A Portable pH Apparatus with Micro-analytical Electrode and saturated Calomel Electrode.

By

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Introduction:

This paper deals with a portable form of apparatus for determination of hydrogen ion concentration with a special electrode for micro-analysis and also with a convenient type of saturated calomel electrode.

In recent years, the concentration of hydrogen ions has received much attention in many fields of investigation as well as in industries, for instance the following scheme indicates approximately the extent of its use:

- Field of application.
  - Scientific.
    - Medicine,
    - Biology,
    - Chemistry (agricultural, engineering, medical etc.)
  - Applied.
    - Sanitation & Manufacture.
      - sewage, drainage.
      - soap industry.
      - tannery.
      - paper mills.
      - thread mills.
      - pharmacy.
      - zymo-industry.
      - canning.
    - Agriculture.
      - milk, cheese and butter.
      - plant cultivation.
      - plant extracts.
      - fruits.
      - soil and soil solution.
      - fertilizers.

Part. I. A Portable pH Apparatus. (Itano)

As it is well known, the determination of hydrogen ion concentration has

been carried out mainly by two methods, namely the colorimetric and the electric. Although the former method is inexpensive and easy to operate and for these reasons it is used widely, it has certain disvantages such as personal factor, difficulties encountered with the colored materials as well as source of light. On the other hand, the latter method is quite expensive and some of them are difficult in their manipulation although it gives exact and accurate results. To meet with these drawbacks, the following convenient form of electric apparatus was designed, based on the Biilmann's quinhydrone method. The entire apparatus is shown in Plate VIII.

The apparatus consists of the following parts:

1. millivoltmeter (400 millivolts divisions.)
2. galvanometer (700 ohms resistance and 5×10^{-7} ampere sensitivity.)
3. switch board (commutator; revolving resistances 600 and 30 ohms each; 10,000 ohms resistance for galvanometer protection; main switch from battery.
4. dry battery.
5. three glass vessels (two have platinum electrode and the middle one contains only concentrated KCl; these vessels are connected by means of agar bridges.)
6. leveling device with a tripod for the outdoor work.

These parts are set up and connected as shown in Fig. I.

Manipulation.

The instrument can be manipulated as follows.

1. Place an unknown solution in a vessel as shown in Fig. I, and a small amount quinhydrone is added and connected up as indicated there in.
2. Open up 10,000 ohms switch and place 600 and 30 ohms resistance on "0" and "5" respectively.
3. Put on the current from the battery by turning its main switch.
4. Turn slowly the 600 ohms resistance watching the galvanometer needle until it strikes a point of apparent balance.
5. Close the 10,000 ohms resistance switch.
6. Adjust the 30 ohms resistance to get the balancing point of the galvanometer.
7. After the galvanometer is balanced, obtain the reading on the millivoltmeter which is in the pH Table[1] and the corresponding pH is found.

The temperature correction[2] is applied, if so desired.

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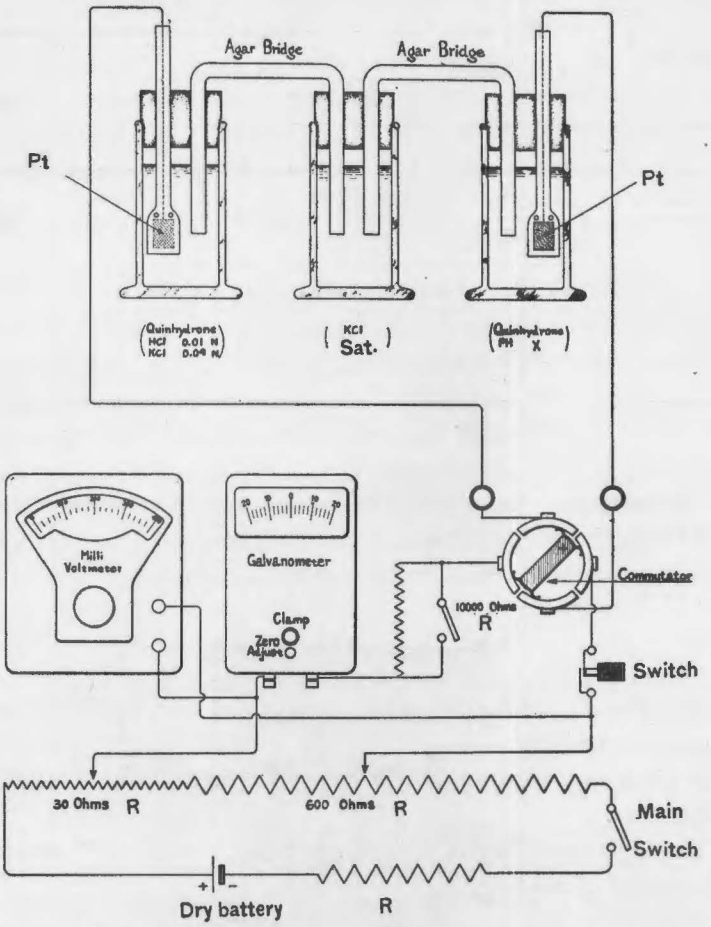
1) A. ITANO and K. HOSODA, Berichte d. Ōhara Inst. etc, Bd. III, 206, 1926.
2) ibid, 205, 1926.

Fig. I.
Wiring of the apparatus.



R ..... Resistance.

Experimental :

The accuracy of this apparatus was checked against the Type K Potentiometer of Leeds & Northrup Co., taking the buffer solutions of three known pH determined by the hydrogen electrode. Four different people experimented and obtained the following results as shown in Table I :

As Table I indicates, there is very fair agreements among the results obtained by different experimentors, using these different apparatus. As a whole the pH determined by Itano's apparatus are slightly lower than those obtained by the other. Especially it is remarkable to note that the experimentor H. is a girl helper in our laboratory who learned the method in twenty minutes and obtained very good comparative results.

Table I.

Comaparative Results of Itano's Apparatus and Type K Potentiometer.

Experimentors	Type of Instrument.	Solutions.		
		I.	II.	III.
		pH. 7.15*	pH 4.70*	pH 8.00*
I.	Itano's.	7.17	4.71	8.02
	K.	7.19	4.74	8.02
A.	Itano's	7.12	4.64	7.92
	K.	7.17	4.73	8.02
M.	Itano's	7.08	4.70	7.91
	K.	7.18	4.74	8.02
H.	Itano's only.	7.08	4.64	8.02

Notes: Experimentor H. is a girl helper who learned the method in twenty minutes.
* These values were obtained by the hydrogen electrode and the others wers obtained by the quinhydrone method.

Summary for Part I.

1. This Itano's apparatus can be manipulated very easily by those who have no previous training.

2. It gives very accurate results comparing with those obtained by Type K potentiometer.

3. The high sensitivity of the galvanometer, $1^{\circ}=5\times10^{-7}$ ampere enables a fine adjustment of reading.

4. Very little time is required to make a determination.

5. The posts of each part are visible so that each part can be used with any other apparatus in the laboratory.

6. It can be carried round very conveniently and its maintenance costs very little.

Part II. Electrode for Micro-pH-determination :

Recently the micro analytical methods have made such a progress that many branches of chemical investigations have been profited greatly. In the determination of hydrogen ion concentration, often only a very small amount of sample is available. In such a case, the colorimetric method has been used

frequently. But it is made possible to use the quinhydrone method in such a small sample as 0.02 cc. or less in quantity by using an electrode which was devised by the auther as shown in Fig. II.

Fig. II.

" A " Type Electrode.

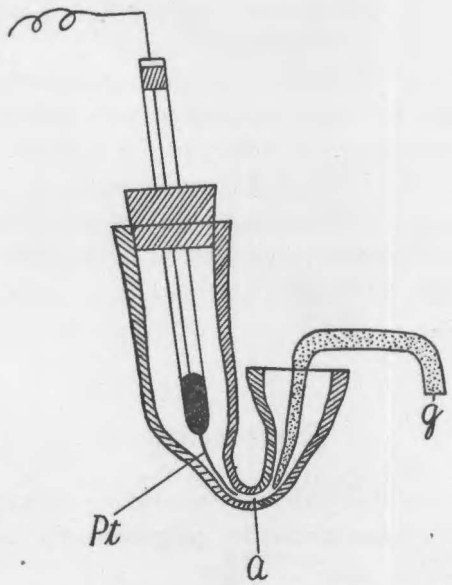


Fig. II. shows the electrode which can be used with quinhydrone. Only 0.02 cc. or less sample is required to carry out a determination. It consists of a fine capillary tube, less than 1 mm. in diameter with wide open ends in which a platinum electrode Pt is inserted in one and an agar bridge with a sharp point, in the other. It can be used as follows :

1. The platinum electrode and the agar bridge are taken out first.
2. A minute quantity of quinhydrone is placed in part (a) by means of a fine glass rod.
3. By means of a capillary pipette, a small sample (0.02 cc. or less) is transfered into part (a) and mixed with the quinhydrone thoroughly.
4. Then, the electrode and agar bridge are replaced in their respective position and connected up as usual so that the determination is made.

The electrode described above is used only with quinhydrone, and for the hydrogen electrode, another form of electrode vessel is designed and it is in course of construction at present, and will be reported later if successfull.

Part III. Investigation on a saturated Calomel Electrode.

In the first part of this publication, it was noted that the standard quinhydrone electrode is used in the portable apparatus. Later however it came to the author's attention that a saturated calomel electrode which is prepared very easily and resists shaking, can be used satisfactorily. Consequently an enquiry is made as to its adequecy as noted below :

As noted previously, the standard quinhydrone electrode has an advantages that it can be prepared easily and reproduced with greater accuracy than the N/10 KCl calomel electrode, and withstand the shaking. For these reasons it is useful for some works although it must be renewed at every fourty eight hours or so. Consequently it is desirable to use the calomel electrode which resists shaking specially in connection with an investigation, extending any considerable length of time, since the calomel electrode can be kept in good condition more than a year.

Experimental :

The following calomel electrodes were used for the comparison :

I. N/10 KCl calomel electrode, prepared very carefully according to the standard method.

II. Saturated KCl calomel electrode which was prepared as follows : Six grams of purified calomel, 15 cc. of pure mercury and 50 cc. of saturated KCl were shaken thoroughly for five minutes in a closed vessel in absence of air, and transfered into a special electrode vessel.

Clark's buffer solution of pH 7.26 was used as the test solution.

Table II. gives the results obtained :

Table. II.

Comparative Results of N/10 and saturated Calomel Electrode.

Temp. ° C.	Known pH	Kind of Calomel Electrode.	Millivolts.	pH Determined*
28.	7.26	I.	−0.054	7.25
〃	〃	II.	+0.036**	7.27

* An average of several determinations by three different experimentors.

** From 0.036 m. v. which was read on the millivoltmeter, pH was calculated according to the following equation :

$$(x \times \text{T.F.}) - 0.0875 = \pi \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \quad (A)$$

Where

x, — reading on the millivoltmeter.

T. F. — temperature facter.

0.0874, — difference of potential between N/10 and saturated calomel electrode at 18°C.

π, — E. M. F. noted in Table for pH Values etc. (ITANO, loc. cit. p. 206)

In this case, therefore

$(0.036 \times 0.966) - 0.0874 = -0.0526$ or pH 7.27

Again from the results obtained above, the potential of such saturated calomel electrode was calculated and found to be as follows ;

The following formula was used which is derived from the Nernst's equation originally :

$$pH = \frac{(0.7042 - E_0) - x}{0.0577} \quad \cdots \cdots \cdots \cdots \cdots \quad (B)$$

where

0.7042, — potential of quinhydrone electrode in respect to the hydrogen electrode at 18° C., using humid hydrogen, given by Billmann.

E_0 — potential of calomel electrode.

x — reading on the millivoltmeter.

0.0577 — thermodynamical facter.

Substituting the experimental data in equation (B), the value for E_0 can be calculated as follows :

$$7.27 = \frac{(0.7042 - E_0) - 0.0348}{0.0577}$$

$$E_0 = 0.2514$$

Considering this value with that is given by Michaelis for the standard saturated calomel electrode at 18° C. which is 0.2503, there is a difference of 0.0011. Again the variation among the newly prepared electrodes, is very small so far as the author's experimence is concerned. Consequently excepting those cases where an extreme accuracy is required, this type of saturated calomel electrode can be used very conveniently with satisfactory result.

Summary and Conclusions.

The contents of this paper may be summarized as follows :

1. A portable type of apparatus designed by the author for determination of hydrogen ion concentration is described.

2. The results which are closely comparable with those obtained with Type K potentiometer, are obtained by this apparatus.

3. The apparatus is inexpensive and easily carried round, and the cost of maintenance is very low.

4. Each part in the apparatus is independent so that it can be used separately, if so desired.

5. An eletrode for determination of pH in a minute quantity of sample viz. 0.02 or less, is described.

6. The results of comparative study of N/10 standard and a saturated calomel electrode of special preparation are given, and they indicate that the latter gives very close result to those obtained with the former.

7. An equation is given by which Table of pH for N/10 calomel electrode can be used for the saturated calomel electrode, as follows:

$$(x \times \text{T. F.}) - 0.0874 = \pi$$

8. The potential of such a saturated calomel electrode was calculated and found to be 0.2514 at 18° C.

PLATE VIII.

Portable pH apparatus.