Precise Potentiometric Titrations Using Glass Electrodes

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Summary Precise potentiometric titrations may be made using high resistance glass electrodes: potentials are measured and interpreted on a routine basis to ± 0.01 mV, a precision equal to that attainable with hydrogen electrodes.

THE reasons for the wider use of glass electrodes than of either hydrogen or quinhydrone electrodes to measure hydrogen ion activities or concentrations are well known.[1] In 1955 it was shown[2] to be possible to measure and interpret the potentials of e.m.f. cells with low resistance (*ca.* 0.5 MΩ) glass electrodes with a precision equal to that attained in the best work with hydrogen electrodes (± 0.01 mV).[3] However, low resistance glass electrodes suffer from the disadvantages of being bulky, fragile and, most recently, commercially unavailable. Most workers have preferred to use high resistance ($50 < R < 500$ MΩ) glass electrodes in spite of the lower precision (± 0.1 mV) attainable even with the best commercial pH meters.

TABLE 1

Glass	Electrodes External ref.	Measuring circuit (Reading)
Electronic Inst. Ltd GHS/33B	Ag/AgCl (thermal–electrolytic preparation)	Vibron electrometer 62A, backed off with Cropico vernier Potentiometer P10; final 1mV displayed on Hitachi 159 recorder.
		(Oxford)
Activion 17SR	Ag/Ag+ (electrolytic preparation)	Solartron digital voltmeter LM1867C with impedance converter (Analog Devices operational amplifier 311K; Coutant power supply OA10)

However, a more precise determination of hydrogen ion concentrations is essential, for example, in studies of

equilibria involving ternary (mixed, protonated,[4] or hydroxo) complexes, or of binary mononuclear complexes at high hydrogen ion concentrations.

Recently, our groups have independently developed routine methods of potentiometric titration in which a

of the glass electrode, fluctuations in the asymmetry and stress potentials are <0.01 mV within the time span of the titrations. A typical determination of $E_{\ominus}$ for the electrochemical cell at Oxford gives a standard deviation of ± 0.01 mV (on ten points) as compared with ± 0.1 mV from

TABLE 2

$\bar{j}$ Range[a]	No. of points	Medium	10^4 K_1/l mol^{-1}	Ref.
0.4—0.6	5	H_2O	5.697 ± 0.006[b]	Reading
			5.705	10
			5.711	10
0.1—0.8	12	3M-NaClO$_4$	10.280 ± 0.007	Oxford
			10.33[c]	11
			10.28[d]	12
			10.35	13

[a] $\bar{j} = [HA]/A = [HA]/([A^-] + [HA])$. [b] Confidence limits, $\pm \sigma$. [c] $A \leqslant 1.0M$. [d] $A \leqslant 0.05M$.

precision of ± 0.01 mV is achieved with cells incorporating high resistance glass electrodes, using the standard commercial equipment indicated in Table 1. Comparable precisions are achieved by using the transfer technique[2] (at Reading) and a potentiometric titration technique[5] (at Oxford) which avoids any movement of the glass electrode between its calibration and use.[6] Both groups use solutions under an atmosphere of purified and appropriately presaturated nitrogen and also use analyses based upon linear Gran plots.[7,8] The transfer technique is designed to compensate for small changes in asymmetry potential. However, the precision and internal consistency of the Oxford technique indicates that, in the absence of movement

a similar titration using a Radiometer pH meter 4. The calculation of $E^{\ominus}$ is performed by the program GRAN, using procedure LINEFITTING.[9] The use of properly weighted data is demonstrably superior to a simple least squares treatment.

Typical determinations of the protonation constant K_1 of the acetate ion at 25.00 °C are in Table 2.

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