the PH to 8.55 and then N/100 HCl was added one cc. at a time. The results are given in Table III. and Graph II.

Table III.

Titration of the Soil Solution. 14°C.

cc. N/100 HCl	Q - C		Q - Qs	
	π	PH	π	PH
0.	−0.1258	8.55	0.3700	8.54
1.	−0.1123	8.33	0.3580	8.33
2.	−0.0949	8.01	0.3370	7.96
3.	−0.0578	7.37	0.3014	7.34
4.	−0.0228	6.75	0.2670	6.74
5.	0.0050	6.26	0.2400	6.25
6.	0.0350	5.73	0.2073	5.68
7.	0.0770	5.00	0.1676	4.97
8.	0.1173	4.29	0.1266	4.26
9.	0.1422	3.85	0.1010	3.79

Graph II.

Titration of the Soil Solution.

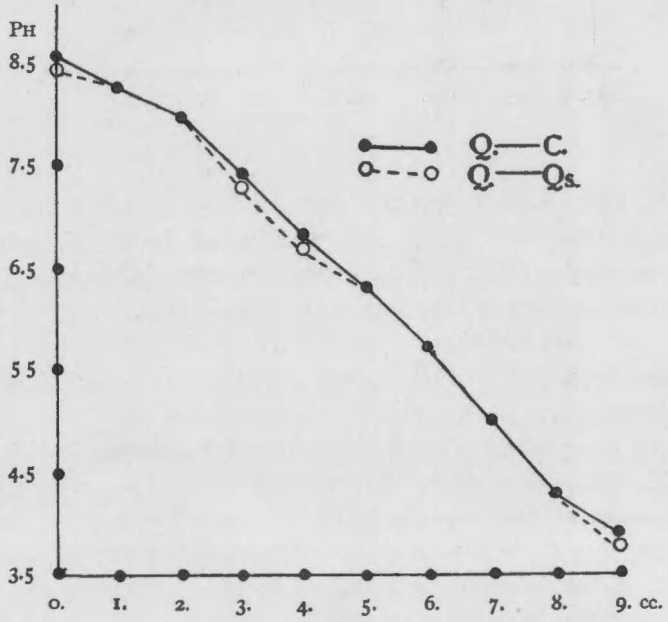


Table III. and Graph II. indicate that the electrode in both of these chains gave very close readings, and very little buffer action exist in the solution.

Solution C. Soil Filtrate.

50 gm. of the air dried soil, the same soil which was used for preparation of the soil solution, was mixed with 250 cc. of the distilled water and let the

mixture stand over night, and filtered through the filter paper. The filtrate thus prepared was found to be PH 6.45. Previous to the titration, the PH was made to 8.29 by adding N/20 NaOH, and was titrated with N/100 HCl by adding one cc. at a time. The results are shown in Table IV. and Graph III.

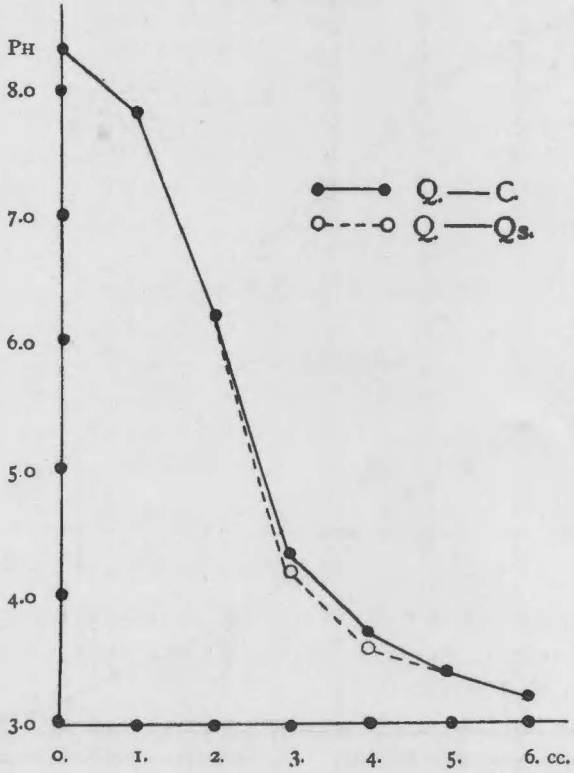
Table IV.

Titration of the Soil Suspension. 14°C.

cc. N/100 HCl	Q—C		Q - Qs	
	π	PH	π	PH
0.	—0.1110	8.29	0.3550	8.26
1.	—0.0803	7.75	0.3278	7.78
2.	0.0087	6.19	0.2340	6.15
3.	0.1180	4.29	0.1250	4.23
4.	0.1528	3.68	0.0905	3.63
5.	0.1681	3.40	0.0757	3.37
6.	0.1778	3.23	0.0667	3.20

Graph III.

Titration of the Soil.



It is interesting to note that a marked buffer action was observed from PH 4.3 and lower. This may be due to the presence of colloidal matter in the filtrate, thus prepared, more than in the solution which was used in the preceding experiment.

Solution D. Nutrient Broth.

The standard nutrient broth was used. The PH value of the broth was 7.22, and the reaction was adjusted to PH 8.39 with N/10 NaOH previous to the titration with N/50 HCl of which results are given in Table V. and Graph IV.

Table V.

Titration of the Nutrient Broth. 14°C.

cc. N/50 HCl	Q−C		Q−Qs	
	π	PH	π	PH
0.	−0.1160	8.39	0.3600	8.37
2.	−0.0808	7.77	0.3250	7.76
4.	−0.0514	7.25	0.2971	7.26
6.	−0.0300	6.87	0.2750	6.88
8.	−0.0122	6.56	0.2565	6.55
10.	0.0115	6.14	0.2330	6.13
12.	0.0385	5.67	0.2065	5.66
14.	0.0630	5.24	0.1815	5.23
16.	0.0828	4.89	0.1618	4.88
18.	0.0990	4.62	0.1451	4.59
20.	0.1135	4.32	0.1308	4.34
22.	0.1265	4.13	0.1170	4.10
24.	0.1378	3.92	0.1065	3.91

Graph IV.

Titration of the Nutrient Broth.

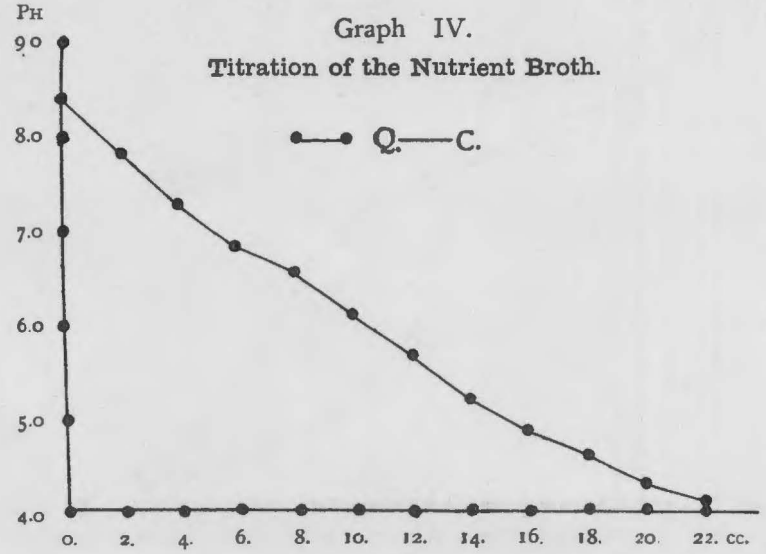


Table V. and Graph IV. indicate the presence of buffer action as it is naturally expected from the nature of the solution

Solution E. Medium for the Cellulose Fermenter.

The pH of this solution was 6.70, and N/10 HCl was added to bring it to PH 3.08 and was titrated with N/20 NaOH. The results are shown in Table VI. and Graph V.

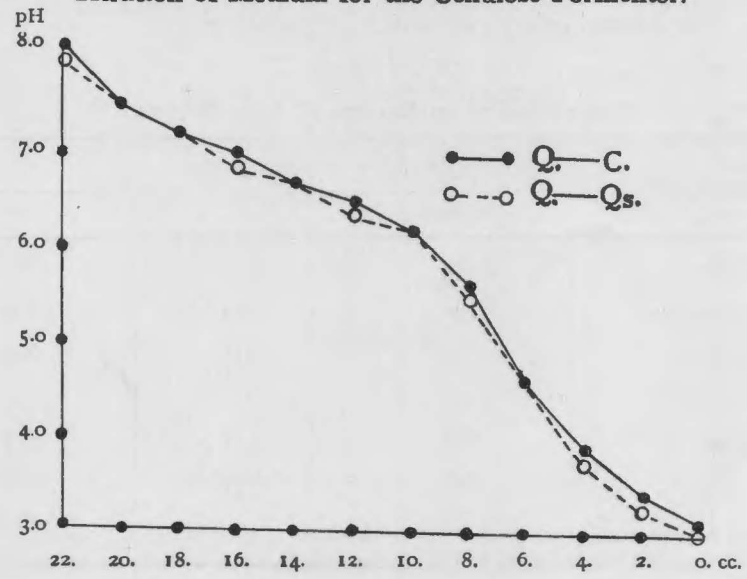
Table VI.

Titration of Medium for the Cellulose Fermenter. 14°C.

cc. N/20 NaOH	Q - C		Q - Qs	
	π	PH	π	PH
0.	0.1884	3.08	0.0560	3 08
2.	0.1704	3.37	0.0736	3.32
4.	0.1416	3.87	0.1024	3.84
6.	0.1005	4.62	0.1431	4.55
8.	0.0440	5.57	0.2000	5.54
10.	0.0082	6.21	0.2384	6.21
12.	−0.0065	6.47	0.2500	6.43
14.	−0.0210	6.71	0.2650	6.69
16.	−0.0348	6.96	0.2786	6.93
18.	−0.0490	7.22	0.2927	7.17
20.	−0.0663	7.51	0.3091	7.47
22.	−0.0980	8.07	0.3425	8.04

Graph V.

Titration of Medium for the Cellulose Fermenter.



The marked buffer action is noted, which is due to the presence of such salts as phosphates and calcium. There is a slight difference among the results obtained by two chains but it is so small that practically no significance.

Solution F. Ashby solution.

The determination of pH in Ashby solution was carried out by various chain to see if the presence of $CaCO_3$ in excess has any influence on the results.

Table VII.

Determination of PH in Ashby Solution.

Ashby solution \ Chain	H_2-C	$Q-C$	H_2-Qs	$Q-Qs$
Filtrate.	7.85	7.64	7.89	7.70
$CaCO_3$	7.76	7.65	7.84	7.69

As the above results indicate, the various chain, in both cases, with or without $CaCO_3$ makes little difference.

Experiment III. Investigation on the Use of Agar Bridge.

This experiment was carried out in two parts, as described below:

Part I. To test the efficiency of the agar bridge in connection with the determination of hydrogen ion concentration of the soil in suspension and the filtrate: the agar bridge was prepared according to MICHAELIS[1] in two shape, as illustrated in Fig. I. A and B. The bridge B was used by placing the solid potassium chloride in a arm-cup (c). The soil sample was prepared by taking 100 gm. of the rice-field soil and 200 cc. of distilled water, shaken for half an hour. A portion of the suspension was filtered and the remainder was used without. The determination was carried out as follows:

Table VIII.

Investigation on the use of Agar Bridge.

Materials.	Agar Bridge		
	Without	A	B
Filtrate:			
H_2-C	6.12	6.24	6.04
$Q-C$	6.19	6.21	6.16
Suspension:			
H_2-C	6.14	6.27	5.71
$Q-C$	6.00	6.00	5.66

1) MICHAELIS, L., Praktikum der Physikalischen Chemie, 1922, 161.

As the table indicates, with the filtrate both chains with or without any one of the bridge gave very close results. However with the suspension, a chain (Q−C) gave higher concentration especially with the bridge B. The diffusion of solid KCl in the bridge seems to cause the difference. PIERRE[1] stated that the use of a new bridge, in the soil work, gives the higher hydrogen ion concentration which is due to a slight diffusion of KCl from the ends of the agar bridge. To eliminate this error, he recommends the soaking of the newly prepared agar bridge for one hour in conductivity water before the use, and to keep it in contact with the soil suspension only while the successive readings are taken. The results obtained in our experiment with the bridge B confirms his statement.

Part II. To test the effect of agar bridge on the determination of hydrogen ion concentration under various conditions.

The bridge is inserted as shown in Fig. VI. in the chain A. and B. as follows:

Chain A.

Hg·HgCl	N/10 KCl	Sat. KCl	Bridge	Unknown solution + Quinhydrone	Pt (blank)

Chain B.

Pt (blank)	Quinhydrone HCl 0.01 N KCl 0.09 N	Sat. KCl	Bridge	Unknown solution + Quinhydrone	Pt (blank)

The buffer solution (Clark), PH 5.84 was used for the determination with different chain as noted in the table:

Table IX.

Determination of Hydrogen Ion Concentration with the Bridge.

Method	PH determined
H_2-eletrode	5.84
Chain A.	5.84
„ „ , without bridge	5.93
Chain B.	5.84
„ „ , without bridge	5.93

Table IX. indicates that with or without insertion of the bridge makes very little difference, if the diffusion is eliminated.

Next the bridge was subjected to the different treatments as follows:

1. The bridge was kept in the quinhydrone mixture for 30 minutes.
2. ibid for 2 hours.
3. ibid for 4 hours.

1) PIERRE, W. H., Soil science, 20, 1925, 287.

4. The bridge was soaked in the distilled water for 2 hours.
5. ibid in the saturated KCl for 2 hours.

Table X.

The Agar Bridge and various Treatment.

Chains	Treatments	PH Determined
A.	1.	5.84
„	2	5.89
„	3.	5.88
„	4.	5.91
„	5.	5.88
B.	1.	5.86
„	2.	5.92
„	3.	5.90
„	4.	5.96
„	5.	5.92

Table X. indicates that various treatments of the bridge do not effect the results appreciably, and an old bridge can be used repeatedly with due precautions such as thorough immersion of the bridge in distilled water and kept in the saturated KCl solution.

Summary and conclusion:

1. The quinhydrone electrode can be used satisfactorily for determination of the hydrogen ion concentration and also for the titration of all the solutions used in this investigation.

2. The electrode gives close results, with any chain as illustrated in this paper.

3. Various treatments given to the bridge, have practically no effect except a fresh bridge, and bridge B. with an addition of solid KCl.

4. The old agar bridge can be used repeatedly with due precautions.

5. The soil filtrate has a stronger buffer action than the soil solution.

6. A complex medium such as the cellulose medium used in our investigation has a strong buffer action, and the electrode does not suffer the presence of various salts.

7. The presence of a alkali salt viz. $CaCO_3$ dose not effect the results of determination by the quinhydrone electrode.

Fig. I.

Fig. II.

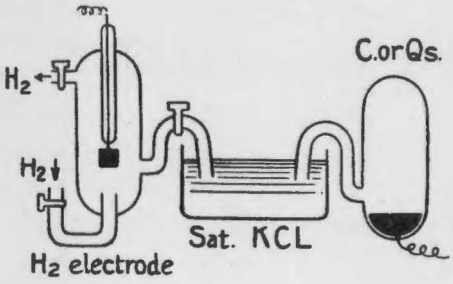


Fig. III.

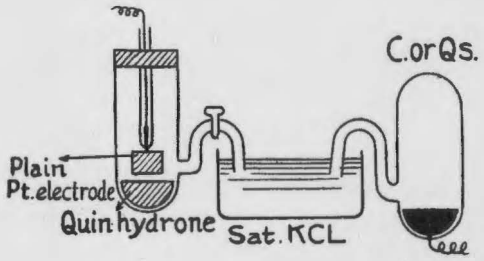


Fig. IV.

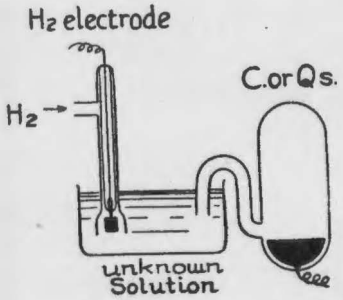


Fig. V.

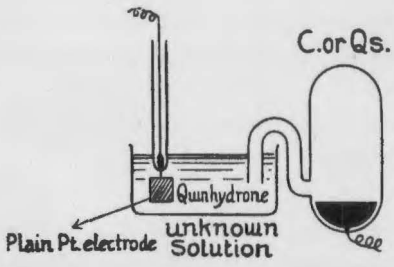


Fig. VI.