Investigation on Antimony Electrode for Determination of Hydrogen Ion Cencentration.

I. Standardization of an antimony electrode in the buffer solutions and calculation of PH.

By

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In the electrometric metheds for determination of the concentration of hydrogen ions, the hydrogen electrode has been used extensivly and regarded as the standard. Recently the quinhydrone[1] and hydro-quinhydrone[1] electrodes are used to a large extent on account of their simplicity. However all these electrodes are inadequate in some instances when some poisonous substances are present in the samples. For example, the hydrogen electrode is known to be poisoned by hydrogen sulfide[1&2], sodium sulfite[3&4], arsenic[4], and several other substances[5]. On the other hand, the other two electrodes are inadequate in presence of free sulfur dioxide[3] and they are not satisfactory in solutions which contain oxidizing and reducing agents. For these reasons, the use of antimony electrode is recommended especially where these causes of error for the other electrodes may be present.

The use of antimony electrode in measuring the hydrogen ion concentration was investigated in 1923 by UHL and KESTRANEK[6], and KOLTHOFF and HARTONG[7] in 1925. In 1928, FRANKE and WILLAMAN[3] have made a study of the antimony electrode and its application to the determination of hydrogen ion concentration of paper-mill liquor; SNYDER[8] applied the method to the determination of the PH values of soils and reported some promising preliminary results in comparison with the hydrogen electrode in some soils ranging in PH values from about 3.6 to 9.2.

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1) BIILMANN, E., J. Chem. Soc. (London) 125, 1954, 1921.
2) DAWSON, Sugar. 28, 211, 310, 369, 2926.
3) FRANKE, K. W. and J. J. WILLAMAN, J. Ind. Chem. 20, 88. e928.
4) BREWSTER and RAINES, Intern. Sugar J. 25, 88. 1923.
5) CLARK, M., The Determination of Hydrogen Ions, 1923, 265—270.
6) UHL, A. and KESTRANEK, W., Monatsh. Chem. 44, 29—34, 1923.
7) KOLTHOFF, I. M. and B. D. HARTONG, Rec. Trav. Chim. Pays-Bas., 44, 113, 1925.
8) SNYDER, E. F., Soil Science, 26, 107, 1928.

This paper reports on some comparative results obtained by hydrogen and antimony electrodes in the buffer solutions, and later it is intended to test with various types of soils under various conditions.

Theoretical.

It was found by UHL and KESTRAEK[1], and KOLTHOFF[2] that a metallic antimony used as a test electrode, gives a definite potential and $\overset{+}{SbO}$ is produced, as follows

$$Sb_2O_3 + 2\overset{+}{H} \rightleftarrows 2\overset{+}{SbO} + H_2O.$$

The potential difference between the antimony electrode and the solution is governed by the concentration of $\overset{+}{SbO}$ which is in turn depend upon the concentration of hydrogen ions. On the other hand, the solubility of Sb_2O_3 in N/10 HCl and N/10 NaOH is so small that it does not influence the concentration of hydrogen ions in the solution.

The equation for calculation of PH measured against N/10 Calomel electrode at 14° C. are given by KOLTHOFF and HARTONG[3], as follows

(I) $E = 0.0415 + 0.0485\ PH$, at 18° C. (from PH 1—5)

(II) $E = 0.009 + 0.0536\ PH$; at 14° C. (above PH 9)

On the other hand, FRANKE and WILLAMAN[4] offers the equation below :

(III) $E = 0.050 + 0.054\ PH$, at 25° C.

The results given in this publication are based on the equation (III), corrected for N/10 calomel electrode at 18° C., which is shown below ;

$$(IV) \qquad PH = \frac{E - 0.104}{0.054},$$

For,

Hg—HgCl	N/10 KCl	sat. KCl	agar bridge	unknown solution	Sb_2O_3

1) UHL and KESTRANEK, Loc. cit.
2) KOLTHOFF, Loc. cit.
3) KOLTHOFF and HARTONG, Loc. cit.
4) FRANKE and WILLAMAN, Loc. cit.

Experimental.

A stick of metallic antimony of about 7 mm. in diameter and about 40 mm. long which was smoothed with a file and with emery, and soldered to a copper lead was used. As the control, the HILDEBRAND's hydrogen electrode was used as usual.

The readings for the antimony electrode were taken at the end of one minute while the content of the vessel being shaken by a girl assistant as uniformly as possible, having a part of the electrode immersed in the solution constantly.

A series of KOLTHOFF's and CLARK's buffer solutions were used as indicated in Table I.

The results are given in Table I and Fig. I.

Table I.

Comparative Study of H_2- and Antimony Electrode.

	No. of Solution. / Chain.	# I.	# II.	# III.	# IV.	# V.
KOLTHOFF's	$H_2 - C_{10}$	3.80	4.86	6.82	7.86	8.47
	$Sb - C_{10}$	3.67	4.81	6.92	7.79	8.17
CLARK's	$H_2 - C_{10}$	3.97	5.24	6.06	7.74	8.50
	$Sb - C_{10}$	4.00	5.20	6.11	7.85	8.26

N. B. The results were corrected for 18° C., by using the temperature factor prepared by the author and published together with the table for calculation of PH.

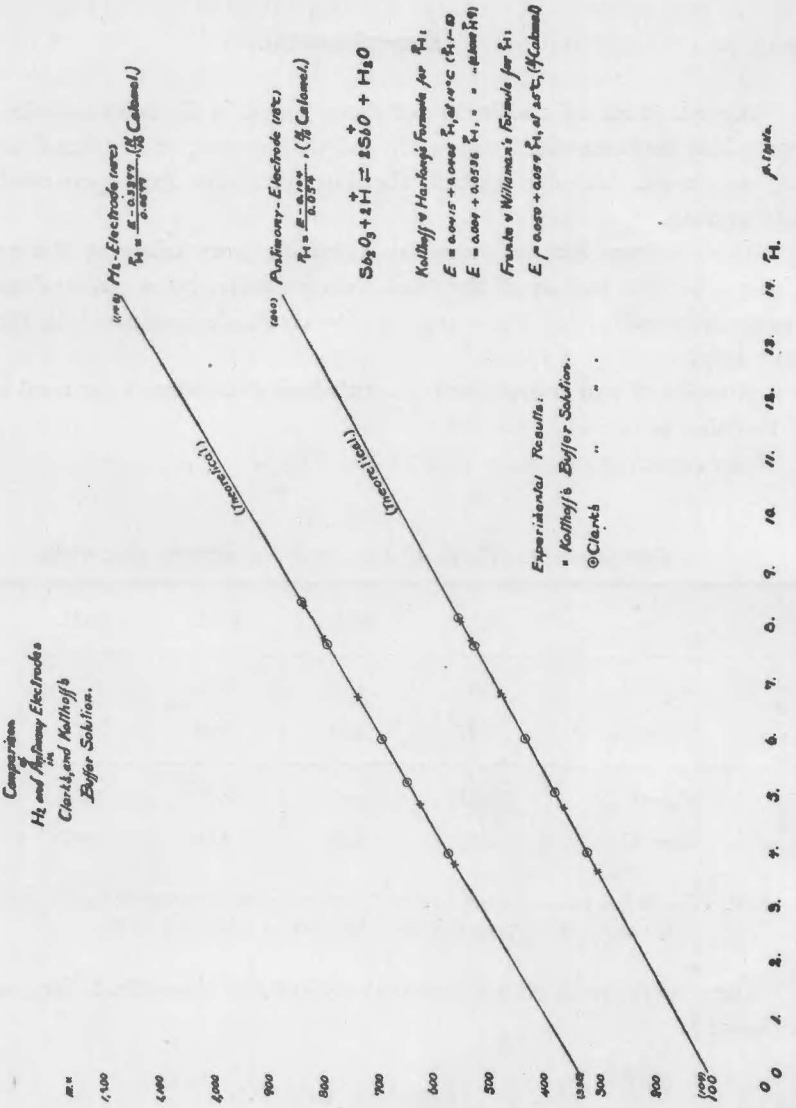
The experimental data are plotted against the theoretical line, and shown in Figure I.

(Fig. I. s. P. 276.)

As Table I. indicates, the antimony electrode gives very close readings to those obtained by the hydrogen electrode, and the experimental data obtained by both of these electrodes are in close agreement with the theoretical line as shown in Fig. I. However somewhat a larger difference is obtained in the alkaline solutions where the PH values become larger than 8, and this matter will be investigated further in the next paper.

Fig. 1.

Comparison of H_2- and Antimony Electrode.



Summary and Conclusion.

The comparative study of the hydrogen and antimony electrodes in the CLARK's and KOLTHOFF's buffer solutions was carried out, and the results may be summarized as follows :

1. Formula IV, $P_H = \frac{E - 0.104}{0.054}$, which is based on FRANKE and

WILLAMAN's equation, $E = 0.050 + 0.054\ P_H$, at 25° C., can be used satisfactorily for the chain and conditions noted previously.

2. The antimony electrode used in this investigation gave close readings to these obtained by the hydrogen electrode in both the CLARK's and KOLTHOFF's buffer solutions.

3. Somewhat larger variation among the results were noted in the alkaline solutions which will be investigated further in future together with some other factors such as manner and duration of shaking, and condition of the electrode.

4. In general, an equilibrium was obtained at the end of one minute, shaken by hand.

The adequecy of the antimony electrode for determination of the hydrogen ion concentration of soils together with some experimental factors, will be investigated further and reported in future.