Investigation on the Biilmann's* Quinhydrone Electrode. I.

By

A. Itano and K. Hosoda.

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This paper deals with several practical and some theoretical points concerning the quinhydrone method of BIILMANN for determination of hydrogen ion concentration.

The said method has been in use for the past few years in Europe and America with good advantage over the H_2 electrode especially in the agricultural investigations such as the soil and dairy. We however began to employ the method only recently since Professor L. MICHAELIS visited us and recommended it very highly.

In a course of preparation of the method, several practical as well as some theoretical points which may be worthy of mention, were noted in regard to : 1. Arrangement of the apparatus; 2. Working formulae; 3. Size of blank platinum eletrode; 4. Preparation of quinhydrone; 5. Effect of calomel; 6. Limitation of the method. These points will be considered separately and contrasted with the standard H_2 electrode together with some literature on the method.
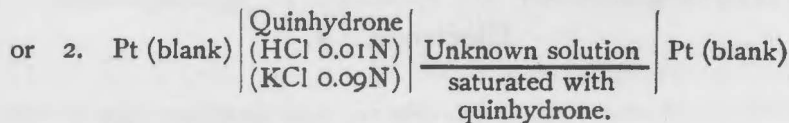
I. Arrangement of the Apparatus.

In order to make the quinhydrone method clearly understood, it will be contrasted with an ordinary gas chain as follows :

A.   An ordinary gas chain, as well known, is arranged as below :

$$\text{Hg-HgCl} \mid \text{N/10 KCl} \mid \text{Sat. KCl} \mid \text{Unknown solution} \mid \text{PtH}_2$$
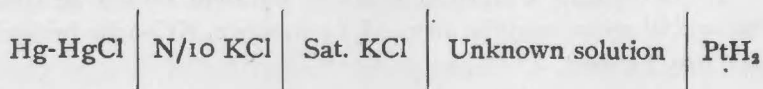
B.   The quinhydrone method may be adopted to either one of the following arrangement :

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1.   Hg-HgCl | N/10 KCl | Sat. KCl | <u>Unknown solution</u> | Pt (blank)
                                      saturated with
                                      quinhydrone.

or 2.   Pt (blank) | Quinhydrone (HCl 0.01N) (KCl 0.09N) | <u>Unknown solution</u> | Pt (blank)
                                                            saturated with
                                                            quinhydrone.

As it is noted, in this method no hydrogen gas is used since the method is based upon the constancy of dissociation of the quinhydrone in the range of certain PH serving as a source of hydrogen. It may be briefly described as follows:

$$C_6H_4O_2H_2 = C_6H_4O_2 + H_2 \text{[1]}$$

Thus the hydroquinone serves as a hydrogen source and gives a " hydrogen pressure ", and it gives the same potential regardless of the electrolytes and of the concentration of quinhydrone.

In connection with the arrangement described above, there are several points in particular should be carefully followed:

1.   Connection of the chain to the potentiometer;

In the chain, arranged as in B_1, the quinhydrone electrode forms the positive, and the calomel electrode, the negative when the PH of a solution is smaller than 6.35 while the reverse is true when the PH is larger up to the limitation.

2.   Preparation of the Standard Quinhydrone Electrode;

The direction given in the literature which were available for our review, is somewhat vague as to the concentration and proportion of HCl and KCl used in the preparation. It is generally expressed as follows:

Pt | Quinhydrone
      (HCl 0.01N)
      (KCl 0.09N)
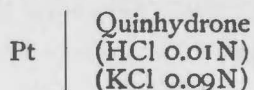
It means that one part of N/10 HCl mixed with nine parts of N/10 KCl. After the solution is made up, it is simple to prepare the standard electrode by merely saturating it with a small amount of the quinhydrone. It keeps in good condition for at least fourty eight hours and it can be reproduced with a greater accuracy than in case of the N/10 KCl calomel electrode.[2]

3.   In forming a chain, a factor of diffusion should be considered, and some special means may be adopted, for instance, KCl-agar bridge[3] of various shape may be used.

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1) E. BIILMANN, J. Agr. Science, 14, 1924, 232;—& Lund, Annales de Chimie 9, 15, 109, 1921; ibid, 18, 321, 1921.

2) STIG VEIBEL, J. Chem, Soc., 123, part 2, 1923, 2205.

3) L. MICHAELIS, Praktikum der Physikalischen Chemie, 1922, 191.

II. Working Formulae.

SÖRENSON's working formula for an ordinary gas chain, using N/10 KCl calomel electrode is as follows:

$$P_H = \frac{P - 0.3377}{0.0577 + 0.0002\,(t - 18)} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots (I)^{[1]}$$

For the quinhydrone electrode, there are three formulae each of which is used according to what kind of chain is formed in the determination.

$$P_H = 6.35 - \frac{\pi}{0.0577 + 0.0002\,(t - 18)} \quad \dots \quad \dots \quad \dots \quad \dots (II)^{[2]}$$

where-

6.35- P_H of the quinhydrone electrode at 18°C.

π- measured potential of the quinhydrone electrode in relation to the calomel electrode.

0.0577 etc ,- thermodynamical factor with temperature correction.

This formula gives the P_H of an unknown solution when a measurement is taken by a quinhydrone electrode against a decinormal calomel electrode through a saturated KCl.

From this equation, it is clear that:

$\pi = 0$ when P_H of an unknown solution $= 6.35$

$\pi = $ positive,   ibid < 6.35

$\pi = $ negative,   ibid > 6.35

Also changing the poles in the arrangement of apparatus becomes a neccessary part of manipulation.

$$P_H = 2.04 + \frac{\pi}{0.0577 + 0.0002\,(t - 18)} \quad \dots \quad \dots \quad \dots \quad \dots (III)^{[3]}$$

where

2.04- P_H of a standard quinhydrone electrode.

This formula is used when a standard quinhydrone electrode is used in place of the calomel electrode. Some authors give 2.03 instead of 2.04 for the P_H value of a standard quinhydrone electrode. The authors found that it is safe to determine the actual value of the electrode by means of the H_2 electrode.

In our case it was found to be 2.04.

$$P_H = \frac{(\pi - 0.2485) - 0.3377}{0.0577 + 0.0002\,(t - 18)}$$
$$= \frac{\pi - 0.5862}{0.0577 + 0.0002\,(t - 18)} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots (IV)^{[4]}$$

where-

0.3377 potential of calomel electrode.

0.2485 difference of potential between calomel and standard quinhydrone electrode.

1) SÖRENSEN S. P. L., Ergebnisse d. Physiologie, 12, 416, 1912.

2) BIILMANN, Loc. cit., p. 233.

3)   ibid

4) This formula is based on VEIBEL's work, loc. cit.

This formula is used when a measurement is taken with the H_2 electrode against the standard quinhydrone electrode.

III. Size of Blank Platinum Electrode.

As it is indicated in the literature, the size of electrode has effect on the sharpness of reading the potential.   From our experience, it was found that an electrode of 1 × 1.5 cm. gives very good reading when it was used in combination with type K potentiometer with a galvanometer.

The direction for cleaning the electrode which is given by BIILMANN[1] found to be helpful and quoted below :

If the electrodes require thorough cleaning, they should be treated with a hot mixture of chromic acid and strong sulfuric acid, then washed with distilled water and heated to glowing-point over an alcohol vapor lamp or a benzine blow-lamp, but not in gas flame.

IV. Preparation of Quinhydrone.

For our immediate use some quinhydrone (Kahlbaum) was given to us by Professor MICHAELIS.   But we found that it was difficult to obtain further supply in this country.   Consequently we prepared some in our laboratory according to the direction given by BIILMANN[2] by using the chemicals obtained from our local dealer :

100 g. ferric ammonium alum are dissolved in 300 c.c. water at ca. 65°C and this solution is poured into a warm solution of 25 g. hydroquinone in 300 c.c. water.   The quinhydrone precipitates in fine dark needles.   The mixture is cooled in ice and filtered by suction and the precipitate then washed four to five times with cold water.   Yield 15—10 g.   The preparation may contain a slight trace of iron, which is without serious effect !

The hydroquinone which was used, was "Hydroquinone Ciba", manufactured by Soc. of Chem.   Industry in Basle (Switzerland) and which is commonly used in the photographic work.

The ferric ammonium alum was (Reine Reagens) by S. ISHIZU, Osaka.

The experimental results which will be given later indicate that our preparation is very satisfactory.

V. Effect of Calomel upon the Quinhydrone Electrode.

Since our buffer solutions have been kept by an addition of a small

1)   BIILMANN,   Loc. cit. p. 237.
2)   ibid   p. 238.

amount of calomel from an infection of molds, it was investigated to ascertain if it has any effect. As it will be seen from the results obtained, it has no effect and keeps the solution from an infection.

VI. Limitation of the Method.

BIILMANN recommended the use of the quinhydrone electrode first only in acid solutions, and later he states that it can be used in basic solutions up to PH ca. 8.5[1] in the case of soil-water mixture. The author cites that KOLTHOFF used the electrode at PH 8 (Rev. Trav. Chim. Pays Bas, 42, 186, 1923). Since this reference is not available here, we have experimented in solutions of which PH larger than 7 and the results will be given in the experimental part.

Experimental.

The following experiments were carried out to find out the efficacy of the quinhydrone electrode and to demonstrate its relative merits against the H_2 electrode.

The apparatus used were type K potentiometer with a galvanometer $\sharp$2420-C and other accessories as used in the determination of hydrogen ion concentration.

Experiment 1. Determination of the PH of MICHAELIS' standard acetate solution :[2] by forming various chain as follows ;

Series.	Chain.	π	Formula.	PH found.
1.	H_2 — C.	0.6024	I	4.635
2.	H_2 — Q_1s.	0.8507	IV	4.632
3.	Q_1 — Q_1s.	0.1415	III	4.518
4.	Q_1 — C.	+ 0.1056	II	4.512
5.	Q_2 — Q_2s.	0.1414	III	4 516
6.	Q_2 — C.	+ 0.1055	II	4.502

Notes: H_2 —hydrogen electrode; C—calomel electrode; Q_1—quinhydrone (Kahlbaum).
        Q_1s—standard quinhydrone (Kahlbaum) electrode;
        Q_2 —quinhydrone (prepared here);
        Q_2s—standard quinhydrone (prepared with Q_2) electrode.
                        (These notations will be used in our publication.)

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1) BIILMANN, Loc. cit. p. 233.
2) The solution was sent to us from Professor MICHAELIS at Aichi Ikadaigaku.

The results obtained in this experiment indicate :

1. Correctness of the apparatus used.
2. Standard quinhydrone electrode gives close readings to those obtained by the H_2 electrode, or within 0.1 or. so PH which may be considered satisfactory for most works.
3. Quinhydrone prepared here gives very good results.

Also it was noted that the H_2 electrode takes much longer time to reach the equilibrium than the quinhydrone electrode which on average requires only three to five minutes. However the former gives sharper reading than the latter either against calomel or standard quinhydrone electrode in general.

Experiment 2. Determination of PH of a buffer solution (Clark) which has been preserved by an addition of calomel, by means of the quinhydrone electrode.

Temperature 16°C.

$H_2 - C$	$Q - C$	$Q - Qs$
π 0.6518	π + 0.0335	π 0 2150
0.6690	+ 0.0335	0.2152
0.6710	—	0.2152
0.6712	—	— —
0.6712	—	—
PH 5.820	5.765	5.795

The results seem to indicate that the calomel has no effect on the determination while the buffer solution has been kept in good condition for seven months already.

Experiment 3. Determination of higher limit of PH in the CLARK's buffer solutions by means of the quinhydrone electrode.

Solution.	$H_2 - C$	$Q - C$	$Q - Qs$	Temp.
A.	π 0.7917	π − 0.0858	π 0.3343	15°C
	0.7932	− 0.0858	0.3343	
	0.7938	− 0.0858	0.3343	
	0.7939	—	—	
PH	7.982	7.852	7.802	
B.	0.7953	− 0.1060	0.3531	15°C
	0.3056	− 0.1060	0.3530	

Solution.	$H_2 - C$	$Q - C$	$Q - Q_s$	Temp.
	π 0.8086	π —	π 0.3530	°
	0.8105	--	—	
	0.8105	—	—	
PH	8.280	8.203	2.222	
C.	0.8173	− 0.1167	0.3680	15°C
	0.8216	− 0.1200	0.3680	
	0.8226	− 0.1200	0.3680	
	0.8234	—	—	
	0.8234	—	—	
PH	8.506	8.452	8.485	
D.	0.8367	− 0.1314	0.3844	13°C
	0.8365	− 0.1320	0.3842	
	0.8365	− 0.1320	0.3844	
	—	—	0.3843	
PH	8.674	8.674	8.818	
E.	0.8415	− 0.1314	0.3896	13°C
	0.8452	− 0.1405	0.3908	
	0.8452	− 0.1390	0.3903	
	—	− 0.1395	0.3909	
	—	− 0.1395	0.3913	
PH	8.951	↓	↓	
F.	0.8581	− 0.1422	0.3953	13°C
	0.8581	− 0.1450	0.3977	
	—	− 0.1462	0.3981	
	—	− 0.1493	0.4002	
	—	− 0.1499	0.4023	
	—	− 0.1523	0.4025	
	—	− 0.1536	0.4050	
	—	− 0.1557	0.4062	
PH	8.951	↓	↓	

Solution.	$H_2 - C$	$Q - C$	$Q - Qs$	Temp.
G.	π 0.9335	π $- 0.1934$	π 0.4493	13°C
	0.9340	$- 0.1963$	0.4490	
	0.9340	$- 0.1997$	0 4508	
	—	$- 0.2042$	0.4540	
	—	$- 0.2068$	0.4555	
	—	$- 0.2100$	0.4565	
	—	$- 0 2151$	0.4614	
	—	$- 0.2185$	0.4653	
Ph	10.516	↓	↓	

Notes : The arrow indicates that no equilibrium is reached.
The readings were taken at five minutes interval except for the calomel electrode.

As the results indicate, the quinhydrone electrode gives very good com-. parative readings up to Ph 8.506 and slightly above. However no equilibrium is reached in Ph 8.951 or higher. Also it is interesting to note that the equilibrium was obtained by the quinhydrone electrode where its use was applicable.

Summary and Conclusions.

1. The Biilmann's quinhydrone method for determination of hydrogen ion concentration is very satisfactory, and easily adopted by those laboratories which have the gas chain method in operation. Again it can be installed in any laboratory where a few physical apparatus such as meter-bridge, galvanometer or capillary electrometer and other accessories are found.

2. The results obtained by this method are sufficiently accurate for most of the agricultural investigation and general biological work.

3. The method has several merits, namely :—
   a. Simplicity in its manipulation, and equipment.
   b. Quicker saturation of the electrode.
   c. The quinhydrone electrode (standard) can be prepared much easier and reproduced with greater accuracy than the calomel electrode.
   d. No platinization of the platinum electrode is necessary, and seldom poisons the electrode.

4. An addition of a small amount of calomel to a testing solution has no effect on the electrode while it keeps the solution in good condition for some time.

5.   The limitation of the method in the basic solution according to our test with CLARK's buffer solution, seems to be about PH 8.5 or so, and in higher PH no equilibrium is obtained.

6.   The formulae given in this publication may be used for general purpose according to a chain formed.

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