XXXVIII. THE USE OF THE HYDROQUINHYDRONE ELECTRODE FOR p_H DETERMINATION IN THE FLUIDS OF THE ORGANISM.

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IN the beginning of the year 1925 I began the investigation of the applicability of Biilmann's [1921] quinhydrone electrode to determine the p_H of serum, cerebrospinal fluid and blood. There has since appeared a number of papers showing that there is a divergence of opinion as to the suitability of this electrode for these purposes. The different experiences have recently been reviewed by Mislowitz [1926] who adheres to his opinion, expressed earlier [1925], that the quinhydrone electrode can be employed to determine the p_H of blood.

My first measurements with a quinhydrone electrode gave unsatisfactory results. The potential was quite unstable. By diluting the serum several times with physiological saline solution I obtained somewhat better results. However, having made several measurements which did not give consistent results, I gave up the quinhydrone electrode and tried the hydroquinhydrone electrode, also invented by Biilmann [1921]. The difference between the quinhydrone and the hydroquinhydrone electrodes is that, instead of quinhydrone, an excess of a quinol (hydroquinone) and quinhydrone mixture is used. Biilmann and Lund [1921] recommend 0.1 g. of quinhydrone and 1 g. of quinol for 15 cc. of fluid. Part of this mixture is dissolved, the rest remains as a precipitate. The platinum wire of the electrode must be almost completely immersed in the precipitate.

The reaction in such an electrode consists in the transformation of stable quinhydrone into stable quinol:

The electromotive force of the chain: Pt/quinol, quinhydrone, solution A/KCl/solution A, H_2 /Pt, according to Biilmann and Lund [1921] = 0.6179 volts at $t = 18^\circ$, instead of 0.7042 in the case of the quinhydrone electrode.

With serum the potential became rapidly stable and the values obtained for p_H were consistent. They differed, however, from those obtained with the hydrogen electrode (see Table I).

Table I.

Pig-serum. $t = 22^\circ$.

No.	Hydrogen electrode				Hydroquinhydrone electrode					
	Volts	Average	p_H	Average	Volts	Average	p_H	Average	Δp_H	p'_H
1	0.708*		7.93		-0.068†		7.67			
2	0.707	0.7075	7.91	7.92	-0.070	-0.687	7.70	7.68	0.19	7.87
3					-0.068		7.68			

Ox-serum. $t = 18^\circ$.

1	0.691		7.76		-0.066		7.63			
2	0.692	0.693	7.78	7.79	-0.067	-0.0667	7.65	7.64	0.18	7.82
3	0.695		7.83		-0.067		7.65			

* These values are for chain: Pt/H₂, serum/KCl/satur. KCl, Hg₂Cl₂/Hg.† These values are for chain: Pt/quinol, quinhydrone, serum/KCl/satur. KCl, Hg₂Cl₂/Hg.

After satisfying myself that my determinations of the p_H of pig-serum with the hydrogen electrode were correct, I repeated the measurements on ox-serum with both electrodes. I again obtained with the hydroquinhydrone electrode a similar difference from those obtained with the hydrogen electrode. Having previously tested this electrode upon standard solutions with $p_H < 7$ and found it to be very exact, I proceeded to ascertain its behaviour with slightly alkaline but well buffered solutions.

For this purpose I prepared a series of Sørensen's phosphate solutions and determined their p_H values with a hydrogen, a quinhydrone and a hydroquinhydrone electrode respectively (see Table II).

I obtained, as seen from Table II, differences between p_H determined with the hydroquinhydrone electrode and the quinhydrone electrode, increasing as the fluid became more alkaline.

Upon the ground of these determinations I arrived at an empirical formula for the correction to be applied when using the hydroquinhydrone electrode on a fluid with $p_H > 7$, namely, $\Delta p_H = 0.24 \times 2^{p_H - 7} - 0.21$.

If we take into consideration $p_H = 7.00$ – 8.00 , that is the widest limits in which p_H can balance in the serum, blood, or cerebrospinal fluid of men and animals, then the rectification Δp_H will vary from 0.03 to 0.21. For body fluids Δp_H will not on the average exceed 0.13.

These corrections are introduced in the tables, and it will be seen that the values with the hydrogen and the hydroquinhydrone electrodes then become almost identical.

I am now working on the theoretical confirmation of the rectification, Δp_H , introduced by me, as was done by La Mer and Parsons [1923] for the aberrations of the quinhydrone electrode in alkaline solutions.

A hydroquinhydrone electrode possesses many advantages over a hydrogen electrode for determining the p_H in serum, blood, etc., both as to simplicity and rapidity in making determinations. Further, there are many conditions under which the hydrogen electrode cannot be used at all.

Table II.

No.	Hydrogen electrode			Quinhydrone electrode			Hydroquinhydrone electrode			
	Volts	Average	p_H average	Volts	Average	p_H average	Volts	Average	p_H average	Δp_H average
Mixture of equal volumes of $M/15$ Na_2HPO_4 and $M/15$ KH_2PO_4 ; according to Sørensen $p_H=6.80$.										
1	0.634			0.0680			-0.0180			
2	0.636	0.6347	6.79	0.0680	0.0680	6.81	-0.0185	-0.0182	6.81	0.01
3	0.634			0.0680			-0.0180			
Mixture of 61 volumes of Na_2HPO_4 and 39 volumes of KH_2PO_4 , with $p_H=7.00$.										
$t=18^\circ$.										
1	0.646			0.0570			-0.0260			
2	0.648	0.647	7.00	0.0570	0.0570	7.00	-0.0270	-0.0267	6.97	0.03
3	0.647			0.0570			-0.0270			
Mixture of 80 vol. of Na_2HPO_4 and 20 vol. of KH_2PO_4 , with $p_H=7.36$.										
$t=19^\circ$.										
1	0.669			0.0345			-0.0460			
2	0.671	0.670	7.38	0.0345	0.0347	7.38	-0.0465	-0.0465	7.28	0.10
3				0.0350			-0.0470			
Mixture of 87 vol. of Na_2HPO_4 and 13 vol. of KH_2PO_4 , with $p_H=7.60$.										
$t=19^\circ$.										
1	0.683			0.0230			-0.0555			
2	0.680	0.681	7.56	0.0230	0.0232	7.56	-0.0560	-0.0557	7.43	0.13
3	0.680			0.0235			-0.0555			
Mixture of 60 vol. of borate and 40 vol. of 0.1 N HCl , with $p_H=8.27$.										
$t=18^\circ$.										
1	0.719			-0.0150			-0.0850			
2	0.720	0.719	8.25	-0.0160	-0.0155	8.26	-0.0850	-0.0855	7.98	0.275
3	0.718			-0.0155			-0.0855			
Mixture of 84 vol. of borate and 16 vol. of 0.1 N HCl , with $p_H=8.99$.										
$t=18^\circ$.										
1	0.760			-0.0570			-0.1150			
2	0.762	0.7607	8.97	-0.0560	-0.0560	8.96	-0.1150	-0.1145	8.49	0.475
3	0.760			-0.0550			-0.1135			

I, therefore, made parallel determinations of the p_H of serum, blood and cerebrospinal fluid with the hydroquinhydrone and hydrogen electrodes. These are set forth in Table III.

We see that after introducing the correction for the hydroquinhydrone electrode, the results obtained with this electrode and those obtained with the hydrogen electrode, given in Table III, are almost identical. I made measurements in the following way: I poured from 1.5 to 3 cc. of physiological salt solution into a small electrode vessel and added a mixture of dry quinhydrone and quinol in quantities more or less such as I have mentioned above; I stirred the contents of the small vessel, poured in 1.5 cc. of blood—that is, diluted it from 1 : 1 to 1 : 2—stirred the contents of the vessel well and after about three minutes read the potential of this electrode. The more the blood is diluted, the better and the more rapidly the potential of the electrode becomes

stable. The relative amounts of quinhydrone and quinol need not necessarily be exactly those recommended by Büllmann. After one has made several measurements, one can judge sufficiently correctly by eye, but the greatest part of the short platinum wire must be immersed in the precipitate.

Table III.

No.	Hydrogen electrode			Hydroquinhydrone electrode				
	Volts	Temp.	p_H	Volts	Temp.	p_H	Δp_H	p'_H
<i>Human serum.</i>								
1	0.6855	20	7.63	-0.0625	20	7.51	14.5	7.655
2	0.6820	18	7.61	-0.0580	18	7.50	14.5	7.645
3	0.6810	18	7.59	-0.0550	18	7.45	13	7.58
4	0.6820	20	7.56	-0.0560	20	7.40	12	7.52
5	0.6820	19	7.59	-0.0560	19	7.43	13	7.56
<i>Cerebrospinal fluid.</i>								
1	0.6910	20	7.72	-0.0640	20	7.53	15	7.68
2	0.6900	20	7.70	-0.0625	19.5	7.51	15	7.66
3	0.6830	20	7.58	-0.0615	20	7.48	14	7.62
4	0.6840	18	7.64	-0.0550	18	7.45	13	7.58
5	0.6850	18.5	7.65	-0.0580	18	7.50	14.5	7.645
<i>Rabbit blood.</i>								
1	0.678	17.5	7.55	-0.050	17.5	7.38	0.12	7.50
2	0.671	18	7.42	-0.048	18	7.33	0.11	7.44
3	0.6805	17.5	7.59	-0.054	17.5	7.45	0.13	7.57
4	0.673	17	7.48	-0.046	16.5	7.35	0.115	7.465
5	0.683	18.5	7.62	-0.056	18.5	7.46	0.13	7.60
<i>Human blood.</i>								
1	0.669	18	7.39	-0.045	18	7.28	0.10	7.38
2	0.675	18.5	7.47	-0.047	18	7.31	0.11	7.42
3	0.668	18	7.37	-0.043	18	7.25	0.10	7.35
4	0.674	18	7.45	-0.050	18.5	7.34	0.115	7.455
5	0.678	18.5	7.53	-0.053	18	7.42	0.125	7.545

Making several measurements on the same blood, for instance that of the rabbit, diluted with 0.85 % NaCl solution, I obtained with the hydroquinhydrone electrode almost identical values, for instance, 7.52, 7.52, 7.54. The quinhydrone electrode in the case of serum as in that of blood gave improbable and drifting results.

I attempted too, to use with blood the quinoquinhydrone electrode also invented by Büllmann [1921] for which a mixture of quinone and quinhydrone is employed. The reaction consists in the transformation of stable quinone into stable quinhydrone:

This electrode is unsuitable for blood as it has a very drifting potential. It is also inferior to the hydroquinhydrone electrode for serum.

I have found that the quinhydrone, hydroquinhydrone and especially the quinoquinhydrone electrode, as pointed out by La Mer and Parsons, cannot be used for fluids with $p_H > 9$, because the quinol oxidises too rapidly.

I have tried the gold electrode recommended by Dixon and Quastel [1923], Corran and Lewis [1924] and Mislowitzer [1925] but have not found it satisfactory. Mislowitzer [1926] has also abandoned it in favour of platinum.

SUMMARY.

To determine the p_H in physiological fluids such as, for instance, serum, plasma, blood, cerebrospinal fluid, etc., the hydroquinhydrone electrode is more exact and simpler than the hydrogen electrode and more generally applicable and, if a correction varying with the alkalinity of the solution is applied, affords results which agree with those obtained with the hydrogen electrode.

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