Investigation on Antimony Electrode for Determination of Hydrogen Ion Concentration.

II. Determination of the hydrogen ion concentration of soils.

By

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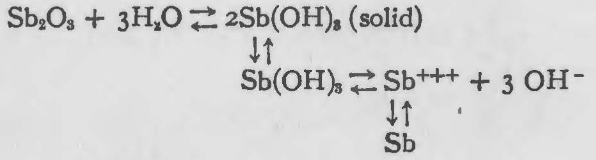
In the previous publication[1], the senior author published on the standardization of an antimony electrode in the buffer solutions and calculation of p_H value. This paper presents the results obtained in determination of the hydrogen ion concentration of the soils by using the antimony electrode together with some factors such as shaking, time of immersion and various treatment of soil samples.

Theoretical.

A brief theoretical consideration was given in the previous paper, and further discussion on the oxidation and reduction of the antimony electrode has been published by LAVA and HEMEDES[2] and will be noted below:

The oxidation-reduction reaction at the antimony electrode was formulated as follows;



$$\begin{array}{lll} Sb_2O_3 + 3H_2O \rightleftarrows & 2Sb(OH)_3 \text{ (solid)} & \\ & \quad\downarrow\uparrow & \\ & Sb(OH)_3 \rightleftarrows & Sb^{+++} + 3\,OH^- \\ & & \;\downarrow\uparrow \\ & & \;Sb \end{array}$$

The mass action equation for the ionization of the hydroxide is

$$\frac{(Sb^{+++})\,(OH)^3}{[Sb(OH)_3]} = K$$

Then, the potential at the oxidation-reduction electrode (Sb electrode) may be written as follows;

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[1] ITANO, A., Berichte des Ōhara Inst. etc., Band IV, Heft 2, 273, 1929.

[2] LAVA, V. G. and HEMEDES, E. D., The Philippine Agric., 17, 337, 1928.

$$E = E_1 - \frac{RT}{nF} \ \mathrm{In} \ \frac{(\mathrm{Red.})}{(\mathrm{Oxi.})} \qquad (1)$$

where

E = potential at the Sb electrode.

E_1 = constant, involving electronic concentration of metal and the equilibrium constant of the oxidation-reduction.

(Red.) and (Oxi.) = concentration of the reductant and oxidant.

R = gas constant in volt coulomb (8.3129).

T = absolute temperature (273.09 + 18).

n = valency of Sb or 3.

F = Faraday constant (96494).

In = natural logarithum.

Therefore, the potential at the Sb electrode may be written as follows:

$$E = E_1 - \frac{RT}{3F} \ \mathrm{In} \ \frac{(\mathrm{Sb})}{(\mathrm{Sb}^{+++})}$$

$$\text{or} \quad E = E_1 - \frac{RT}{3F} \ \mathrm{In} \ \frac{(\mathrm{Sb})\,(\mathrm{OH}^-)^3}{K[\mathrm{Sb(OH)}_3]} \qquad (2)$$

In which $Sb(OH)_3$ is very insoluble and it may be presumed that the amount of the Sb_2O_3 mixed with the metal is sufficient to keep the concentration of the hydroxide constant, and also the value of (Sb) may also be considered as constant.

Since $(OH^-) = \frac{10^{-14}}{(H^+)}$, the equation (2) may be written as

$$E = E_1 - \frac{RT}{3F} \ \mathrm{In} \ \frac{(\mathrm{Sb})\,(10^{-14})^3}{K[\mathrm{Sb(OH)}_3]\,(H^+)^3}$$

Gathering the constants,

$$E = E_0 - \frac{RT}{F} \ \mathrm{In}\,(H^+) \qquad (3)$$

or at 18°C, the value of $\frac{RT}{F}$ is 0.0577 and calculating for P_H,

$$P_H = \frac{E_0 - E}{0.0577} \qquad (4)$$

Since the potential at the Sb electrode is negative to calomel, equation (4) is equivalent to

$$P_H = \frac{E - E_0}{0.0577}$$

Which is the working formula for determination of P_H, by any other electrode. The value of 0.0577, in case of the antimony electrode is questioned from the experimental standpoint. Theoretically the said value is correct but experimentally 0.054[1] gives closer results to those obtained by the hydrogen electrode.

In our investigation, the following equations were used according to the chain emloyed:

$$p_H = \frac{E - 0.104}{0.054}, \text{ is used}$$

for Hg—HgCl | N/10 KCl | sat. KCl | agar bridge | Sb_2O_3, at 18°C

$$p_H = \frac{E - 0.017}{0.054}, \text{ is used}$$

for Hg—HgCl | sat. KCl | sat. KCl | agar bridge | Sb_2O_3, at 18°C

The results noted in this publication were calculated according to the p_H table, prepared by ITANO[2] after the value of E was obtained.

Experimental.

I. Arrangement of apparatus:

The antimony electrode was arranged as shown in Figure I, so that it can be used conveniently in conjunction with the portable p_H apparatus devised by ITANO[3].

(Figure I. s. P. 386.)

II. Procedure:

1. A sufficient amount of the sample is placed in the receptacle A and the electrode and an end of the agar bridge are immersed. Then, it is shaken by hand while the reading is taken and in other cases the shaking is eliminated.

2. The readings were taken until the constant value was obtained consecutively. On the average ten seconds to two minutes were sufficient to reach the equilibrium.

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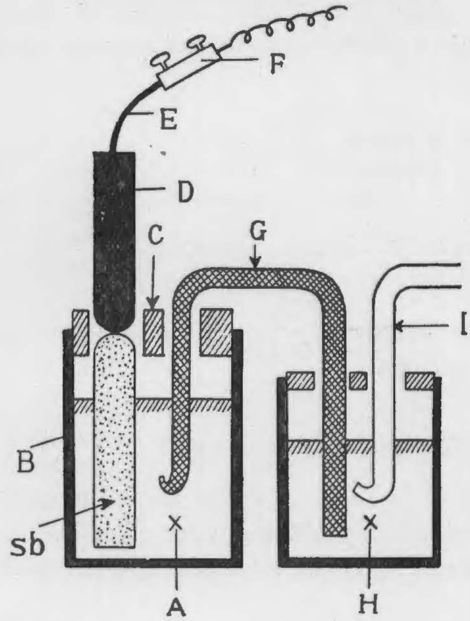
[1] FRANKE, K. W. and WILLAMAN, J. J., J. ind. Chem. 20, 88, 1928.; substantiated by others also.

[2] ITANO, A., Loc. cit. p. 199.

[3] 〃 〃 〃 〃 p. 19.

Fig. I.
Chain of Antimony Electrode.



A.	Sample.	F.	Terminal.
B.	Vessel.	G.	Agar bridge.
C.	Rubber stopper.	H.	Sat. KCl.
D.	Rubber tube.	I.	KCl-calomel electrode.
E.	Copper wire.	Sb.	Antimony electrode.

Experiment I.

The accuracy of antimony electrode was investigated further using the SÖRENSEN's buffer solutions (P_H 2.96—12.79). The results are shown in Table I.

Table I.
Comparison of Antimony and H_2-electrode in Buffer Solutions.

No. of experiment.	H_2-electrode.		Antimony.		diff. P_H
	π*	P_H	π	P_H	
1.	0.5093	2.96	0.2710	3.09	(—) 0.13
2.	0.5735	4.07	0.3234	4.06	(+) 0.01
3.	0.6013	4.55	0.3538	4.63	(—) 0.08
4.	0.6294	5.03	0.3701	4.93	(+) 0.10
5.	0.6512	5.42	0.3944	5.39	(+) 0.03
6.	0.6760	5.86	0.4141	5.74	(+) 0.12
7.	0.7144	6.52	0.4511	6.43	(+) 0.09

No. of experiment.	H_2-electrode.		Antimony.		diff. p_H
	π*	p_H	π	p_H	
8.	0.7359	6.90	0.4766	6.91	(−) 0.01
9.	0.7851	7.74	0.5196	7.70	(+) 0.04
10.	0.8704	9.21	0.5949	9.09	(+) 0.12
11.	0.9098	9.91	0.6293	9.72	(+) 0.19
12.	0.9543	10.63	0.6683	10.45	(+) 0.18
13.	1.0358	12.10	0.7498	11.96	(+) 0.14
14.	1.0760	12.79	0.7981	12.85	(−) 0.06

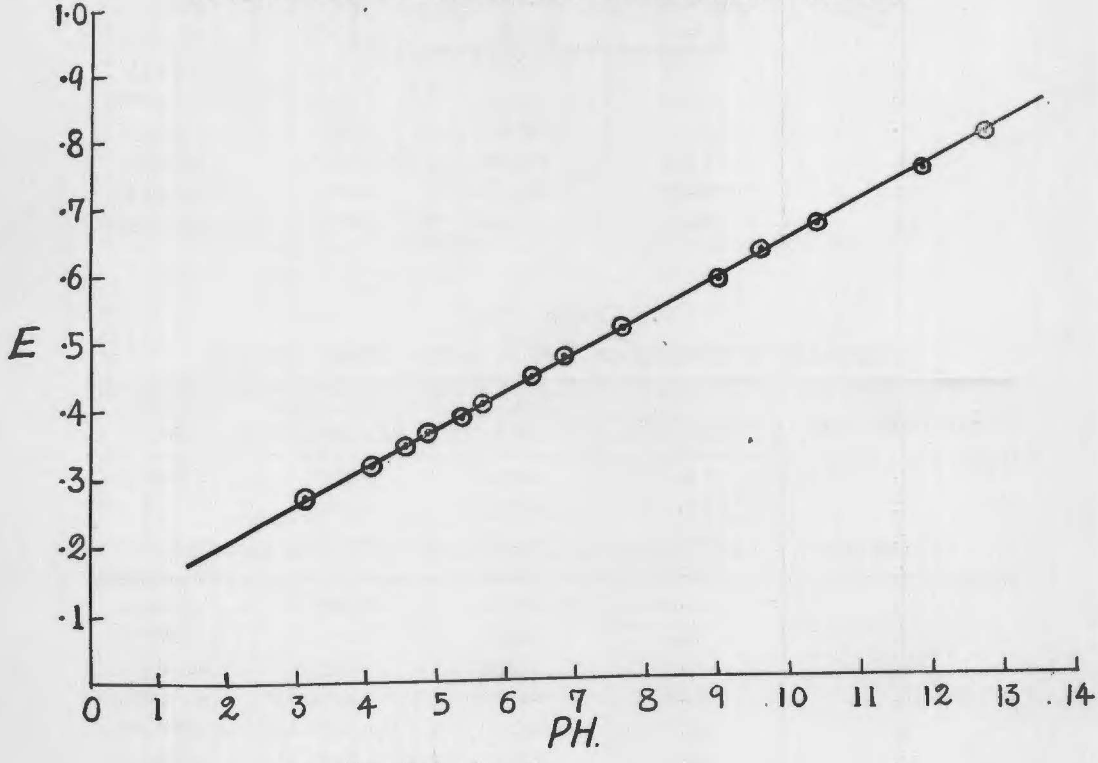
* Determined at 18°C., against N/10 KCl-calomel electrode.

Table I indicates that the antimony electrode gives a slightly smaller p_H value than the H_2 electrode.

The comparison of the theoretical and practical results is shown in Figure II.

Fig. II.

Comparison of Theoretical and Practical Results obtained.



— theoretical value.

⊙ practical value obtained by antimony electrode.

Figure II also indicates that the antimony electrode gives smaller p_H value.

Experiment II.

The significance of shaking on the readings was investigated in A.) buffer solution, B.) soil extract, and the results are given in Table II and III respectively:

Table II.

Influence of Shaking on E. M. F. in Sörensen's Buffer Solutions.

No. of experiment.	P_H of Buffer solution.	Shaken.	Without shaking.	Change of π
		π	π	
1.	2.96	0.2710	0.2893	(−) 0.0183
2.	4.07	0.3234	0.3281	(−) 0.0047
3.	4.55	0.3538	0.3591	(−) 0.0053
4.	5.03	0.3701	0.3702	(−) 0.0001
5.	5.42	0.3944	0.3967	(−) 0.0023
6.	5.86	0.4141	0.4136	(+) 0.0005
7.	6.52	0.4511	0.4488	(+) 0.0023
8.	6.90	0.4766	0.4603	(+) 0.0163
9.	7.74	0.5196	0.5145	(+) 0.0051
10.	9.21	0.5946	0.5851	(+) 0.0098
11.	9.91	0.6293	0.6212	(+) 0.0081
12.	10.63	0.6683	0.6620	(+) 0.0063
13.	12.10	0.7498	0.7616	(−) 0.0118
14.	12.79	0.7981	0.8240	(−) 0.0259

Table III.

Influence of Shaking on E. M. F. in Soil Water Extract.

No. of experiment.	No. of soils.	Shaken. (π)	Without shaking (π)	Change of π
1.	1.	0.4773	0.3702	(+) 0.0071
2.	8.	0.4121	0.3995	(+) 0.0126
3.	10.	0.4340	0.4361	(−) 0.0021
4.	13.	0.4594	0.4272	(+) 0.0322
5.	30.	0.4153	0.4178	(−) 0.0025
6.	34.	0.4632	0.4477	(+) 0.0155
7.	37.	0.4252	0.4253	(−) 0.0001
8.	42.	0.4224	0.4185	(+) 0.0039
9.	44.	0.4110	0.3987	(+) 0.0123
10.	46.	0.4072	0.3977	(+) 0.0095
11.	50.	0.4257	0.4231	(+) 0.0026
12.	52.	0.5087	0.5095	(−) 0.0008
13.	55.	0.4221	0.4166	(+) 0.0055
14.	60.	0.3989	0.4127	(−) 0.0138

Table II and III indicate that the shaking has influence on the readings and the influence varies according to the p_H value. That is toward either extreme, the difference was greater, and without shaking the higher value for E was obtained. Although HARRISON and his coworker¹⁾ claimed that the shaking did not make any difference, it was found differently in our experiment.

Experiment III.

The influence of duration of immersion of electrode was investigated. The readings were taken soon after the electrode was immersed and five minutes later in both the buffer solution and soil extract. The results are given in Table IV and V.

Table IV.

Influence of Time of Immersion of Electrode in Buffer Solutions.

No. of experiment.	p_H of solutions.	At once.		5 minutes after.		Change of E. M. F.	
		π	p_H	π	p_H	π	p_H
1.	2.96	0.2893	3.43	0.2900	3.44	(−) 0.0007	(−) 0.01
2.	4.07	0.3281	4.15	0.3328	4.24	(−) 0.0047	(−) 0.09
3.	4.55	0.3591	4.72	0.3611	4.76	(−) 0.0020	(−) 0.04
4.	5.03	0.3702	4.93	0.3664	4.85	(+) 0.0038	(+) 0.08
5.	5.42	0.3967	5.43	0.4027	5.54	(−) 0.0060	(−) 0.11
6.	5.86	0.4136	5.74	0.4110	5.69	(+) 0.0026	(+) 0.05
7.	6.52	0.4488	6.39	0.4476	6.37	(+) 0.0012	(+) 0.02
8.	6.90	0.4603	6.59	0.4662	6.70	(−) 0.0059	(−) 0.11
9.	7.74	0.5145	7.61	0.5085	7.50	(+) 0.0060	(−) 0.11
10.	9.21	0.5851	8.91	0.5845	8.91	(+) 0.0006	(±) 0.00
11.	9.91	0.6212	9.57	0.6209	9.57	(+) 0.0003	(±) 0.00
12.	10.63	0.6620	10.23	0.6657	10.41	(−) 0.0037	(−) 0.08
13.	12.10	0.7616	12.19	0.7675	12.30	(−) 0.0059	(−) 0.11
14.	12.79	0.8240	13.33	0.8340	23.52	(−) 0.0100	(−) 0.19

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1) HARRISON, W. H. and VRIDHACHALAM, P. N., Memoirs Dept. Agric. India, 10, 157, 1929.

Table V.

Influence of Time of Immersion of Electrode in Soil Paste.

No. of experiment.	No. of soils.	At once.		5 minutes after.		Change of E. M. F.	
		π	p_H	π	p_H	π	p_H
1.	1.	0.4633	6.65	0.4785	6.94	(−) 0.0152	(−) 0.29
2.	8.	0.3907	5.32	0.3947	5.39	(−) 0.0040	(−) 0.07
3.	10.	0.4380	6.19	0.4281	6.00	(+) 0.0099	(+) 0.19
4.	13.	0.4063	5.59	0.4063	5.59	(±) 0.0000	(±) 0.00
5.	30.	0.3447	4.46	0.3465	4.50	(−) 0.0018	(−) 0.04
6.	34.	0.4498	6.41	0.4526	6.46	(−) 0.0028	(−) 0.05
7.	37.	0.3975	5.44	0.3952	5.39	(+) 0.0023	(+) 0.05
8.	42.	0.4012	5.50	0.4012	5.50	(±) 0.0000	(±) 0.00
9.	44.	0.4067	5.61	0.4062	5.59	(+) 0.0005	(+) 0.02
10.	46.	0.3942	5.37	0.3936	5.37	(+) 0.0006	(±) 0.00
11.	50.	0.3973	5.43	0.3988	5.46	(−) 0.0015	(−) 0.03
12.	52.	0.5235	7.78	0.5308	7.91	(−) 0.0073	(−) 0.13
13.	55.	0.4046	5.57	0.4021	5.52	(+) 0.0025	(+) 0.05
14.	60.	0.3902	5.30	0.3895	5.30	(+) 0.0007	(±) 0.00
15.	67.	0.4221	5.89	0.4213	5.87	(+) 0.0008	(+) 0.02
16.	72.	0.4356	6.15	0.4361	6.15	(−) 0.0005	(±) 0.00
17.	91.	0.4070	5.61	0.4005	5.50	(+) 0.0065	(+) 0.11
18.	105.	0.3934	5.35	0.3894	5.28	(+) 0.0040	(+) 0.07
19.	111	0.3924	5.33	0.3872	5.24	(+) 0.0052	(+) 0.09
20.	125.	0.3967	5.43	0.3982	5.44	(−) 0.0015	(−) 0.01
21.	168.	0.3870	5.24	0.3903	5.30	(−) 0.0033	(−) 0.06
22.	200.	0.3858	5.22	0.3821	5.15	(+) 0.0037	(−) 0.07
23.	208.	0.3800	5.11	0.3814	5.13	(−) 0.0014	(−) 0.02
24.	212.	0.5161	7.63	0.5222	7.74	(−) 0.0061	(−) 0.11
25.	239.	0.3792	5.09	0.3774	5.06	(+) 0.0018	(+) 0.03

Table IV and V indicate that five minutes immersion did not make an appreciate difference in either case.

Experiment IV.

The comparative study of hydrogen, quinhydrone and antimony electrode was undertaken by using soil extract (1 part of soil to 5 parts of water) for hydrogen and antimony electrode and extract (1 : 1) for quinhydrone. The results are noted in Table VI.

Table VI.

Comparative Study of H_2, Quinhydrone and Antimony Electrode.

No. of expt.	No. of soils.	Nature of soils.	H_2	Q	Sb.	H_2-Sb.	Q.-Sb.
			p_H	p_H	p_H	p_H	p_H
1.	1.	clay loam.	7.02	6.97	6.94	(+) 0.08	(+) 0.03
2.	3.	sandy.	6.13	6.26	6.13	(±) 0.00	(+) 0.13
3.	8.	clay loam.	5.89	5.95	5.70	(+) 0.19	(+) 0.25
4.	10.	fine clay loam.	6.15	6.33	6.11	(+) 0.04	(+) 0.22
5.	11.	sandy loam.	6.33	6.47	6.20	(+) 0.13	(+) 0.27
6.	13.	fine loam.	6.69	6.32	6.57	(+) 0.12	(−) 0.25
7.	15.	fine clay loam.	6.67	6.40	6.30	(+) 0.37	(+) 0.10
8.	19.	sandy.	5.38	5.57	5.44	(−) 0.06	(+) 0.13
9.	20.	sandy.	5.88	5.99	5.82	(+) 0.06	(+) 0.17
10.	30.	red soil.	5.79	6.09	5.76	(+) 0.03	(+) 0.33
11.	31.	clay slate shale.	7.00	7.21	7.04	(−) 0.04	(+) 0.17
12.	32.	sand stone shale.	7.47	7.41	7.33	(+) 0.14	(+) 0.08
13.	34.	clay loam.	6.71	6.76	6.65	(−) 0.06	(+) 0.11
14.	37.	ditto.	5.98	6.16	5.94	(+) 0.04	(+) 0.22
15.	42.	light ditto.	5.96	5.93	5.89	(+) 0.07	(+) 0.04
16.	44.	fine loam.	5.79	5.88	5.69	(+) 0.10	(+) 0.18
17.	46.	ditto.	5.74	5.85	5.60	(+) 0.14	(+) 0.25
18.	50.	loam.	6.09	6.11	5.96	(+) 0.13	(+) 0.15
19.	52.	ditto.	7.57	7.51	7.50	(+) 0.07	(+) 0.01
20.	55.	ditto.	6.02	6.04	5.89	(+) 0.13	(+) 0.15
21.	60.	clay loam.	5.84	6.04	6.08	(−) 0.24	(−) 0.04
22.	67.	sandy loam.	5.79	6.21	6.07	(−) 0.18	(+) 0.14
23.	72.	ditto.	5.84	6.33	6.18	(−) 0.34	(+) 0.15
24.	91.	loam.	5.86	6.07	5.99	(−) 0.13	(+) 0.08
25.	105.	ditto.	5.73	6.00	5.70	(+) 0.03	(+) 0.30
26.	111.	clay loam.	5.46	5.80	5.92	(−) 0.46	(−) 0.12
27.	125.	sandy loam.	6.02	6.07	6.07	(−) 0.05	(±) 0.00
28.	142.	ditto.	5.31	5.33	5.43	(−) 0.12	(−) 0.10
29.	167.	clay loam.	5.42	5.47	5.61	(−) 0.19	(−) 0.14
30.	168.	sandy loam.	5.66	5.63	5.57	(+) 0.09	(+) 0.06
31.	200.	sandy.	6.08	6.09	5.89	(+) 0.19	(+) 0.20
32.	208.	volcanic.	5.74	5.88	5.55	(+) 0.19	(+) 0.33
33.	212.	loam.	7.30	7.34	7.01	(+) 0.29	(+) 0.33
34.	239.	laterit.	6.21	5.93	6.14	(+) 0.07	(−) 0.21

As Table VI indicates, the difference between the hydrogen and antimony electrode lies between p_H (+) 0.37 and (−) 0.46 with an average of (±) 0.20 while quinhydrone and antimony electrode vary within p_H (+) 0.33 to (−) 0.25

with an average of (±) 0.30. In case of quinhydrone, it was found that the results are slightly higher than the hydrogen electrode so that the difference between the antimony electrode becomes naturally higher.

Experiment V.

The comparative determination of the p_H value in the soil extract and paste was undertaken. The soil paste was prepared by adding just sufficient amount of water to make it into the paste form.

The following results, as shown in Table VII, were obtained:

Table VII.

Determination of pH in Soil Extract and Paste.

No. of experiment.	No. of Soils.	Soil water extract. p_H	Paste. p_H	Difference of p_H
1.	1.	6.94	6.94	(±) 0.00
2.	8.	5.70	5.39	(+) 0.31
3.	10.	6.11	6.00	(+) 0.11
4.	13.	6.57	5.59	(−) 0.02
5.	30.	5.76	4.50	(+) 1.26
6.	34.	6.65	6.46	(+) 0.19
7.	37.	5.94	5.39	(+) 0.55
8.	42.	5.89	5.50	(+) 0.39
9.	44.	5.69	5.59	(+) 0.10
10.	46.	5.60	5.37	(+) 0.23
11.	50.	5.96	5.46	(+) 0.50
12.	52.	7.50	7.91	(−) 0.41
13.	55.	5.89	5.52	(+) 0.37
14.	60.	6.08	5.30	(+) 0.78
15.	67.	6.07	5.87	(+) 0.20
16.	72.	6.18	6.15	(+) 0.03
17.	91.	5.99	5.50	(+) 0.49
18.	105.	5.70	5.28	(+) 0.42
19.	111.	5.92	5.24	(+) 0.68
20.	125.	6.07	5.44	(+) 0.63
21.	168.	5.57	5.30	(+) 0.27
22.	200.	5.89	5.15	(+) 0.74
23.	208.	5.55	5.13	(+) 0.42
24.	212.	7.01	7.74	(−) 0.73
25.	239.	6.14	5.06	(+) 1.08

Table VII indicates that the soil paste gave higher p_H value than the soil extract corresponding to that of soil extract and suspension in case of quinhydrone where the soil suspension gave higher p_H value. Especially soil ♯52 and ♯212 which were alkaline gave the opposite results.

Experiment VI.

The antimony and quinhydrone electrode were compared in determination of hydrogen ion concentration in soil extract prepared with KCl. The soil sample was treated with N/10 KCl and the extract was made. The results are shown in Table VIII:

Table VIII.

Comparison of Antimony and Quinhydrone Electrode in KCl Soil Extract.

No. of experiment.	No. of soil.	Quinhydrone.	Antimony.	Difference of p_H
1.	11.	5.95	5.61	(+) 0.34
2.	15.	5.92	5.54	(+) 0.38
3.	19.	5.43	5.15	(+) 0.28
4.	20.	5.17	4.93	(+) 0.42
5.	21.	7.20	6.93	(+) 0.27
6.	31.	7.19	6.63	(+) 0.56
7.	32.	7.10	6.52	(+) 0.48

As Table VIII indicates, the antimony electrode gave lower p_H value, ranging 0.30—0.50 than quinhydrone electrode.

Experiment VII.

The p_H value in water which has been known to contain hydrogen sulfide was determined by both quinhydrone and antimony electrode. The quinhydrone electrode failed to give an equilibrium while the antimony electrode gave the steady readings as shown in Table IX.

Table IX.

Determination of pH in Presence of Hydrogen Sulfide.

No. of samples.	Fresh water.	Water disposed.		Remark.
	p_H	p_H	acidity, total. (cc.)	
1.	7.56	6.61	4.0	slightly turbid.
2.	7.51	6.73	3.0	turbid.
3.	7.55	6.80	2.0	ditto.
4.	7.60	3.07	1.6	H_2S odor, turbid.
5.	7.68	3.50	1.3	ditto.
6.	7.58	9.10	(−) 8.0	slightly turbid.
7.	7.50	3.30	13.0	H_2S odor, turbid.
8.	7.53	8.67	(−) 3.0	slightly muddy, turbid.
9.	7.44	9.20	(−) 7.0	ditto.
10.	7.60	6.11	6.0	slightly turbid.

Summary and Conclusions.

This investigation was undertaken to ascertain the accuracy and applicability of antimony electrode in determination of hydrogen ion concentration of soil, and water which contains hydrogen sulfide. The following summary and conclusions may be made:

1. The following formulae can be used satisfactorily in calculating p_H value;

$$p_H = \frac{E - 0.104}{0.054}, \text{ for } (p_H\ 1-14.) \text{ with N/10 KCl-calomel electrode.}$$

$$p_H = \frac{E - 0.017}{0.054}, \quad \text{ibid} \quad , \text{ with sat. KCl-calomel electrode.}$$

2. In the buffer solution, the antimony electrode gives the results within p_H 0.2 compared with those obtained by the hydrogen electrode.

3. The shaking gives better results, reaching the equilibrium within 10 seconds to 2 minutes. It is particulary so in dealing with the solution of which p_H value is above 12.

4. The variation of reading caused by leaving the electrode immersed is not definite and some cases slightly higher p_H values were obtained in the alkaline soils which were determined in paste form.

5. The hydrogen ion concentration of thirty four soil samples was determined by both quinhydrone and antimony electrodes and found that they agree within p_H $(\pm)$ 0.2.

6. The antimony electrode gives in general higher p_H value in soil water extract than in the paste,

7. With soil extract prepared with N/10 KCl, the quinhydrone electrode gives 0.3 – 0.4 higher p_H value than those obtained by the antimony electrode.

8. The antimony electrode can be used satisfactorily with water containing sulfurous substance where the quinhydrone electrode fails.