

**POISED SOLUTIONS FOR VERIFICATION OF REDOX ELECTRODE BEHAVIOR<sup>1</sup>**

There are severe theoretical limitations to the interpretation of redox potentials measured by electrodes in natural water samples (Hostettler, 1984; Morris and Stumm, 1967; Stumm, 1966; Thorstenson, 1984). Despite this, such measurements can be useful as qualitative indicators of redox conditions and continue to be widely reported. Reliable electrode potential measurements must be made with attention to many practical difficulties. These can be satisfactorily addressed by careful, reproducible pretreatment of the measuring (working) electrode (Lindberg, 1983) followed by verification of the electrode behavior. Information regarding solutions useful for verification of redox electrode behavior is very widely scattered in the literature and not easily recovered. We have assembled some of this information and tried several poised solutions under many conditions. This paper reports our recommendations in order to facilitate more consistent and correct practice.

Solutions that resist change in their Eh are called poised (Clark, 1923). An appropriate solution for verifying the

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behavior of apparatus for Eh measurement is based on a redox couple that is: 1) reversible, 2) labile to electron transfer, and 3) moderately soluble. The solution must also 4) be easily formulated in a condition which is partially reduced to an accurately known degree, 5) be stable over hours or days, and 6) have a known, thermodynamically interpretable Eh which is close to that of the sample. For general applications, it is desirable to have the solution in the half-reduced/half-oxidized state where its poisoning capacity will be at a maximum (Nightingale, 1958). Near this point, a two-electron transfer offers greater poisoning capacity than a one-electron transfer (Nightingale, 1958).

Solutions of quinhydrone meet the above conditions and have long been used to verify the performance of a Pt measuring electrode. Quinhydrone is a readily available solid that consists of approximately equal proportions of quinone (the oxidized form) and hydroquinone (the reduced form). A few grams will saturate 100 mL of pH buffer resulting in a solution that exhibits stable measured redox potentials (Jones, 1966). Because the standard potential for the quinone-hydroquinone couple is +699 mV, the Eh of a pH 4 solution of quinhydrone is +462 mV and that of a pH 7 solution +285 mV at 25 °C.

The most widely used redox standard is an equimolar solution of ferric and ferrous cyanide. Among geochemists, at least, a solution that is 3.33 mM  $K_3Fe(CN)_6$  and 3.33 mM  $K_4Fe(CN)_6$  in 0.10 M KCl is known as the ZoBell solution (ZoBell, 1946). Nordstrom (1977) has studied the thermodynamics of the ZoBell solution in detail. His equation for the temperature dependence of its Eh gives +430 mV at 25 °C. The ZoBell solution is subject to

oxidation and should be refrigerated and used within a few days of preparation.

A solution of iron salts that gives exceptionally stable measured redox potentials is 0.100 M  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  and 0.100 M  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$  in 1.00 M  $\text{H}_2\text{SO}_4$ . In our laboratory, we call this the "Light solution" because it was proposed by Light (1972). It is now recommended for standard practice by the ASTM (1979). The Light solution has an Eh of +675 mV at 25 °C and is stable for many months without special precautions.

There are other formulations with useful properties that have not been used by geochemists because one conjugant must be prepared in a separate step and/or cannot be stored or easily dispensed. For example, Smith and Banick (1959) used poised solutions composed of vanadate and vanadyl ions in sulfuric acid solution. A portion of a  $\text{VOCl}$  solution was oxidized to vanadate with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (the excess oxidant was destroyed by boiling). Equal portions of the two solutions were combined to form a poised solution. The Eh's are quite high: ranging from +0.910 V in 0.10 F  $\text{H}_2\text{SO}_4$  to +1.226 V in 6.0 F  $\text{H}_2\text{SO}_4$ .

Hydroquinone, ZoBell, and Light solutions are appropriate when electrode measurements are to be made on materials from oxidizing environments. However, poised solutions with low redox potentials are desirable to verify electrode performance when measurements are to be made in reducing systems. Unfortunately, no such convenient solutions exist and recourse has been made to unsatisfactory, makeshift formulations. For example, Barrio-Lage et al. (1986) reported to have calibrated their redox potential

measurement apparatus at 0 mV with a pH 7 buffer solution supersaturated with hydroquinone. The concentration ratio of reduced to oxidized forms of such a solution will differ from one to some unknown degree which depends on the kinetics of oxidation of hydroquinone by dissolved oxygen and the relative solubilities of quinone and hydroquinone. When we measure the redox potential of such a solution we observe an Eh of approximately +220 mV. This corresponds to a hydroquinone/quinone concentration ratio between 10 and 100. Also redox and acid/base reactions of the hydroquinone necessary to insure saturation may exceed the capacity of common buffer solutions. The result is lower pH's and higher Eh's than intended.

Poised solutions with low redox potentials and the ideal characteristics stated above can only be obtained when work is done under a strictly anoxic atmosphere. Under these circumstances, we have found redox indicator dyes make suitable poised solutions. They are available containing a variety of functional groups and spanning a wide range of standard potentials (Bishop 1972). They have Eh-pH dependent colors, moderate solubility, and, usually, low toxicity. For example, we have found that a 5 mM solution of indigo carmine is a convenient and reliable solution when used in an inert-atmosphere glove box. It can be reduced by bubbling  $H_2$  over Pd coated ceramic beads in a chromatography column. The oxidized and reduced forms can be mixed in known proportions and pH adjusted to achieve solutions poised at potentials from +100 mV to -200 mV. The theoretical redox potential of the solution can be calculated with the

following form of the Nernst equation

$$E_h = E^{\circ'} + (RT/2F)\ln(C_o/C_r) + (RT/2F)\ln([H^+]^2 + K_{r1}[H^+])$$

where  $E^{\circ'}$  is the formal potential, +291 mV, and  $K_{r1}$  is the acid dissociation constant for the first hydroxyl group of the reduced form,  $10^{-7.4}$  (Bishop, 1972).

Poised solutions with low redox potentials have been used widely in the study of biochemical electron transfer and so the biochemical literature contains a great deal of useful information regarding redox poisoning. In general, biochemists have also relied on redox indicator dyes (e.g. Loach, 1966; Swartz and Wilson, 1971) but many biochemicals have also been tried; for example amino acids, porphyrins, and flavins.

Finally, three caveats deserve mention. First, a redox poised standard such as the Light solution is formulated to give constant, reproducible electrode potentials which are independent of the measuring electrode material and the condition of its surface. Erratic inter- and intra-electrode behavior will be more apparent when the apparatus is used to make measurements in less ideal systems (Jacob, 1970; Lindberg, 1983). Second, measuring electrodes may exhibit a "memory effect" especially after soaking in the strongly poised solutions recommended herein. To obviate this problem, Lindberg (1983) suggested using the poised solution to verify electrode performance only after taking the sample measurement. This is defensible but inefficient and we have found that using a poised standard solution with a potential similar to that expected of the sample

and copious rinsing of the measuring electrode adequately minimizes the memory effect. Third, measured redox potentials are influenced by many factors that should not just be concealed by calibration. The poised solution should only be used to verify that the Eh measurement apparatus is sensitive and reading within approximately 30 mV of the expected value. If it fails this, the measuring electrode should be reconditioned, the reference electrode checked, etc. until the apparatus is working properly. A constant correction factor should be applied only under exceptional circumstances.

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