

RESEARCH PAPER RP634

*Part of Bureau of Standards Journal of Research, vol. 12, January 1934*A GLASS ELECTRODE POTENTIOMETER SYSTEM FOR THE DETERMINATION OF THE pH VALUES OF WEAKLY BUFFERED SOLUTIONS SUCH AS NATURAL AND TREATED WATERS¹

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ABSTRACT

In the electrometric measurement of the pH values of buffered solutions more dilute than $M/10,000$ by means of quinhydrone and hydrogen electrodes the resistance of the solution, escape of carbon dioxide, acid properties of the quinhydrone, and polarization of the electrodes are so disturbing that the emf readings may vary as much as 5 to 30 mv or 0.1 to 0.5 pH unit. The isohydric-indicator technique is apparently applicable within 0.1 pH to such solutions, and distilled water, but has not heretofore been compared with a reliable emf method. By adding Varley shunts to a modification of the vacuum-tube potentiometer used by Partridge, keeping the grid attached to the circuit, and using a Thompson glass electrode, emf readings can be made within 0.1 to 2.0 mv on weakly-buffered solutions and distilled water, and the pH values agree with those obtained by the isohydric-indicator method. This apparatus is also suitable for measuring the pH of solutions containing active oxidizing or reducing agents, such as chlorine or tannins, where the hydrogen and quinhydrone electrodes and indicator methods might fail.

CONTENTS

	Page
I. Introduction.....	67
II. The glass electrode potentiometer system.....	68
III. The pH measurements.....	71
IV. Summary.....	72

I. INTRODUCTION

The methods most frequently used for determining hydrogen-ion concentrations include the hydrogen electrode, the quinhydrone electrode, and indicators. All have their limitations, either as to the range of concentration in which they are applicable or to the type of solutions in which they can be used. For example, oxidizing agents such as chromates and chlorine interfere. The glass electrode, on the other hand, has been shown² by Hughes, MacInnes, Thompson, and others to be applicable in solutions of oxidizing and reducing agents, and of heavy metal salts, when the pH values are less than 11 or 11.5. There are no data showing the lowest concentrations in which the glass electrode is applicable.

¹ Presented before the Division of Water, Sewage, and Sanitation Chemistry at the Eighty-Fifth Meeting of the American Chemical Society, Washington, D.C., Mar. 27 to 31, 1933.

² For extensive references see M. R. Thompson, B.S.Jour. Research, vol. 9, p. 852, 1932.

In connection with our work on the determination of the pH and total acidity of the weakly-buffered extracts of paper and farm-waste fibers and of sugar acids in equilibrium with their lactones and salts, it became necessary to devise a method applicable to both the solutions and the natural and distilled water used as solvents. It was found by Fawcett and Acree,³ and confirmed by ourselves, that the hydrogen electrode is not very sensitive in solutions more dilute than $N/10,000$, due to the high resistance and polarization at the electrode; in such cases the readings with portable galvanometers are not reliable within several tenths of a pH unit. Furthermore the pH will rise steadily as the hydrogen removes carbon dioxide from the solution. In the use of the quinhydrone electrode the quinhydrone itself, as an acid, lowers the pH steadily as it gradually dissolves and the error is consequently large, in some cases several tenths of a pH unit, with very dilute buffers such as natural and distilled waters. On the other hand the above authors have shown that consistent pH readings can be obtained on dilute buffers or distilled water by the isohydric-indicator method, in which a final check is made by adding indicator adjusted to the pH of the unknown as determined in preliminary tests. As the high resistance of dilute solutions or even pure water in the usual glass-electrode vessels is small in comparison with that of the glass itself, which is generally greater than 10 megohms, this emf method looked promising. It has proven useful within its range in this field for giving a very desirable comparison between the pH values obtained by its use and by the isohydric-indicator technique. The method is particularly promising for measuring the hydrogen-ion activity of organic acids and acid salts (buffers) and applying the mass law in extremely dilute solutions that approach pure water.

Check readings with the glass electrode on even double-distilled water do not vary more than 2 to 3 mv which is satisfactory for most purposes. Although only meager data are available, the results of Thompson⁴ are supported regarding the salt errors of the glass electrode, which gives approximately the same pH as the isohydric-indicator technique below pH 7.0. The object of this paper is therefore to present data obtained by these four methods in very dilute or weakly-buffered solutions and distilled water, and particularly to show the usefulness and agreement of the glass electrode and the isohydric-indicator methods, and the sources of error of the hydrogen and quinhydrone electrodes.

II. THE GLASS ELECTRODE POTENTIOMETER SYSTEM

The equipment consists essentially of a Leeds and Northrup type K potentiometer and type R 500 ohm 2500-e galvanometer, sensitive to 0.01 mv per mm and with a period of 3 seconds, a Thompson metal-jacketed electrode and saturated calomel electrode, and a modified Partridge⁵ vacuum-tube galvanometer containing a special Duovac triode requiring 2 volts for the filament and -1.5 volts on the grid. The authors' more recent work is being done with the FP 54 G.E. tube, which is even more suitable for the purpose. Figure 1 illustrates in the upper sketch the approximate values of the resistances and the

³ Edna H. Fawcett and S. F. Acree, *Jour. Bacteriology*, vol. 17, no. 3, March 1929; *Jour. Ind. Eng. Chem. An. Ed.*, vol. 2, p. 78, Jan. 15, 1930.

⁴ See reference 2, p. 67.

⁵ H. M. Partridge, *Jour. Am. Chem. Soc.* 51, 1, 1929, *Microchemie*, 11, 326, 337, 1932.

changes made in the Partridge system which is shown in the lower diagram. The letters show the positions of the switches in the Partridge instrument. In following the directions furnished for the Partridge apparatus the A and B batteries are turned on and reach fairly stable conditions in about 30 minutes as shown by the milliammeter. The grid circuit is left open, and the galvanometer deflection is brought to zero by sliding its movable contact terminal along the B battery negative line. The grid-circuit contact is then closed and moved

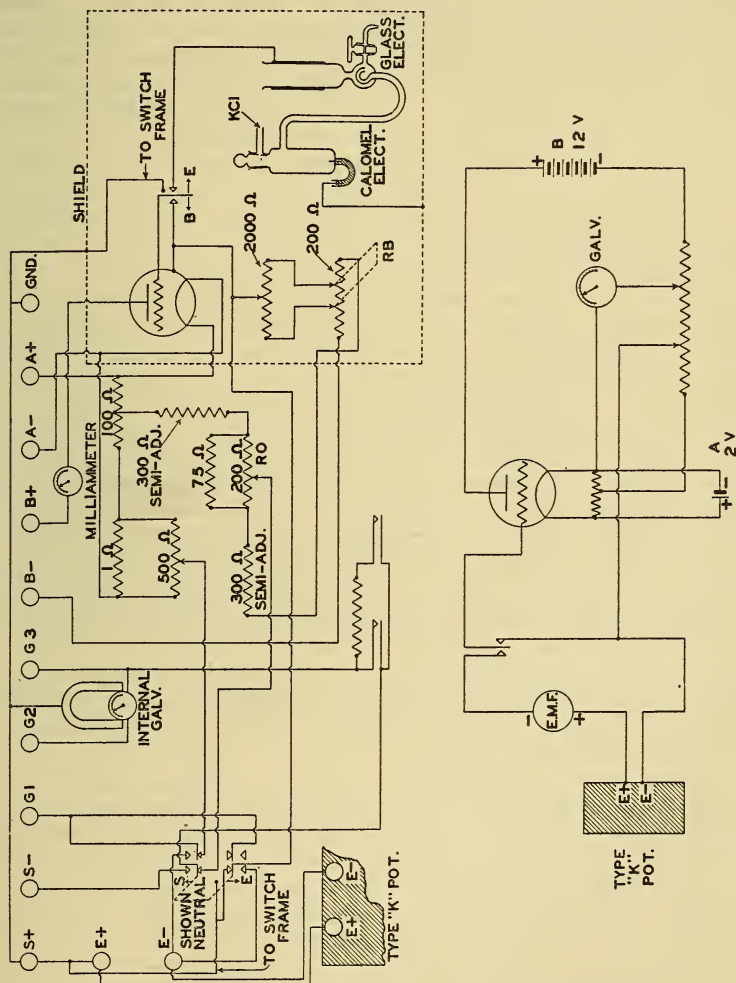


FIGURE 1.—Diagrams of wiring and resistance in the glass electrode potentiometer system. Upper diagram, circuit as modified in this work. Lower diagram, schematic Partridge circuit.

along the B battery negative line to balance the galvanometer again. These operations are repeated until the galvanometer deflection is zero regardless of whether the grid circuit is closed or open. The electrode system and potentiometer are then switched into series with the grid, and the emf of the electrode system is found by adjusting the potentiometer until the galvanometer reading is again zero. All this manipulation takes time for readings to 0.1 mv and is rendered difficult by the disturbing effect of stray charges on the free grid po-

tential which good shielding cannot completely overcome around heavy-current equipment.

We have noted that the balances are more easily obtained with the grid circuit closed because they are then less affected by stray electrical impulses. All balancing with a free grid is therefore omitted. Simply contact the grid lead with the B battery negative line at approximately the correct position, adjust the movable galvanometer terminal on the B battery negative line until zero reading is established, and then switch the potentiometer-electrode system in series with the grid and find the emf necessary to bring the galvanometer to zero again. This procedure increases the speed and precision. To avoid the inherent "jumps" in the galvanometer position arising from corresponding increments in emf as the sliding contacts move from one turn to the next in the spiral wire-resistances, we have replaced these junctions with Varley shunts⁶ having the approximate resistances shown in the upper half of figure 1. Another change is the shift of the galvanometer contact from the A battery negative line to a 1 to 500 ohm Varley shunt at the negative terminal of the center tap resistor across the filament as indicated in figure 1. In making the changes it was possible to bring the two knobs of each Varley shunt close together on the dial panel for convenience of manipulation, and to get higher precision in emf readings. The resistances have been suited to the use of 2-volt A and 12-volt B batteries, which are run continuously to give steady emf readings.

The method of grounding and shielding is shown. It is very important to make the leads for the batteries, galvanometer, and potentiometer-electrode system as short as possible and to shield them thoroughly; electrode leads 10 feet long give trouble even when covered with a braided-steel sheath grounded at both ends. The greatest uncertainty arises on damp days from electrical leaks across the moisture condensed on the leads, switches, galvanometer, and potentiometer, which should therefore be coated with paraffin and kept in a thoroughly dry container if possible. Heavy duty storage batteries should be used, at constant temperature if possible, and charged frequently; operation of the batteries by the floating charge method, even through transformer-rectifier systems, causes noticeable galvanometer deflections from line surges.

The sensitivity of this modified equipment with the Leeds and Northrup 2500-e galvanometer and the Thompson glass electrode of about 60-megohms resistance, made from Corning no. 015 glass, is about 0.004 mv per mm scale division with $M/1,000$ sodium-acid phthalate, 0.007 mv with $M/10,000$ solution, and 1 mv for double-distilled water. Standard cells can be checked to within 0.1 mv with this vacuum-tube potentiometer equipment. With the Thompson glass electrode the readings are therefore made easily to within 0.1 mv, are reproducible with double-distilled water to within 2 or 3 mv, and become better as the buffer concentration increases.

⁶ The Varley shunt was made by arranging an ordinary radio potentiometer with two insulated sliding contacts close together, and shunting them with another potentiometer. A knob on the main potentiometer gives the coarse adjustment and the knob on the shunt potentiometer gives very fine adjustments in emf.

III. THE pH MEASUREMENTS

The purpose of this work was to learn the limiting dilutions of organic buffer salts in which each of the methods mentioned can be used and to get similar data on natural, treated, and distilled waters generally used as solvents. We therefore first used each of the four methods to measure the pH of solutions of sodium-acid phthalate (NaHPh in the tables) whose concentrations ranged from one tenth to one hundred thousandth molar. We also determined the pH of tap water, boiler water, and double-distilled water by the four methods. Leather extracts and chlorine solutions were studied as examples of reducing and oxidizing agents. The results of these measurements are shown in table 1.

TABLE 1.—pH values of solutions of various concentrations obtained by different methods

	Hydrogen electrode	Quinhydrone electrode	Glass electrode	Isohydric indicator method
M/10 NaHPh.....	3.93	3.93	3.92	3.90
M/100 NaHPh.....	4.05	4.06	4.04	4.05
M/1,000 NaHPh.....	4.34	4.37 to (4.33)	4.35	4.30
M/10,000 NaHPh.....	4.85	4.82 to (4.72)	4.84	4.90
M/100,000 NaHPh.....	5.68 to (5.95)	5.34 to (5.20)	5.61	5.70
Tap water.....	8.42 to (8.98)	7.11	7.58	7.70
Boiler water.....	11.74	(^a)	11.52	11.70
Double distilled water.....	6.18 to (7.66)	6.05 to (5.71)	6.57	6.50
Leather extract.....	5.28	5.40	5.25	(^b)
M/100 buffer containing 0.07 g chlorine per liter ^c	4.59	4.66	4.72	(^d)
M/100 buffer containing 1 g chlorine per liter ^e	(^f)	0.20	1.90	(^d)

^a Solution too alkaline for quinhydrone electrode.

^b Solution too deeply colored for indicator method.

^c This solution was prepared by diluting 50 ml of M/20 KHPH-NaOH solution (pH=4.80) and 5 ml of saturated chlorine water (pH=1.71) to 250 ml.

^d Indicator faded quickly.

^e This solution was prepared by passing chlorine gas into M/100 KHPH-NaOH solution (pH=4.80).

^f Solution removed plating from electrode.

In making measurements, all at about 25 C, 5 mm by 10 mm gold sheets plated with palladium sponge were used as hydrogen electrodes; 5 mm by 10 mm gold plates were used with the quinhydrone; and saturated calomel electrodes were used as reference standards. No correction was made for the contact potentials which were of course constant in the comparisons of the emf given by hydrogen, glass, and quinhydrone electrodes in any given buffer. The usual sulphonphthalein indicators adjusted in pH values were employed.⁷

It is to be observed that when tap water, distilled water, or other solutions containing carbonates were measured with the usual hydrogen electrodes the escaping hydrogen removed carbon dioxide and the pH rose in one half hour from the initial values stated to those shown in the parentheses in table 1, and was still rising at the end of that time. Solid quinhydrone added to a very dilute acid solution slowly dissolved and because of the weak acidic properties of this oxidation-reduction reagent the pH gradually decreased in about one half hour from the initial value stated to a constant reading given in the parentheses in table 1. Leather extracts gave the same

⁷ See reference 3, p. 68.

readings with the glass and hydrogen electrodes, but the quinhydrone electrode and the indicator method were found inapplicable in confirmation of other workers,⁸ especially Pleass, and Wallace and Beek. Chlorine present in *M*/100 sodium acid phthalate to the extent of only 0.07 g per liter decolorized the indicator and gave drifting emf readings in the hydrogen and quinhydrone electrodes which became constant at distinctly low values when the chlorine was consumed. When chlorine was present to the extent of 1 g per liter the palladium sponge was dissolved from the hydrogen electrode and the quinhydrone method gave large errors. It was observed, however, that no such drifts or uncertainties arose in this work with the glass electrode even in very dilute solutions and water. Table 2 shows the precision of successive emf readings made on the same solution in the glass electrode at about 1-minute intervals after rebalancing each time. Practically identical results were obtained with fresh portions of the solution placed in the electrode and hence polarization errors may be considered negligible. Table 2 shows the average and maximum deviations from the mean values. As Thompson emphasized, the glass electrode should be recalibrated at least daily against one or more standard buffer solutions.

TABLE 2.—Average emf values and average and maximum deviations for various solutions in the glass electrode

Solution	Average of five readings	Average deviation from mean	Maximum deviation from mean	Solution	Average of five readings	Average deviation from mean	Maximum deviation from mean
	<i>Volts</i>	<i>Volts</i>	<i>Volts</i>		<i>Volts</i>	<i>Volts</i>	<i>Volts</i>
<i>M</i> /10 NaHPh.....	+0.0439	0.0001	0.0003	Tap water.....	-0.1696	0.0006	0.0016
<i>M</i> /100 NaHPh.....	+0.0372	.0003	.0005	Boiler water.....	-.4003	.0006	.0016
<i>M</i> /1,000 NaHPh.....	+0.0188	.0004	.0006	Double-distilled water.....	-.1113	.0010	.0018
<i>M</i> /10,000 NaHPh.....	-.0106	.0001	.0001	Leather extract.....	+0.0492	.0003	.0004
<i>M</i> /100,000 NaHPh.....	-.0551	.0005	.0014	Buffer containing chlorine ^a	-.0039	.0004	.0006

^a This solution was prepared by diluting 50 ml of *M*/20 KHPH-NaOH solution (pH=4.80) and 5 ml of saturated chlorine water (pH=1.71) to 250 ml.

IV. SUMMARY

In summarizing the results of this work the following conclusions may be drawn.

1. The hydrogen electrode appears to be applicable in solutions whose concentrations are one ten-thousandth molar or greater. It is not generally suitable for determining the pH of distilled water or tap water. In the case of tap water the difficulty may be a disturbance of the carbonate-bicarbonate ratio rather than too low a concentration of electrolyte. The hydrogen electrode is suitable for determining the pH of the boiler water used in this work, but may not be for all boiler waters. Oxidizing and reducing agents may give erroneous results.

2. The quinhydrone electrode is not reliable in solutions whose concentrations are less than one-thousandth molar. This combined with its inapplicability in solutions having a pH greater than 8.5 or containing oxidizing agents or other compounds acting on the quinone or hydroquinone, makes it less satisfactory than the other methods studied.

⁸ Pleass, *J. Soc. Chem. Ind.*, 48, p. 152T, 1929; E. L. Wallace and John Beek, Jr., *B.S. Jour. Research* vol. 4, p. 737, 1930.

3. The glass electrode appears to be applicable throughout the entire range of concentration from one-tenth molar to double-distilled pH 7 water, with an accuracy of 0.1 pH or better. The solubility of Corning 015 glass is low enough to prevent errors even with distilled water, especially if the solution is flowed through the electrode or kept in it only long enough for measurements.

The glass-electrode method would therefore seem to be valuable as an alternative and hence an electrometric check upon the isohydric-indicator technique in these extremely dilute solutions. It is also generally useful for solutions which are turbid, highly colored or containing oxidizing or reducing agents.

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