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## APPENDIX II

### REPORT OF THE SOIL REACTION COMMITTEE ON THE INVESTIGATION OF THE GLASS ELECTRODE METHOD

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The Soil Reaction Committee of Commission II, which was set up at Budapest in 1929, reported its work on the Quinhydrone method for soil reaction in 1930 ("Soil Research," 1930, Volume 2, 77-139). Its Report and Recommendations were adopted at the Second International Soil Congress in Leningrad 1930 ("Soil Research," 1930, Volume 2, 141-144). At the Copenhagen Conference of the Second Commission of 1933 attention was drawn to the advantages of the glass electrode, especially in soils containing manganese oxides and therefore unsuited for the quinhydrone method. The Soil Reaction Committee was instructed to carry out a co-operative study of the glass electrode method in comparison with the quinhydrone method.

It was decided to use for the study 18 soil samples from the series originally prepared in 1929 and described in the 1930 Report, together with three American soils, selected by Professor R. Bradfield as being manganeseiferous and therefore subject to large quinhydrone errors. Quinhydrone measurements were made on these soils in the way described in the 1930 Report, voltage readings being taken rapidly (between 8 and 15 seconds at different laboratories) and again at 60 seconds after adding the quinhydrone. The latter readings were accepted as standard for the quinhydrone method for the 12 soils without appreciable drift, and the rapid readings were accepted as the best available quinhydrone figures for the 9 soils in which the potential changed rapidly within the first half minute after adding quinhydrone.

Quinhydrone readings at a series of intervals after adding the quinhydrone were given for the original soil samples in the 1930 Report and similar data are given below for the three new American soils (Table III).

Two forms of glass electrode were employed, viz. :—

- Type 1.* The Kerridge pattern with a re-entrant thin glass membrane within a stout bulb, as used for soils by S. G. Heintze (*J. Agric. Sci.*, 1934, 24, 28-40).
- Type 2.* The MacInnes-Dole pattern as used for soils by R. Bradfield ("Soil Research," Vol. 3, 1933, 222-246). A thin membrane of "Corning" glass is sealed over the end of a stout soft glass tube.

The following summary gives the names and Institutes of the collaborators, the types of glass electrode and electrical measuring

apparatus employed, and the index letter under which the results are presented in the following Tables.

**Gr.** *Dr. Jac. van der Spek, Groningen, Holland.*

MacInnes glass electrode, Pye galvanometer (sensitivity  $10^{-7}$  amps. per scale division), Wolff potentiometer and valve amplifier.

**R.** *Miss S. G. Heintze, Rothamsted, England.*

Kerridge and MacInnes glass electrodes, used with Philips Electrometer Triode amplifying valve, as described by S. G. Heintze (*loc. cit.*), and simple Cambridge potentiometer.

**C.** *Prof. S. Touborg-Jensen, Copenhagen, Denmark.*

MacInnes glass electrode, Wolf potentiometer and Lindemann electrometer as null-point indicator. Two Veibel electrodes were used as reference electrodes.

**BP.** *Dr. G. di Gleria, Budapest, Hungary.*

MacInnes glass electrode and quadrant electrometer.

**B.** *Dr. M. Trénel, Geologische Landesanstalt, Berlin, Germany.*

Special As-free Schott-Jena glass in MacInnes' pattern, E. Leybold (Cologne) valve potentiometer and Trénel acidimeter.

**O.** *Prof. R. Bradfield and Mr. C. F. Simmons, Columbus, Ohio, U.S.A.*

Kerridge and MacInnes glass electrodes, with a Lindemann quadrant electrometer as null point instrument, and a Leeds and Northrup type K potentiometer. As reference standards saturated calomel electrodes were used.

#### QUINHYDRONE RESULTS

Table I gives pH values for readings made as rapidly as possible after adding quinhydrone, and again at 60 seconds after the addition. The times for rapid readings varied from 8 to 15 seconds. Dr. di Gleria's final figures are for 300 seconds instead of 60 seconds. For convenience in comparison with the glass electrode figures, the soils in Table I are grouped into two sets: viz. without and with appreciable drift in potentials between the initial and the final readings.

#### GLASS ELECTRODE RESULTS

Table II gives the pH values by the glass electrode method together with the difference between the quinhydrone and the glass electrode values. For the purpose of this comparison the 1930 recommendations of the Soil Reaction Committee were followed, i.e., readings at 60 seconds for soils without quinhydrone drift and readings at 8-15 seconds for soils with considerable drift.

The discrepancies between the glass electrode and the quinhydrone electrode would, of course, be greatly increased by using the 60 second quinhydrone readings for soils with large drifts.

In comparing the values obtained by different workers by the same method it should be remembered that 18 of the 21 samples were prepared and distributed in 1929, and that the changes in pH and salt content on storage for five years may have varied considerably from laboratory to laboratory. Dr. Trénel found that the quinhydrone pH values in 1935 were appreciably different from those of 1930 when the measurements were made in water, though the changes were much less for measurements made in 0.1 N.KCl. With these qualifications the six sets of glass electrode measurements agree fairly satisfactorily. Comparison of the two methods at a single laboratory generally gave much closer agreement. Thus, for the 12 soils free from quinhydrone drift the maximum discrepancies between the glass and quinhydrone electrodes (60 second values) were 0.13 at Rothamsted, 0.11 at Groningen and 0.09 at Copenhagen. Wider differences were obtained at

Ohio, Budapest and Berlin. For the 9 drifting soils the maximum differences at Groningen and Berlin between glass electrode and quinhydrone electrode at 10 seconds were 0.26 and 0.34 respectively. The wider discrepancies at the other laboratories may be due to greater disturbances by manganese oxides by longer contact or more intimate mixing. The possibility of obtaining such large errors shows the danger of relying on quick readings to overcome the quinhydrone error.

TABLE I  
pH values with the quinhydrone electrode  
Rapid QH readings  
One minute QH readings

Laboratory: Time of reading (sec.)	Rapid QH readings				One minute QH readings							
	R.	Gr.	C.	O.	BP.	B.	R.	Gr.	C.	O.	BP.	B.
	15	10	15	16-20	8	10	60	60	60	60	300	60
	A. Soils showing no drift in QH measurements.											
Berlin I	4.63	4.53	4.44	—	4.75	—	4.60	4.52	4.46	—	4.73	—
Berlin II	3.85	3.85	3.87	—	3.74	—	3.80	3.84	3.76	—	3.72	—
Berlin III	4.00	4.00	3.79	—	4.02	—	4.00	3.99	3.78	—	4.03	—
Groningen A	5.82	5.85	5.62	5.74	5.98	5.35	5.72	5.83	5.55	5.76	6.08	5.30
Groningen C	6.83	7.01	6.50	6.74	6.30	6.25	6.83	6.83	6.55	6.70	6.25	6.36
Lyngby C	7.24	7.38	—	—	7.08	7.00	7.29	7.40	—	—	7.13	7.20
Lyngby D	7.16	7.26	—	—	—	7.06	7.16	7.31	—	—	6.61	7.15
Lyngby E	4.73	4.94	—	—	4.69	4.62	4.75	4.93	—	—	4.78	4.54
Rothamsted V	5.06	5.16	4.89	5.10	5.21	5.15	5.08	5.16	4.96	5.10	5.30	5.10
Sigmond C	5.34	5.61	5.57	5.46	5.95	6.24	5.36	5.58	5.59	5.52	5.96	6.35
Sigmond D	7.87	7.92	7.78	7.74	7.68	7.80	8.05	7.90	7.81	7.84	7.65	7.96
Sigmond E	9.38	9.46	9.40	9.04	8.90	9.65	9.44	9.51	9.36	9.06	8.80	9.62
	B. Soils showing drift in QH measurements											
Groningen B	7.14	7.06	6.80	7.16	6.81	6.55	7.60	7.36	7.11	7.59	6.99	7.12
Rothamsted I	6.67	6.09	6.19	6.83	6.22	6.18	7.19	6.74	6.62	7.24	6.30	6.18
Rothamsted III	7.88	7.52	7.53	7.70	8.01	7.60	8.40	7.93	7.75	8.05	7.92	8.15
Scherf B	8.21	8.25	7.91	8.01	8.01	8.10	8.65	8.59	8.16	8.18	8.18	8.40
Scherf C	7.60	7.51	7.18	7.47	7.58	7.50	7.80	7.87	7.58	7.62	7.36	7.78
Scherf D	6.19	5.92	5.92	6.02	6.55	6.15	6.23	6.25	6.05	6.11	6.56	6.08
Bradfield 1	6.00	5.85	5.32	6.10	6.39	6.12	6.56	6.12	6.10	6.72	6.38	6.22
Bradfield 2	6.84	5.74	6.02	7.32	4.86	5.64	6.74	6.89	6.85	7.61	6.22	5.74
Bradfield 3	7.48	6.50	—	7.94	6.67	—	7.31	6.73	—	8.05	7.23	—

TABLE II  
*pH* values with the glass electrode, and comparison between glass electrode and *QH* values

Laboratory:	Glass electrode <i>pH</i> values			Difference <i>QH</i> —Glass electrode		
	R.	Gr.	O. BP.	R.	Gr.	O. BP.
A. Soils showing no drift in <i>QH</i> measurements (one minute <i>QH</i> readings)						
Berlin I	4.60	4.47	4.42	—	4.58	—
II	3.83	3.77	3.85	—	3.72	—
III	3.99	3.98	3.76	—	3.91	—
Groningen A	5.72	5.76	5.55	5.78	6.17	5.38
C	6.96	6.94	6.61	7.08	6.91	6.35
Lyngby C	7.23	7.32	—	—	7.27	7.06
D	7.20	7.23	—	—	6.88	6.98
E	4.73	4.90	—	—	5.10	4.58
Rothamsted V	5.04	5.09	4.87	5.03	5.47	4.93
Sigmond C	5.34	5.55	5.50	5.45	5.86	6.08
D	8.03	7.85	7.78	7.91	7.66	7.70
E	9.86	9.60	10.07	9.80	8.98	9.91
B. Soils showing drift in <i>QH</i> measurements.						
Groningen B	7.07	7.02	7.14	7.16	6.61	6.88
Rothamsted I	5.99	6.04	6.05	5.99	6.10	6.01
III	8.00	7.62	7.73	7.72	7.18	7.42
Scherf B	8.13	8.14	8.18	8.03	7.79	8.06
C	7.57	7.59	7.42	7.43	7.31	7.40
D	5.92	6.18	5.79	5.95	6.09	6.03
Bradfield I	5.71	5.88	5.39	5.72	6.10	5.78
2	5.55	5.56	5.38	5.51	5.78	5.40
3	6.32	6.46	—	6.35	6.41	—

  

<i>QH</i> —Glass electrode for <i>QH</i> values at, —				
15 sec.	1s.	15s.	16-20s.	8s. 10s.
+0.07	+0.04	-0.34	0.00	+0.20
+0.68	+0.05	+0.14	+0.84	+0.12
-0.12	-0.10	-0.20	-0.02	+0.83
+0.08	+0.11	-0.27	-0.01	+0.05
-0.03	-0.08	-0.24	+0.03	+0.27
+0.27	-0.26	+0.13	+0.07	+0.46
+0.29	-0.03	-0.07	+0.38	+0.29
+1.29	+0.18	+0.64	+1.81	+0.92
+1.16	+0.04	—	+1.59	+0.26

## OTHER DETERMINATIONS

Three laboratories extended the 1930 work to the three highly manganiferous soils from the United States. Table III shows that the drift in these soils amounts to about a pH unit. At Groningen, but not at Rothamsted or Berlin, the most rapid reading agreed with the glass electrode value.

TABLE III  
*pH measurements of highly manganiferous soils from U.S.A.*  
Mean values of duplicates

Soil	Institute	Glass Electrode	QH readings after Seconds				
			10-15	30	60	300	900
No. 1 Greenville	Groningen	5.88	5.85	5.95	6.12	6.82	6.84
	Rothamsted	5.71	6.00	6.24	6.56	6.64	—
	Berlin	5.78	6.12	6.13	6.22	—	—
No. 2 Alabama	Groningen	5.56	5.74	6.42	6.89	6.77	6.47
	Rothamsted	5.55	6.84	6.91	6.74	6.35	—
	Berlin	5.40	5.64	5.70	5.74	—	—
No. 3 Honolulu	Groningen	6.46	6.50	7.13	6.73	6.17	5.80
	Rothamsted	6.32	7.48	7.51	7.31	6.49	—

Professor Tovborg-Jensen illustrated the extent of the interaction between quinhydrone and soil by making glass electrode measurements on comparable suspensions with and without quinhydrone (Table IV). There was no effect due to quinhydrone in the soils which rapidly gave stable quinhydrone potentials but large discrepancies in the soils showing drifts.

TABLE IV  
*Glass electrode measurements on soils with and without quinhydrone. (Tovborg-Jensen's data)*  
Soils without QH drift      Soils with QH drift

	Soil			Soil	
	Soil	+ QH		Soil	+ QH
Berlin I	4.38	4.40	Groningen B	7.14	7.69
" II	3.73	3.75	Rothamsted I	6.05	7.09
" III	3.66	3.66	" III	7.76	8.55
Groningen A	5.51	5.68	Scherf B	8.24	8.60
" C	6.65	6.73	" C	7.37	7.85
Rothamsted V	4.90	4.99	Bradfield 1	5.23	7.30
Sigmond G	5.46	5.51	" 2	5.38	6.64
" D	7.85	7.87			
" E	10.13	9.08 (not stable)			

Miss S. G. Heintze and Prof. R. Bradfield compared the two types of glass electrode on the same suspension. It is unnecessary to tabulate the results for with 16 soils at Rothamsted and 11 soils at Ohio the difference was 0.05 or less and for 5 soils at Rothamsted and 4 soils at Ohio the difference was 0.05-0.12. Professor Bradfield notes that care had to be taken with the Kerridge type to prevent entrapping of air-bubbles and that leakage seemed to be a little more serious with the MacInnes type due to its high resistance.

Dr. di Gleria, however, failed to get satisfactory stable potentials with the Kerridge type of electrode.

## SUMMARY

The glass electrode method proved satisfactory on all soils tested.

The agreement between the quinhydrone and the glass electrode methods is satisfactory for soils without quinhydrone drift, i.e., for soils which give closely similar potentials about 10 seconds and 60 seconds after adding the quinhydrone. For soils with quinhydrone drift the glass electrode results are similar to those measured by quinhydrone after about 10 seconds. Such rapid measurements by quinhydrone are not reproducible and for soils with large quinhydrone drifts the pH values should be measured by the glass electrode.

In order to decide whether the quinhydrone method is appropriate, determinations should always be made rapidly (preferably within 10 seconds) and again after 60 seconds, and the latter readings used when the drift is small.