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New perspective on the powers and limitations of potentiometric redox measurements, a possible game changer

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The redox potential (Eh) is a master variable affecting speciation and fate of nutrients and pollutants in aqueous environments. To date, direct potentiometric measurements using redox electrodes are the only viable means of monitoring Eh in-situ and continuously. While some scholars indicated the quantitative value of this direct Eh measurement, many have argued that because there are often discrepancies between the measured Eh and the measured speciation of redox active species in solution, the electrode measurements can be regarded as qualitative at best. The ambiguity regarding the quantitative power of potentiometric Eh measurements has led many to disregard this important analytical tool. The question is raised – are there environments in which redox electrodes give a more reliable representation of the redox state than others? We investigated this question in a simplified system of solubilized Fe in different concentrations and various ratios of FeCl₃ to FeSO₄. HCl and KCl were added to achieve different pH value (in the range of 2-4) and ionic strength levels (10-100 mM). The solutions were maintained stirred and were monitored continuously and simulatenously using 7 permanently installed redox electrodes with a data logger. The electrode readings were compared with the Eh calculated by external measurement of Fe speciation and the known solution inputs. In the initial solution, where only the ferrous iron form was added, a standard deviation of ~10mV was found between the electrodes used in this study; additions of Ferric iron to these solutions led to a decrease in standard deviation between electrodes down to ~2mV and concurrently to a convergence between electrode readings and the Nernst-based calculated Eh. The increased deviation in low ferric iron concentrations occurred regardless of the measuring device or if an external reference electrode was used. These findings suggest that potentiometric measurements have an effective range for which they can be used, which has been widely overlooked in the literature. We examined different indices to define the effective range. Using the standard deviation as the index of the effective range, it was determined that in the tested solutions deviations increased when Fe⁺³ molar activity was <20 nM at an ionic strength of 10-20mM; but the rise occurred at a lower value (<5nM) in solutions with ionic strength ~100mM. The increased effective range at higher ionic strength points towards electron shuttling as a possible effector of the electrode range; if so, it is postulated that in natural systems, electron shuttling by organic matter may greatly increase electrode effective range. We believe that once the understanding that potentiometric redox measurements have an effective range is further established and explored it may be a game changer which will promote both the development of methods to define the effective range and

technical improvements to increase electrode effective range so that potentiometric redox measurements can be more widely utilized as a quantitative tool.