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Comments on "Calibration of a chalcogenide glass membrane ion-selective electrode for the determination of free Fe^{3+} in seawater: I. Measurements in UV photooxidised seawater" by De Marco and Mackey (Marine Chemistry 68 (2000) 283–294) [☆]

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De Marco and Mackey have attempted to determine the low ambient free metal ion concentrations in seawater using ion-selective electrodes (ISEs). Their attempts are to be applauded as it would clearly be convenient if such measurements could be made, and they are brave because it can be a little risky to get exposed to critical comments by using an unconventional method. However, there are fundamental problems with the method, which remain to be solved.

It is claimed in the paper by De Marco and Mackey that free Fe^{3+} ions at levels down to 10^{-25} M can be determined in natural pH seawater using an ISE. However, it appears from this paper, and previous ones (De Marco et al., 1997; Zirino et al., 1998), that it is not clear what is being measured. It is important that readers realise what is going on so that they do not waste their time with these electrodes and use them in suitable conditions, and I hope this will also inform prospective reviewers of similar work. I will give here two reasons why it is impossible to measure low ionic iron (or other metal

ion) concentrations at low ambient iron concentrations using an iron-containing chalcogenide electrode, and then I will try to explain what they are actually measuring. Firstly, I should mention that these ISEs are composed of the metal being determined, mixed with other compounds to provide a conductive and solid electrode surface. The response of the electrode requires some dissolution of the metal and a reversible exchange between the metal and its ions in solution.

At ionic iron concentrations less than 10^{-24} M, there is less than one ion per litre of solution: It is at least unusual to claim that this ion can be detected; after all, it might not be in the bottle. A step forward would be to say that the electrode responds to all inorganic iron (mostly hydroxide species), and that it is likely that kinetic effects would alter the response. Generally, it is unrealistic to expect that an ISE of the poorly reversible type, which is being used for these experiments, will work at levels below 10^{-6} or 10^{-7} M total iron, because it cannot generate a sufficient flux of metal ions to maintain a stable gradient to satisfy the Nernst equation. A comparison to pH measurements is not valid: at pH 14, the ionic concentration of H^+ may be 10^{-14}, but the pH electrode is based on surface exchanges of H^+, as

well as OH^-, and, clearly, there are lots of OH^- at pH 14.

It is fundamentally impossible to measure low ionic iron (or other metal) concentrations at low ambient concentrations, because iron is part of the electrode surface. This iron slowly and steadily oxidises from the electrode surface and dissolves into the measuring solution. The authors attempt to address this point by determining the increase in the iron concentration as a function of time, and it was found that the iron concentration in a 10-ml sea water aliquot increased by 8 nM after 5 min of exposure to the electrode. It is said that this problem can be minimised by using a larger sample. However, the problem is not just that the whole sample becomes contaminated, but the diffusion layer of the electrode is also permanently saturated with inorganic iron diffusing away from the electrode surface into the bulk of the sample. Therefore, indeed, the contamination of the bulk will be less by using a larger sample, but the saturation of the diffusion layer does not change at all.

The diffusion layer (now saturated with iron from the electrode) is the place where Fe^{3+} ions from the bulk are supposed to be determined. Clearly, it is not possible for these ions to travel to the electrode surface, and give a meaningful response, against a concentration gradient, which runs in the opposite direction. Thus, the contamination of the diffusion layer with metal ions makes it fundamentally impossible to detect low ionic metal levels in a bulk solution containing low ambient metal levels, unless the ionic metal concentration is kept low by an excess of ligand, which rapidly complexes the metal being released. The ambient metal concentration has to be high (and the ligand concentration even higher) so that the change in the ratio of $[M^{n+}]/[ML]$ is buffered against changes.

The question now arises what it is that is being measured by these electrodes. For these electrodes to function, it is necessary that the bulk metal ion concentration is greater than that released from the electrode surface (or is stabilised by complexation) due to the ongoing oxidative dissolution; other work has demonstrated that this is effective at total metal concentrations not much below around 10^{-6} M, and only in some conditions valid responses are obtained at lower levels (Bakker et al., 1999). This work with iron ions (De Marco and Mackey, 2000), and previously with cupric ions, was carried out at much lower metal concentrations, and apparently stable responses were obtained. My hypothesis for this behaviour is the following: The electrode surface is oxidised at a constant rate by the diffusion of oxygen to the electrode; metal ions diffuse away at a constant rate, giving a constant background level of inorganic iron, consisting of a mixture of Fe^{2+} and Fe^{3+} and various inorganic complexes (or of cuprous and cupric ions for the copper electrode). This gives a constant response for a constant diffusion layer thickness (i.e. the response may change if you would stir or stir at variable rates). The response would change also with pH as the iron solubility changes, seemingly in line with Nernstian behaviour. The response is furthermore altered in the presence of complexing ligands as the ligands would be binding the metal ions, again at a constant rate due to the diffusion of the ligands to the electrode surface. Therefore, an apparently stable response suggesting a low free metal ion concentration would be obtained if there is a high concentration of complexing ligands in solution (like in the buffer solutions used for their preliminary work), or if the natural seawater contains ligands, which bind some of the metal diffusing away.

Therefore, the response obtained is not due to the ionic iron in the water, but due to the kinetics of iron diffusing away or being complexed by ligands. The response may be related to the complexing capacity of the water and may have some use therein, but it is definitely no measure of the ambient ionic (or inorganic) iron concentration at low total iron concentrations.

References

Bakker, E., Diamond, D., Lewenstam, A., Pretsch, E., 1999. Ion sensors: current limits and new trends. Anal. Chim. Acta 393, 11–18.

De Marco, R., Mackey, D.J., 2000. Calibration of a chalcogenide glass membrane ion-selective electrode for the determination of free Fe^{3+} in seawater: I. Measurements in UV photooxidised seawater. Mar. Chem. 68, 283–294.

De Marco, R., Mackey, D.J., Zirino, A., 1997. Response of the Jalpaite membrane copper(II) ion-selective electrode in marine waters. Electroanalysis 9, 330–334.

Zirino, A., VanderWeele, D.A., Belli, S.L., De Marco, R., Mackey, D.J., 1998. Direct measurement of Cu(II)(aq) in seawater at pH 8 with the jalpaite ion-selective electrode. Mar. Chem. 61, 173–184.