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14. ABSTRACT

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Feature Article

The Influence of Diffusion Fluxes on the Detection Limit of the Jalpaite Copper Ion-Selective Electrode

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Abstract
It has been suggested that electrode dissolution and the concomitant saturation of the electrode's diffusion layer restricts the detection limit of the jalpaite Cu ion-selective electrode (ISE) to samples with total Cu levels above 10^{-6} mol dm^{-3} [1, 2]. This article will use rotating disk electrode (RDE) data for San Diego Bay seawater and Fick's law of diffusion to demonstrate that the static commercial Orion Cu ISE (employing a jalpaite membrane) produces a background level of contamination of $(2.0 \pm 0.5) \times 10^{-8}$ mol dm^{-3} total Cu, and the reduced thickness of the Orion Cu ISE's diffusion layer in the presence of hydrodynamic flow [e.g., at an RDE, or in continuous flow analysis (CFA)] lowers the background contamination of Cu to $< 10^{-9}$ mol dm^{-3}. Furthermore, the RDE Cu ISE employing an electrode fabricated using jalpaite precipitated in 80% excess Na$_2$S, so as to minimize the presence of occluded and leachable Cu^{2+} salts and extraneous phases such as silver sulfide [3–5], reveals an improvement in the lower limit of detection compared to the commercial Orion Cu ISE.

Keywords: Copper ion-selective electrode, Rotating disk electrode, Electrode dissolution, Diffusion flux, Seawater

1. Introduction

The jalpaite Cu ion-selective electrode (ISE) offers an attractive method for the electroanalysis of Cu in natural media, as this approach enables a determination of pCu [i.e., -log(activity Cu)] in the natural medium; an extremely important chemical parameter that is considered a master variable, as it is related to the Cu complexing capacity of the medium, which reflects the medium's ability to regulate the uptake of Cu by the biota [6].

There are several reports on the use of the jalpaite Cu ISE in measurements of pCu in raw and UV-photooxidized seawater, along with total Cu in acidified and UV photooxidized seawater [7–15]. This body of work has demonstrated that the jalpaite Cu ISE is capable of providing data for free and total Cu in seawater that are commensurate with results obtained by using graphite furnace atomic absorption spectrometry (GFAAS), differential pulse anodic stripping voltammetry (DPASV), metal speciation calculations for seawater, and the observed toxicological effects of Cu on marine organisms. Significantly, the work of Jasinski et al. [14] along with Smith and Manahan [15] in the early 1970's demonstrated that, if electrode carry-over and contamination of Cu is minimized by using a suitable electrode cleansing technique (e.g., washing in dilute acid to remove adsorbed Cu), then the Cu ISE is capable of yielding Nernstian response down to total Cu spikes of 5×10^{-9} and 20×10^{-9} mol dm^{-3}, respectively. Furthermore, other studies [7–13] obtained meaningful results over total and free Cu concentration ranges of $10^{-9} < $ [total Cu] $< 10^{-1}$ mol dm^{-3} and $10^{-14} < $ [free Cu] $< 10^{-1}$ mol dm^{-3}, respectively.

The seminal work of Pretsch and co-workers [16–20] has demonstrated a marked improvement in the detection limit of polymer-membrane ISEs through the use of internal filling solutions that incorporate extremely low levels of primary ion (e.g., a Pb-EDTA filling solution for the Pb ISE). This novel approach is based on the elimination of transmembrane fluxes that would normally perturb the local concentrations of primary ions at the surface of polymer-membrane electrodes employing a conventional internal filling solution [e.g., acidified 0.1 mol dm^{-3} Pb(NO$_3$)$_2$ for the Pb ISE]. The recent review by Bakker et al. [20] revealed, in unbuffered media, a Nernstian Pb ISE response down to a total Pb level of 10^{-12} mol dm^{-3}. Furthermore, the pioneering work of Harsanyi et al. [21] along with Lindner and co-workers [22, 23] has ameliorated the deleterious effects of released metal fluxes for both polymeric and solid-state ISE membranes by applying a slight cathodic current to the electrode, and a very recent article [23] has demonstrated Nernstian response down to 10^{-12} mol dm^{-3} Pb for a galvanostatically controlled Pb ISE. This recent advancement demonstrates that ISE detection of ultra-trace levels of metal is possible if the flux of released metal is kept low enough to avoid saturation of the ISE's diffusion layer.

Despite the demonstrated potential of the jalpaite Cu ISE for determinations of free and total Cu in natural media, some workers still hold the perception that the jalpaite Cu ISE is only capable of reliably sensing Cu in samples with total Cu levels $> 10^{-6}$ mol dm^{-3} [1,2], making it unsuitable

for the analysis of natural media containing total Cu levels of about 10^{-9} mol dm^{-3}. This criterion is based on the belief that the dissolution based release of Cu from the ISE saturates the electrode diffusion layer with 10^{-6} mol dm^{-3} Cu, and samples with total Cu levels $<10^{-6}$ mol dm^{-3} (e. g., natural media) are incapable of sustaining an inward flux of Cu to overcome this significant level of background contamination. Unfortunately, this unproven skepticism is impeding the advancement of this important field of electroanalytical chemistry, and the current article will use the laws of electrode kinetics and diffusion, along with some recent rotating disk electrode (RDE) data for San Diego Bay seawater, to show that ISE dissolution and the concomitant saturation of the electrode's diffusion layer is unproblematic, and the Cu ISE functions satisfactorily in natural media.

2. Experimental

Two jalpaite Cu ISEs were employed in this study: a commercial Orion Cu ISE (Model 94-29) in static ISE measurements (assigned as Cu ISE1); a RDE Cu ISE that was fabricated using jalpaite powder prepared by coprecipitation of CuS and Ag$_2$S in the presence of 80% excess of Na$_2$S [24, 25], which was subsequently pressed in a Specac punch and die at 7.9×10^5 kPa, electrically connected to a threaded aluminium stub by using silver epoxy, and encapsulated in clear epoxy (assigned as RDE Cu ISE1).

For RDE Cu ISE studies, the threaded aluminium stub of the RDE was screwed into an epoxy-molded rotator shaft that was inserted into a single element PINE electrode rotator (Model AFCPRB).

All cell potentials were recorded relative to an Orion double-junction sleeve-type reference electrode (Model 900200) on a Radiometer pH/ion meter using a stability criterion of 0.2 mV min^{-1}, i. e., the steady-state potential was recorded when the potential-time transient first acquired a drift rate of 0.2 mV min^{-1}.

The electrodes were calibrated by using Cu-ethylenediamine and Cu-glycine buffers, as has been described elsewhere [10]. Furthermore, the electrodes were cleansed in a sacrificial Cu-ethylenediamine buffer, prior to several washes in the seawater sample to be analyzed, and final electrode equilibration in a fresh seawater sample [7].

3. Results and Discussion

Previous electrochemical impedance spectroscopy (EIS) data for the charge-transfer impedance (i.e., R_{CT}) of RDE Cu ISE1 in unbuffered Cu standards and seawater revealed that the kinetics of the reversible Cu^{2+}/Cu$^+$ reduction process [26], as reflected by the reciprocal of R_{CT}, is accelerated by increasing Cu concentration or by reducing the diffusion layer thickness at elevated rotation speed. This behavior is internally consistent with a dynamic response to facilitated mass transportation of Cu^{2+} from the bulk solution to the electrode surface [26]. If a predominant

dissolution reaction at the electrode surface was saturating RDE Cu ISE1's diffusion layer with a very high level of Cu^{2+} (e. g., 10^{-6} mol dm^{-3}) then the facilitated mass transportation of released Cu^{2+} away from the electrode at elevated rotation speed is expected to diminish the surface concentration of Cu^{2+} (as has been shown elsewhere for an RDE Orion Cu ISE [7]). The aforesaid hypothetical situation would manifest itself as a decrease, not the observed EIS increase, in the rate of the Cu^{2+} controlled Cu^{2+}/Cu$^+$ reduction process at elevated rotation speed. This practical outcome demonstrates that, in fact, the predominant diffusion flux for Cu^{2+} through RDE Cu ISE1's diffusion layer at 10^{-9} mol dm^{-3} total Cu is from the bulk seawater to the electrode surface, not the other way around, as suggested by other authors [1, 2].

3.1. RDE Cu ISE1

The RDE Cu ISE1 system used in this study employed a jalpaite powder that had been precipitated in the presence of 80% excess Na$_2$S. According to Heijne and van der Linden [24], these conditions favor the formation of a very pure sample of jalpaite, and our independent X-ray diffraction (XRD) pattern of the precipitate confirmed its very high purity. Furthermore, Heijne and van der Linden [24] specified that the aforementioned recipe produces electrodes with the best physical and electrochemical characteristics, and we fabricated our electrodes accordingly.

Figure 1 presents RDE Cu ISE1 data as a function of rotation speed in two San Diego Bay seawater samples, viz., (●) sea1 comprising 1.3×10^{-8} mol dm^{-3} total Cu, and (▲) sea2 comprising $<1 \times 10^{-9}$ mol dm^{-3} total Cu. It can be seen that, at both levels of total Cu, the RDE Cu ISE determined pCu values are independent of rotation speed, and are identical to the value obtained using RDE Cu ISE1 under
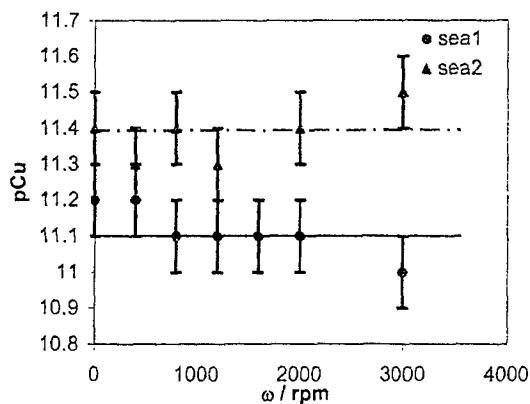

Fig. 1. Jalpaite RDE Cu ISE (coprecipitated copper and silver sulfide in 80% excess Na$_2$S) pCu data in two seawater samples (sea1 contains 1.3×10^{-8} mol dm^{-3} total Cu, and sea2 comprises $<1 \times 10^{-9}$ mol dm^{-3} total Cu, as determined by GFAAS) as a function of electrode rotation speed.

stationary conditions (i.e., $\omega = 0$ rpm). Note, these samples were taken at different oceanic sites, and possess disparate Cu complexing capacities, explaining why ΔpCu (i.e., 0.4) does not mirror the change in total Cu (i.e., 1 order of magnitude).

The behavior of RDE Cu ISE1 in San Diego Bay seawater can be interpreted theoretically by considering the dissolution and diffusion fluxes at the electrode surface [namely, J_{Cu} (dissolution) and J_{Cu}(diffusion)] in accordance with Fick's law of diffusion [27]:

$$J_{Cu}(diffusion) = D(Cu)\left(\frac{\partial C}{\partial x}\right)$$

$$= D(Cu) \times \frac{\left([Cu]_{surf} - [Cu]_{bulk}\right)}{\delta} \qquad (1)$$

where D(Cu) = diffusion coefficient of Cu (5.8×10^{-10} m^2 s^{-1} [28]), δ = thickness of the electrode diffusion layer (1.00×10^{-1} mm for a static electrode [27]), $[Cu]_{surf}$ = surface concentration of Cu, and $[Cu]_{bulk}$ = bulk solution concentration of Cu (10^{-9} mol dm^{-3} in seawater).

If a dominant dissolution process saturates the Cu ISE diffusion layer with 10^{-6} mol dm^{-3} total Cu, as proposed elsewhere [1, 2], then this diffusion controlled process will produce a steady-state ISE potential when J_{Cu}(dissolution) equilibrates with J_{Cu}(diffusion).

For an RDE, it is possible to estimate δ_{RDE} by using the Levich equation [29]:

$$\delta_{RDE} \approx 0.5\ (D/\nu)^{1/3}\ \delta_0 \text{ and } \delta_0 = 3.6\ (\nu/\omega)^{1/2} \qquad (2)$$

where ν = viscosity of water (1.00×10^{-6} m^2 s^{-1} for water [29]), ω = rotation speed (e.g., 314.2 rad s^{-1} or 3000 rpm), and δ_0 = thickness of the hydrodynamic boundary layer. Substitution of the aforementioned conditions into Equation 2 yields $\delta_{RDE} \approx 8.5 \times 10^{-3}$ mm, compared to $\delta = 1.00 \times 10^{-1}$ mm for a static electrode [27].

A presumed high and constant level of background dissolution (i.e., a fixed level of J_{Cu}(dissolution) producing $[Cu]_{surf} \approx 10^{-6}$ mol dm^{-3}) due to release of leachable Cu salts out of the ISE membrane [1, 2] is clearly incommensurate with the observed insensitivity of the RDE Cu ISE to rotation speed, as the hypothetical facilitated mass transportation of released Cu out of the RDE Cu ISE's diffusion layer is expected to reduce ($[Cu]_{surf} - [Cu]_{bulk}$) to a value equal to the ratio of δ's for the RDE and static electrode which, for example at 3000 rpm, corresponds to a ratio of 8.5×10^{-3} to 1.00×10^{-1} mm or 0.085 to 1.00 [i.e., δ_{RDE} relative to δ_{static} obtained by equalizing J_{Cu}(diffusion) values, which are equivalent to the fixed value of J_{Cu}(dissolution), for static and RDE Cu ISEs]. Nevertheless, the aforesaid theoretical rationalization is partially consistent with the observed response of an RDE Orion Cu ISE in San Diego Bay seawater, whereby a gradual increase in pCu (or decrease in Cu activity) was noted up to a plateau of +0.5 pCu unit (or 3-fold decrease in Cu activity) at

>2000 rpm [7], confirming that, for the Orion RDE Cu ISE, the major diffusion flux corresponds to the dispersion of released Cu out of the ISE's diffusion layer.

Clearly, the constancy in pCu for $\omega = 0$–3000 rpm for RDE Cu ISE1 precipitated in 80% excess Na$_2$S, demonstrates that background Cu contamination caused by dissolution of the ISE is lower than the bulk concentration of Cu in either sample, and the major diffusion flux of Cu is from the bulk solution to the electrode surface, not the other way around, as suggested by other authors [1,2]. Furthermore, it is significant to note that potential-time transients for RDE Cu ISE1 in sea1 and sea2, as expected for mass transportation of Cu from the bulk solution to the electrode surface, revealed a shift to positive potentials prior to the attainment of steady-state potentials at a drift rate of 0.2 mV min^{-1}. Moreover, it can be inferred that the background Cu contamination for this Cu ISE is lower than the concentration of total Cu in sea2 (i.e., $< 10^{-9}$ mol dm^{-3}).

3.2. RDE Cu ISE1 and Static Cu ISE1 Data for San Diego Bay

The aforementioned lack of sensitivity of the RDE Cu ISE1 to rotation speed is dissimilar to that for an RDE Orion Cu ISE, which showed a gradual increase in pCu up to a plateau of +0.5 pCu unit at 2000 rpm [7] consistent with facilitated mass transportation and dispersion of released Cu out of the RDE Orion Cu ISE's diffusion layer. This scenario is also consistent with a higher Cu dissolution rate for the Orion Cu ISE that leads to some enrichment of released Cu at the surface layer of the electrode.

A previous XRD study demonstrated that the commercial Orion Cu ISE incorporates a membrane composed almost entirely of jalpaite, and also contains a small amount of silver sulfide [30]. This membrane composition is consistent with precipitation of the jalpaite Orion Cu ISE in 20% excess Na$_2$S [24], and other work [5] suggests a low excess of Na$_2$S in electrode preparation enables re-oxidation of membrane Cu$^+$ to leachable Cu^{2+} salts.

This led to the hypothesis that Cu ISE1 may leach more Cu, yielding a higher detection limit compared to RDE Cu ISE1 fabricated using a higher excess of Na$_2$S. This thesis was tested by analyzing San Diego Bay samples using both static Cu ISE1 and RDE Cu ISE1.

A recent inter-calibration exercise (refer to Figure 2) employing RDE Cu ISE1 at 3000 rpm and static Cu ISE1 in the analysis of San Diego Bay seawater, revealed an average difference of +(0.6 ± 0.1) pCu unit or a (4 ± 1) – fold decrease in Cu activity, noting RDE Cu ISE1 gave this deviation to higher pCu or lower Cu activity, for uncontaminated sites containing nanomolar levels of total Cu (i.e., samples 3–4 with about 5×10^{-9} mol dm^{-3} total Cu), while sites comprising about 10^{-7} mol dm^{-3} total Cu (i.e., samples 1 & 5–7) yielded static Cu ISE1 and RDE Cu ISE1 data that agreed to within ± 0.1 pCu unit. It must be recalled that the data for RDE Cu ISE1 in sea2 (refer to Figure 1) revealed that determined pCu values are independent of rotation
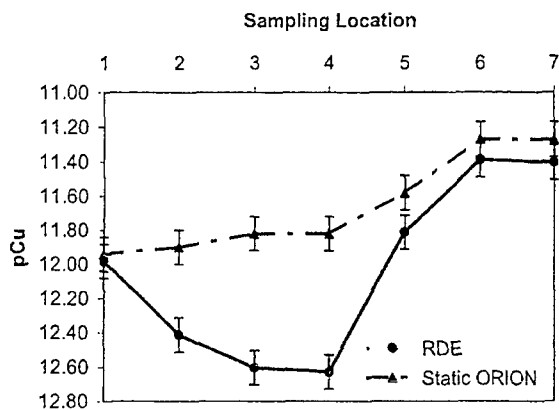
Sampling Location

Fig. 2. Cu ISE pCu data for San Diego Bay seawater samples, as determined by using a static Orion 94–09 jalpaite Cu ISE, and a jalpaite RDE Cu ISE at 3000 rpm employing a membrane prepared by the coprecipitation of copper and silver sulfide in 80% excess Na_2S. San Diego Bay seawater samples have been labelled as follows: 1) Point Loma Bayside (13 nM total Cu); 2) Waterfront (32 nM total Cu); 3) Point Loma Seaside (6 nM total Cu); 4) Point Loma Bay Entrance (5 nM total Cu); 5) Shelter Island (116 nM total Cu); 6) Inner Shelter Island (159 nM total Cu); 7) Commercial Basin (131 nM total Cu). Note, the data in parentheses are GFAAS levels of total Cu.

speed in samples with total Cu levels $<1 \times 10^{-9}$ mol dm^{-3}, symbolizing that RDE Cu ISE1 yields the true thermodynamic activity of Cu. Furthermore, as the Cu complexing capacity for San Diego Bay seawater ligands is approximately constant [13], it is expected that Cu ISE data for free Cu will mirror the GFAAS determined variation in total Cu, which corresponds to $\Delta pCu \approx 1.3$ (cf., total Cu data for samples 3 and 7). Accordingly, the RDE Cu ISE1 data yields $\Delta pCu \approx 1.3$ (cf., samples 3 and 7), and this provides further credence for the notion that RDE Cu ISE1 is measuring the true thermodynamic activity of Cu. By contrast, it will be shown in the proceeding discussion that a low ΔpCu value for static Cu ISE1 is due to surface accumulation of ISE released Cu.
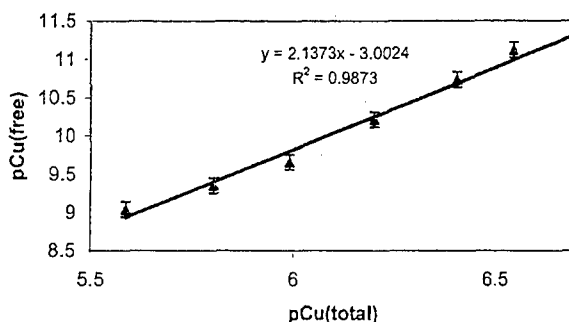
Fig. 3. RDE Cu ISE1 data for pCu(free) [determined against standard calibration buffers] vs. pCu(total) in a standard addition potentiometric analysis of San Diego Bay seawater.

Additional proof for RDE Cu ISE1 sensing the true thermodynamic activity of Cu is provided by the results of a standard addition potentiometric analysis of Cu in San Diego Bay seawater (refer to Figure 3). It can be seen that the response for RDE Cu ISE1 to free Cu follows the variation in total Cu (at high total Cu levels above 10^{-7} M) demonstrating that the ISE is accurately sensing Cu in seawater. Nevertheless, it is also evident that the slope of the plot is double the value of unity that is expected for the simple complexation of added Cu by natural seawater ligands, if the side reaction coefficient for Cu complexation is assumed to be constant. Clearly, this is not the case, as previous work by Belli and Zirino [9] has shown that the side reaction coefficient (i.e., α) for Cu complexation in seawater varies as a function of added total Cu, and equilibrium modelling of the associated Cu complexation demonstrated that the apparent double divalent slope for a standard addition experiment (i.e., 59.16 mV per decade change in total Cu at 298.15 K) is self-consistent with theoretical predictions, i.e., the ISE senses free Cu, but is being forced to erroneously fit total Cu which is not related simply to free Cu. In simple terms, the Belli and Zirino [9] theory predicts correctly an observed slope of 2 for a plot of pCu(free) vs. pCu(total), as the Cu ISE experiences an apparent double sensitivity toward added total Cu.

In summary, the discrepancies in ISE determined pCu values for RDE Cu ISE1 and static Cu ISE1 in seawater are consistent with a diffusion-controlled Cu dissolution process that saturates the stationary Orion electrode's diffusion layer with somewhere between 5×10^{-9} and 10^{-7} mol dm^{-3} Cu.

It is possible to estimate the background level of $[Cu]_{surf}$ for static Cu ISE1 in seawater containing 5×10^{-9} mol dm^{-3} total Cu (i.e., samples 3 & 4) by comparing its response to that for RDE Cu ISE1 in the same samples, which is indicative of the true thermodynamic activity of Cu. The (4 ± 1) – fold increase in activity of free Cu for the static Cu ISE1 compared to RDE Cu ISE1 can be equated to the corresponding ratio for total Cu by assuming a fixed side reaction coefficient between both released and ambient total Cu and the ubiquitous inorganic and organic ligands of seawater. In such a case, $[Cu]_{surf}$ for static Cu ISE1 is estimated at $(2.0 \pm 0.5) \times 10^{-8}$ mol dm^{-3}. Clearly, this level of Cu saturation of the Orion electrode's diffusion layer is far less problematic than the alleged concentration of 10^{-6} mol dm^{-3} [1, 2], and this is the reason why previous reports [7–15] have managed to obtain meaningful Cu ISE data for free and total Cu in various coastal seawater samples, falling within $\pm 0.1 - 0.3$ pCu unit of GFAAS and speciation data.

Nevertheless, a $[Cu]_{surf}$ of $(2.0 \pm 0.5) \times 10^{-8}$ mol dm^{-3} poses a serious uncertainty for the use of the static Orion electrode in open ocean samples that may contain nanomolar or sub-nanomolar levels of total Cu; however, the previous work of Zirino et al. [7] has shown it is possible to reduce $[Cu]_{surf}$ by using a RDE Orion Cu ISE, whereby determined pCu values increased up to $\omega = 2000$ rpm, at which point the pCu reaches a constant value due to the

complete dispersal of released Cu (i.e., $(2.0 \pm 0.5) \times 10^{-8}$ mol dm^{-3} total Cu) under this hydrodynamic flow regime.

Obviously, an RDE Orion Cu ISE can be used to diminish the level of saturation of the electrode's diffusion layer by released Cu. It can be shown using the above-mentioned theoretical arguments [i.e., J_{Cu}(dissolution) $\approx$ J_{Cu}(diffusion) and δ_{RDE} calculated using Equation 2] that $[Cu]_{surf}$ can be reduced from $(2.0 \pm 0.5) \times 10^{-8}$ mol dm^{-3} for a static Orion Cu ISE to $(0.9 \pm 0.2) \times 10^{-9}$ mol dm^{-3} for a RDE Orion Cu ISE at $\omega = 10\,000$ rpm or 1047 rad s^{-1} which is the upper safe limit for laminar flow at an RDE [31], viz., a dilution factor of δ_{RDE} to δ_{static} of 4.6×10^{-3} mm to 1.00×10^{-1} mm or 0.046 to 1.00.

Alternatively, our current analytical strategy utilizes continuous flow analysis (CFA) and a wall-jet cell [11, 12] to facilitate the dispersal of released Cu by the strong eddy currents in the wall-jet cell. Experimental polarization data for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple at a gold electrode [32] in a wall-jet cell was used to derive an empirical relationship for δ_{CFA} as a function of the linear flow velocity, υ, yielding the same dependency for υ as the theoretical expression that has been reported elsewhere [33], viz.

$$\delta_{CFA} = 3.34 \times 10^{-6} \, \upsilon^{-0.44} \qquad (3)$$

where δ_{CFA} is given in units of m, υ in units of m s^{-1}, and the empirical constant has units of m$^{1.44}$ s$^{-0.44}$. It can be shown that the CFA linear flow velocity used by our group (2.55×10^{-1} m s^{-1} or 3 mL min^{-1} for a wall-jet diameter of 0.5 mm [11, 12]) leads to $\delta_{CFA} = 6.1 \times 10^{-3}$ mm compared to $\delta_{static} = 1.00 \times 10^{-1}$ mm, and this is expected to disperse released Cu from $[Cu]_{surf}$ of $(2.0 \pm 0.5) \times 10^{-8}$ mol dm^{-3} for static Cu ISE1 to $(1.2 \pm 0.3) \times 10^{-9}$ mol dm^{-3} in CFA. The use of a higher flow rate (e.g., 4.25 m s^{-1} or 50 mL min^{-1}) can ameliorate contamination by released Cu to $(3.6 \pm 0.9) \times 10^{-10}$ mol dm^{-3} Cu at $\delta_{CFA} = 1.8 \times 10^{-3}$ mm.

4. Conclusion

This article demonstrates that the flux of Cu released by the static Orion Cu ISE is consistent with a surface concentration of $(2.0 \pm 0.5) \times 10^{-8}$ mol dm^{-3}. The significant enhancement in the diffusion flux for the Orion Cu ISE in CFA with a wall-jet cell or at a RDE implies that the surface concentration, and concomitant detection limit of the Cu ISE in the presence of hydrodynamic flow, is 3.6×10^{-10} to 1.3×10^{-9} mol dm^{-3}. Clearly, this level of contamination is insufficient to cause significant errors in CFA or RDE ISE determinations of pCu in natural waters, and this is supported by recent CFA experimental data in natural waters (e.g., pCu data in acidified and poorly buffered seawater at total Cu concentrations of 10^{-9} mol dm^{-3} [11] that fell within $\pm 0.1 - 0.3$ pCu unit of values predicted using the well-known Cu inorganic speciation of seawater, and ISE pCu values in seawater correlated strongly with measured toxicological responses for certain marine organisms [12]). Nevertheless, the constant leaching of a low level

of Cu by the Orion Cu ISE generates a steady-state or quasi-equilibrium diffusion flux, and corresponding interfacial potential, due to the mixing of inward and outward Cu fluxes. In such a case, the kinetics of diffusion of dominant solution species toward and away from the electrode (i.e., ligands and metal ligand complexes) along with the Cu ISE's interfacial chemistry (e.g., metal-ligand complexation and electrochemical processes) are the potential determining processes for the ISE. Nevertheless, it is possible to attain steady-state Orion Cu ISE pCu values approaching the true thermodynamic values by using practices that reduce the thickness of the ISE diffusion layer (e.g., RDE and CFA), ensuring that released Cu is dispersed efficaciously into the bulk solution.

A Cu ISE fabricated using jalpaite precipitated in the presence of 80% excess Na_2S has a superior detection limit of $<10^{-9}$ mol dm^{-3} total Cu compared to that for the commercial Orion Cu ISE. Presumably, this improvement in sensitivity is ascribable to the diminution in water soluble or leachable Cu^{2+} salts in the bulk membrane material, which minimizes the corresponding dissolution flux of the jalpaite Cu ISE, and the concomitant outward diffusion flux, ensuring the inward diffusion flux for Cu from the bulk solution dominates the response of the Cu ISE in natural seawater containing ca. 10^{-9} mol dm^{-3} total Cu.

5. Acknowledgements

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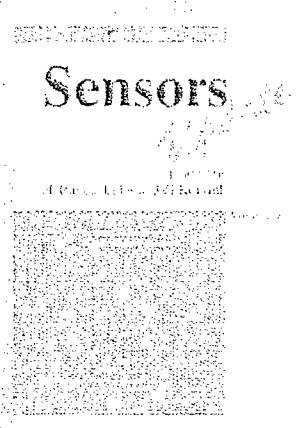[13] A. Zirino, S. L. Belli, D. A. Van der Weele, Electroanalysis 1998, 10, 423.

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