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A COMPARISON OF DIFFERENT TYPES OF GLASS ELECTRODE FOR DETERMINING THE pH OF SOILS

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During the past decade the quinhydrone electrode has been used extensively for determining the hydrogen-ion concentration of soils. It is admirably adapted to the study of reaction in soils due to its simplicity and ease of operation, and to its accuracy in most soils. As is well known, however, its use is restricted to soils having a reaction less than pH 8.0 to 8.5, and to soils containing no oxidizing or reducing substances in sufficient concentration to affect the oxidation-reduction potential of the quinhydrone. In recent years a number of investigators, notably Karraker (5), McGeorge (8), Baver (1), and Heintze and Crowther (4), have noted that erroneous results were obtained when the quinhydrone electrode was used to determine the hydrogen-ion concentration of certain soils having a neutral or even an acid reaction. The presence in soils of comparatively large amounts of manganese dioxide has been found to upset the oxidation-reduction potentials of the quinhydrone and hence to cause an error in the measurement of the hydrogen-ion concentration.

In order to overcome the difficulties encountered in the use of quinhydrone for hydrogen-ion determinations in soils, it has been suggested that the glass electrode be used in its stead. This necessitated a study of the adaptability of the glass electrode for this purpose. As one phase of this study a comparison has been made of the different types of glass electrode that have been used by other workers in the various fields of investigation. The results of this study are presented in this paper.

EXPERIMENTAL

Four types of glass electrode, as shown in fig. 1, were used in this investigation. They were (a) the modified bulb, silver-silver chloride as used by Goodhue (3); (b) the modified bulb quinhydrone made according to the specifications of Leeds and Northrup Co.; (c) the reentrant, silver-silver chloride, a modification of the Kerridge electrode (6); and (d) the MacInnes-Dole (7) type of membrane, silver-silver chloride. The electrodes were made from Corning glass No. 015.

A Leeds and Northrup Hydrogen-ion potentiometer with a saturated calomel half-cell was used with the glass electrodes for measuring the potentials. In order to cut down the resistance, a vacuum tube circuit was used with the potentiometer. It was constructed according to Goodhue's (3) modification of Ellis and Kiehl's (2) vacuum-tube circuit. The temperature during the pH determinations was controlled at 25°C. by the use of a Freas constant temperature oven.

Samples of five different soil types were used in the experiment, namely: Tama silt loam from Marshall county, Grundy silt loam and Shelby loam from Warren county, Marshall silt loam from Audubon county, and Carrington loam from Hardin county. The soils were air-dried and passed through a twenty-mesh sieve. A thirty-gram sample of soil was placed in a 150 cc. extraction flask and mixed with 75 cc. of CO_2-free distilled water. The mixture was shaken for one minute and then allowed to stand for two hours, at which time the supernatant liquid was poured into a specially constructed "U"-shaped tube and the glass electrode introduced into the liquid. The electrode was so adjusted that the surface of the liquid inside the electrode was level with the surface of the liquid outside. Then the KCl-agar bridge making contact with the calomel half-cell was introduced and the potential measured.

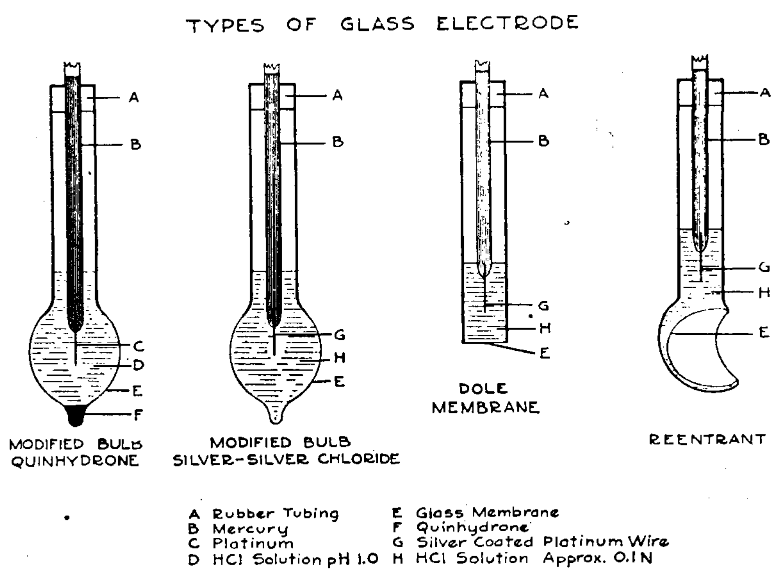

Fig. 1.

The voltage readings given by the electrodes were calculated to pH by the Youden and Dobroschy (9) method.

Before comparisons could be made of the results obtained by the use of different electrodes it was necessary to determine the normal variation to be expected from the use of a single electrode with the soils employed. Hence, the pH of twenty-five replicate samples of each soil was determined by use of the modified bulb, silver-silver chloride electrode of Goodhue. The range of variation, the probable error of the mean and the standard deviation of the items are shown in table I.

Table I — The Variation in pH as Determined on Twenty-five Samples of Each Soil by a Single Glass electrode

Soil Type	Ave. pH	Range	Probable error	Standard deviation
Tama silt loam	4.96	0.06	0.002	0.017
Carrington loam	5.12	0.17	0.007	0.051
Grundy silt loam	5.36	0.12	0.003	0.022
Shelby loam	5.84	0.17	0.006	0.046
Marshall silt loam	7.44	0.22	0.007	0.047

As may be noted, the total range of variation for the twenty-five samples of Tama silt loam was within 0.06 pH unit; fifty per cent of the total number varied within 0.002 of a pH unit above or below the average as indicated by the probable error and two-thirds of the total number varied within 0.017 pH unit above or below the average as indicated by the standard deviation. The data secured with the other soils varied slightly more than this and were most variable in the case of the Marshall silt loam where the range of variation was 0.22 pH unit. Even with this soil, however, the probable error of the mean was not large, being only 0.007 pH unit.

In comparing the reliability of the different types of glass electrode for measuring the pH of soils, the potential of quadruplicate samples of each soil was determined by each of the four types of electrode, the electrodes being used simultaneously on each sample of soil. The results are shown in table II.

Table II — The pH of Quadruplicate Samples of Five Soils as Determined by Four Types of Glass Electrode

Sample number	Types of Glass Electrode			
	Modified Club Ag/Ag Cl	Reentrant	Modified Bulb quinhydrone	MacInnes-Dole
Tama silt loam				
1	5.03	4.98	5.06	5.09
2	5.09	4.99	5.01	4.77
3	5.06	4.99	5.03	5.01
4	5.04	4.99	5.06	5.04
Average	5.06	4.99	5.04	4.98

Table II — Continued.

		Carrington silt loam		
1	5.08	5.13	5.09	5.06
2	5.08	5.09	5.13	5.11
3	5.06	5.06	5.01	5.06
4	5.11	5.06	5.08	5.04
Average	5.08	5.09	5.08	5.07
		Shelby loam		
1	5.82	5.81	5.78	5.84
2	5.87	5.70	5.74	5.79
3	5.96	5.81	5.84	5.81
4	5.89	5.87	5.80	5.79
Average	5.89	5.80	5.79	5.81
		Grundy silt loam		
1	5.40	5.38	5.47	5.43
2	5.35	5.38	5.48	5.47
3	5.40	5.35	5.45	5.45
4	5.31	5.37	5.47	5.45
Average	5.37	5.37	5.47	5.45
		Marshall silt loam		
1	7.46	7.36	7.45	7.56
2	7.46	7.34	7.41	7.53
3	7.46	7.29	7.43	7.56
4	7.45	7.23	7.36	7.55
Average	7.46	7.30	7.41	7.55

In the case of the Tama silt loam, the modified bulb, silver-silver chloride electrode gave a slightly higher average pH value and the reentrant type of electrode gave a slightly lower average pH value than the other electrodes. In the case of the Carrington loam the reentrant type of electrode gave a slightly higher average pH value and the MacInnes-Dole membrane type gave a slightly lower average value than the other electrodes. The modified bulb, silver-silver chloride electrode gave the highest average pH value of the electrodes on Shelby loam and the modified bulb, quinhydrone type the lowest average value. In the case of the Grundy silt loam the modified bulb, quinhydrone electrode gave a higher average pH value than the other electrodes and the modified bulb and reentrant electrodes the lowest average pH values. On the Marshall silt loam the MacInnes-Dole membrane electrode gave the highest average pH value and the reentrant type the lowest average value. It appears that no one type of electrode gave consistently higher or lower results on the various soils than the other electrodes.

While making the determinations on the Marshall silt loam it appeared that the electrodes were not functioning the same as they had in the acid soils. Considerable drift occurred with all electrodes, and inasmuch as the drift in potential was rather large at times, the readings were taken at the point of apparent equilibrium. From two to eight minutes elapsed from the time the electrodes were immersed in the soil suspension until the readings were finally taken. In a later experiment it was found, however, that the potential became constant after approximately 15 minutes. The reason for the potential drift is not definitely known but this point is now being investigated.

In order to determine the extent of variation of the pH values obtained with the different electrodes, the total range of variation, the probable error of the mean, and the standard deviation of the items were calculated from the total number of pH values for each soil. These data are shown in table III.

Table III — The Variation in pH as Determined on Quadruplicate Samples of Each Soil by Four Different Types of Glass Electrode

Soil type	Range	Probable error	Standard deviation
Tama silt loam	0.11	0.006	0.036
Carrington loam	0.12	0.005	0.032
Grundy silt loam	0.17	0.019	0.056
SShelby loam	0.26	0.010	0.060
Marshall silt loam	0.33	0.016	0.098

It may be noted that the range of variation, the probable error of the mean and the standard deviation of the items as secured in this test are very similar to those secured in the previous test where a single electrode was used to determine the pH on twenty-five different samples of each soil. The range of variation of the data secured with the different electrodes was not appreciably wider than that to be expected in the normal distribution of the pH values obtained from a large number of samples of a homogeneous soil as determined by a single electrode. It may be concluded, therefore, that all four types of glass electrode employed in this test gave similar results with the soils studied.

During the progress of this investigation it was observed that certain electrodes were more desirable than others from a practical standpoint for various reasons other than their reliability and accuracy. The modified bulb, silver-silver chloride type of electrode was found most desirable because it is more rugged, and easier to construct and maintain than the other types.

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