

Measurements of Copper in Seawater: The Use and Misuse of the Ion-Selective Electrode*

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Received January 25, 1996; accepted July 1, 1996

Conventional wisdom holds that the copper Ion Selective Electrode (CuISE) is unsuitable for measurements in seawater because of a wide range of effects including; interference by chloride ion, electrode drift, sub- and super-Nernstian response, contamination of the sample and, a lack of sensitivity. While all of these effects have undoubtedly been observed, there have also been reports indicating that the CuISE can give Nernstian response, at 29 mV/decade, down to very low concentrations of free copper ions in saline buffers. The application of experimental techniques for studying changes on membrane surfaces, as well as the use of »clean« techniques that have become standard for studying trace metals at very low concentrations, have enabled us to better understand the processes which lead to the problems listed above. In this paper, we review some of the the literature on the topic and suggest that it may indeed be possible to use the CuISE to provide reliable measurements of copper speciation in marine and estuarine waters.

INTRODUCTION

Two decades ago, conventional wisdom held that the concentration of zinc in seawater was approximately 5 µg/L (75 nmoles/kg) and independent of depth and location, and that complexation by organic ligands was not im-

* Dedicated to Marko Branica on the occasion of his 65th birthday.

portant since it was highly unlikely that organic ligands in seawater were capable of forming complexes that were thermodynamically stable.¹ A few years later, the concentration of zinc was known to vary with location (the Pacific was different from the Atlantic) and increased from values as low as 7 ng/L in surface waters to a maximum of about 500 ng/L in deep waters of the Pacific Ocean.² In addition, recent work has proposed that zinc in seawater is essentially totally complexed by organic ligands^{3,4} even though the lower the total concentration of zinc, the stronger the complexing strength of the organic ligands required to form organic complexes. Similar comments apply to most of the biologically important trace metals and it is generally assumed now that metals such as copper,⁵⁻⁸ nickel,⁹⁻¹² iron,¹³⁻¹⁵ cobalt,^{16,11} lead¹⁸ and cadmium¹⁷ exist in seawater mainly as organic complexes, or in the form of mixed organic/inorganic colloidal particles.¹⁹

The advances in our ability to measure trace elements in seawater have largely been due to our skill in developing »clean« techniques for the collection, storage and analyses of samples. In general, it is not possible to measure the trace metals directly at the low concentrations that occur naturally and some form of preconcentration is required. This must of necessity introduce an element of uncertainty in our experimental procedures if these metals are, in fact, largely complexed by organic ligands capable of forming very strong complexes. In-line cartridges may only extract a fraction of a given trace metal; we make assumptions as to the labile fraction determined by differential pulse anodic stripping voltammetry (DPASV); we assume thermodynamic equilibrium between natural and added ligands in cathodic stripping voltammetry (CSV) and; we assume that naturally occurring metal organic complexes are not adsorbed on to the hydrophobic (teflon, polyethylene) equipment used in all stages of our analytical procedures. It is no longer axiomatic that the lower the concentration determined, the more believable the measurement.

If trace metals in seawater are largely complexed by organic ligands then, from a biological and environmental point of view, the total concentration of trace metal may be largely irrelevant since there is abundant evidence that marine microorganisms respond only to the concentration of free copper,²⁰⁻²² zinc,²³ manganese,²⁴ iron²⁵ and cadmium.²⁶ There is no evidence that naturally occurring metal organic complexes are directly taken up by microorganisms and, although it has been postulated that this may occur for iron siderophores,²⁷ there is no evidence that this occurs although few attempts have been made to detect such compounds.^{28,29} Attempts to calculate the concentration of free trace metal by chemical,³⁰ biological³¹ or electrochemical procedures^{32,33} are difficult, time consuming and generally depend on *a priori* assumptions of thermodynamic equilibrium or of the specific types of metal complexes present in the sample. The effect of kinetics are generally ignored even though the system is far from thermodynamic

equilibrium.¹⁹ Under equilibrium conditions, organic complexes would not exist since all organic matter would be converted to carbon dioxide.

In principle, the free metal concentration can be measured by an appropriate Ion Selective Electrode (ISE) regardless of whether the system is in thermodynamic equilibrium, or whether the trace metal is present as organic or inorganic complexes, in solution, on particles, in colloidal suspension or, as is likely, a combination of all of these. One of the most widely used ISE is the copper ISE (CuISE) and there have been several attempts to use it for the analysis of natural waters.³⁴⁻³⁷

The excellent reviews by Gulens^{38,39} provide much useful information on CuISEs and it is not the purpose of this paper to replicate the information provided in these papers. One of the first preconceptions that needs to be dispelled is that there is only one type of CuISE. There are in fact a large number of CuISEs described in the literature and these have been summarised by Gulens: the sensing membrane can consist of Cu_2S (chalcocite), CuS (covellite), $\text{Cu}_{1.92}\text{S}$, $\text{Cu}_{1.77}\text{S}$, $\text{Cu}_{1.60}\text{S}$, $\text{Cu}_{1.31}\text{S}$,³⁸⁻⁴⁰ a mixture of CuS and Ag_2S , the ternary compounds $\text{Cu}_{0.45}\text{Ag}_{1.55}\text{S}$ (jalpaite),^{39,41} $\text{Cu}_{0.80}\text{Ag}_{1.20}\text{S}$ (macin-styrite),^{39,41,42} $\text{Cu}_{1.07}\text{Ag}_{0.93}\text{S}$ (stromeyerite),^{39,41,42} $\text{Cu}(\text{AgInSeFe})(\text{SSeTe})$,^{39,43} CuSe , $\text{Cu}_{1.8}\text{Se}$, Cu_2Se , Cu_3Se_2 ,^{39,42} AgCuSe ,^{39,44} glasses based on $\text{Cu-As}_2\text{S}_3$, $\text{Cu-As}_2(\text{SeTe})_3$ ^{39,45} or Cu-Ag-As-Se ,^{39,44} bronzes based on β -vanadium oxide such as $\text{Cu}_2\text{V}_{12}\text{O}_{30}$,⁴⁶ compounds containing no copper such as $\text{Ag}_{25}\text{As}_{37.5}\text{Se}_{37.5}$,^{39,44} or mixtures of any of these compounds. Moreover, the surface composition may be far from that of the bulk compound⁴⁷ and the response may be dependent on impurities such as S,^{48,49} and the method of preparation including electrodeposition⁵⁰, direct combination of the elements,⁴⁹ precipitation from acidic⁵¹ or basic⁴¹ solution or under oxidising or reducing conditions.⁴¹

Even describing an electrode as a $\text{CuS-Ag}_2\text{S}$ electrode is misleading since such an electrode may be jalpaite which nominally contains Cu(I) , contain a physical mixture of CuS and Ag_2S with or without jalpaite, or contain other species depending on the method of preparation³⁹ and have different responses to interferences such as chloride depending on the internal construction.⁵² It therefore makes no sense to make sweeping statements about the suitability of the CuISE for a particular analysis. One of the most widely used CuISEs is the Orion 94-29 electrode which is largely composed of jalpaite, and our understanding of this electrode has been greatly helped by the use of »clean« techniques for analysing trace metals and by techniques such as X-ray Photoelectron Spectroscopy (XPS),⁵³⁻⁵⁷ Scanning Electron Microscopy^{53,58,49,42} and Auger Spectrometry⁵⁹ which have allowed characterisation of membrane surfaces both before and after immersion in various synthetic media and in seawater. This information has enabled us to better understand the processes that are reported to make the CuISE unsuitable for the analysis of seawater, such as; a lack of sensitivity, contamination of

the sample and, especially, interference from chloride ions. While all of these effects undoubtedly do occur, they can be overcome and such efforts are more than justified by the prospect of developing a simple, robust, portable instrument that enables the direct *in situ* determination of that fraction of copper that is biologically and environmentally important. Preliminary work has been reported previously.^{60,34}

We will use the expressions Cu_{free} and Cu_{total} when necessary to distinguish between the concentration of free copper ions (*i.e.* $Cu^{2+}(\text{aq})$) and the total concentration of copper in the medium and the expression pCu equals $-\log_{10}[Cu]$. Actually, the CuISE senses directly the activity of free Cu ions; however, if the standards and samples are maintained at constant ionic strength by matrix matching, the activity coefficient remains constant and the ISE can be calibrated in terms of the concentration of free Cu.

DISCUSSION

In the following discussion, reactions occurring on the membrane surface will be described in terms of simple stoichiometric binary compounds such as CuS, or Ag_2S even though the actual surface composition may be non-stoichiometric and/or consist of ternary compounds such as jalpaite. Even the assumption of copper(II) species in the membrane is incorrect as it has been shown that CuS (covellite) contains only copper(I) and that its composition is given by an equimolar mixture of Cu_2S and CuS_2 with the latter containing the $(S_2)^-$ ion.⁶¹

Detection Limit

In unbuffered systems, the detection limit of CuISEs for Cu_{total} is often quoted to be 10^{-4} to 10^{-8} M. Assuming that the ISE has come to equilibrium, this detection limit should be determined by dissolution of the membrane, adsorption and desorption of copper ions and contamination of the sample. While most of the variations in reported detection limits are undoubtedly due to the composition of the membrane, it is also highly probable that many of the early experiments were subject to significant contamination. Few, if any, of these experiments were done under the »clean« laboratory conditions that are now considered mandatory for reliable measurements of copper, and similar metals, at concentrations below 10^{-8} M.

The solubility products of Cu_2S , CuS and Ag_2S are reported to be 10^{-48} , $10^{-35.2}$ and 10^{-49} respectively^{62,63} and hence the simple dissolution of any of these species should be negligible even at low pH as should the formation of soluble sulfide complexes. This should also apply to jalpaite and any dissolution of the Orion membrane must be due to either redox processes, with the formation of sulfur and/or sulfate, or due to the presence of ligands with

an extremely strong affinity for copper or silver. Surface oxidation of CuS membranes leads to the formation of hydroxy-sulfates which have been identified by XPS⁶⁰ and this is one of the reasons why these membranes are unsuitable for the analysis of seawater. Similar process presumably can occur to a greater or lesser extent on other membranes. In natural waters (in the absence of high concentrations of nitrate which potentially may react with the membrane at high concentrations and/or low pH) the main oxidant is oxygen and, possibly, hydrogen peroxide and species produced by photochemical degradation of organic matter. It has been stated that measurements at low Cu_{total} concentrations must be done in deoxygenated samples.^{52,64} This does not appear to be as important for the Orion 94-29 electrode and it has been shown^{60,65} that oxidative dissolution of the membrane, and subsequent contamination of the sample, is much less for the Orion 94-29 electrode than for electrodes made from CuS or $Cu_{1.8}Se$ (Radiometer F1112).

Interferences from surface oxidation and dissolution, and from adsorbed copper,^{66,67} can be minimised by preequilibration (24 hours) of the CuISE in a solution similar to the one being measured and by immersing the ISE in a sacrificial Cu-en buffer ($pCu \approx 15$) prior to measurements. It should be noted that any adsorption of copper by the membrane leads to an increase in the amount of contact adsorbed copper in the inner Helmholtz plane of the ISE's electrical double-layer and is responsible for problems of »carry over« which limits the response of the electrode after it has been exposed to high concentrations of copper. Dissolution of the membrane will contaminate the sample and also lead to an increase in the amount of contact adsorbed copper. Thus, either adsorption or desorption will give rise to high ISE potentials, overestimating the true level of free Cu(II).

Under the conditions described above, De Marco *et al.*³⁴ have been able to demonstrate Nernstian behaviour (slope $\cong 30$ mV/decade) of the Orion CuISE in Milli-Q water down to 1-3 nM. In acidified seawater at pH 2, the corresponding value was 3-7 nM.

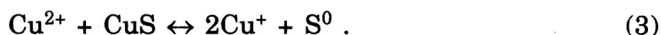
Response Mechanism

For a long time, it has been generally believed that the CuISE responded to Cu(II) by a simple ion-exchange mechanism involving solubility product equilibria, *viz.*³⁹



According to this oversimplified and incorrect mechanism, the Cu(II) activity controls the sulfide ion activity *via* the CuS equilibrium and this, in

turn, influences the Ag_2S equilibrium and the ISE potential. However, the abundant structural evidence³⁹ (*i.e.*, XRD and XPS) clearly shows that the CuISE membrane is a Cu(I) ion conductor that responds directly to Cu(I). Nowadays, it is accepted that the mechanism for CuISE response involves the reductive ion-exchange of Cu(II) at the electrode diffusion layer, followed by direct response to the released Cu(I), *viz.*:⁶⁸⁻⁷⁰



It is important to note that the Cu(I) generated at the ISE surface probably resides within the Cu(I) vacancies of the metal sub-lattice of the membrane and, undoubtedly, the coulombic forces experienced by Cu(I) in this environment stabilise it against disproportionation to Cu(II) and Cu. In essence, the Cu(II) response is based on the interference of Cu(II) on Cu(I), and it has been shown that the Nicolsky equation describes quantitatively this behaviour:⁶⁸

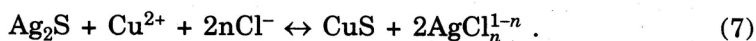
$$E = E^0(\text{Cu}^+) + \frac{RT}{F} \{ \ln [\text{Cu}^+] + K[\text{Cu}^{2+}]^{1/2} \} \quad (4)$$

In Gulens' review,³⁹ it was reported that several authors had obtained selectivity coefficients in the range $\log K = -6.5$ to -5.7 for various CuS/ Ag_2S , Cu(I)S and Cu(I)Se systems. This small value of K indicates that the CuISE is about 10^6 times more selective towards Cu(I) than Cu(II) and this potentially may pose a serious problem for *in situ* measurements of copper in seawater where 5–10% of total copper may be present as Cu(I) as a result of photoreduction.⁷¹ In contrast to laboratory experiments which suggest that Cu(I) has a half life of about 5 minutes in saline media,^{72,73} the half life in seawater at sub-nanomolar concentrations appears to be about 12 hours.⁷¹ Under these conditions, it is anticipated that the Cu(I) signal would totally obscure the Cu(II) response, leading to erroneous readings in the euphotic zone. This alleged source of uncertainty requires further investigation, and the authors plan to undertake a comparative study of the ISE response in acidified seawater containing Cu(II) and UV photoreduced and acidified seawater containing Cu(I).

Many workers have observed non-Nernstian (slope $\neq 30$ mV/decade) behaviour of the CuISE in seawater and have therefore stated that the electrode is unsuitable for the analysis of seawater. Deviations from the theoretical Nernstian slope can arise from two effects. The first is the well known interference by chloride ions and two theories have been proposed to explain the non-Nernstian response. Westall *et al.*⁵² developed a theory that is based on redox processes occurring at the membrane surface which can be summarised as:



In an extension of this theory, Ag_2S and Cu_2S can replace CuS and other chloro-complexes of Ag^+ and Cu^+ are also included.⁴⁸ Confirmation of this mechanism was provided by Lewenstam *et al.*⁴⁹ who identified S on the surface of a CuS membrane exposed to Cu^{2+} and chloride. An alternative mechanism, based on exchange of Ag^+ and Cu^+ has been proposed by Lanza⁷⁴ and can be summarised by the following reactions:



These reactions are basically driven by the formation of chloro-complexes of Ag^+ and Cu^+ and, since these have very similar stability constants,⁶² the interference should be very similar for any membrane containing Ag and/or Cu. The two mechanisms predict essentially the same effects which depend on the absolute and relative concentrations of Cu^{2+} and chloride and both have been used to explain the variations in electrode response in chloride media up to 3 M and for Cu^{2+} concentrations above about 10^{-5} M. Both mechanisms probably prevail at high levels of copper and De Marco showed that the super-Nernstian response of jalpaite at levels of copper between 10^{-7} and 10^{-4} M leads to a slight memory effect characterised by a negative shift in E^0 . XPS identified AgCl on the membrane surface.⁷⁵ At low concentrations of Cu(II) in seawater Cu-en buffers, XPS showed that significantly lower levels of AgCl had formed on the membrane.⁷⁵

Both of these theories predict that, for seawater, the Nernstian slope should increase from the expected 29 mV/decade and approach 59 mV/decade at Cu^{2+} concentrations lower than about 10^{-4} M. The Cu^{2+} concentration at which the slope increases from 29 mV/decade increases as the concentration of chloride increases.⁵² At sufficiently high concentrations of chloride, Westall *et al.*⁵² state that it is impossible to measure Cu^{2+} ion activity directly. However, as pointed out by Belli and Zirino⁷⁶ the experiments of Westall *et al.* were carried out in unstirred, oxygen-free conditions at high concentrations of both chloride and copper and these conditions are not applicable to measurements in seawater. Moreover, the electrode used by Westall *et al.* was a Radiometer (F3000)⁵² of unspecified membrane composition. This membrane obviously behaves quite differently from the Orion 94-29 since Westall *et al.* calculate that AgCl cannot form on the surface of the Radiometer electrode at Cu(II) concentrations below 10^{-4} M in contrast to the results of De Marco described previously.⁷⁵

Moreover, in 1974, Jasinski *et al.*³⁵ had already demonstrated Nernstian response (with a slope of 26.8 mV/decade) for an Orion 94-29 electrode in seawater at concentrations of Cu^{2+} down to $0.6 \mu\text{g/L}$ (9 nM) for samples acidified to pH 3. At pH 8 the response was non-linear with »slopes« in the

range 44–52 mV/decade. In the latter case, the non-ideal behaviour was undoubtedly due to the presence in the sample of organic ligands. This effect has been described previously^{76,77} and Belli and Zirino⁷⁶ showed that, regardless of the presence of halide ions, a CuISE will give a Nernstian response in the presence of organic ligands only if such ligands are present at concentrations, sufficiently in excess of the concentration of Cu^{2+} , that the ratio of Cu_{free} to Cu_{total} remains constant. This is obviously not the case when copper is added to seawater (or freshwater) containing low concentrations of organic ligands which form copper complexes having a wide range of effective stability constants. If copper-organic complexes in seawater are destroyed by UV photooxidation or by acidification to pH 2, Nernstian (30 mV/decade) response is observed down to total copper concentrations of approximately 1 nM.³⁴ This implies that the CuISE can be used to measure total copper in seawater down to comparable concentrations.

The absence of interference by chloride is not due to thermodynamics since equilibrium calculations, based on solubility products, for AgCl formation on Ag_2S in the presence of Cu^{2+} predict that, at a chloride ion concentration of 0.6 M, the reaction is thermodynamically possible at Cu^{2+} concentrations above 3.5×10^{-15} M. The non-interference must therefore be attributed⁶⁰ to the slow kinetics of reactions (5), (6) and (7) at nanomolar concentrations of Cu^{2+} .

Slow kinetics can also explain the fact that the CuISE can give Nernstian behaviour in buffered solutions where Cu_{free} is controlled by ligands such as ethylenediamine (en). Avdeef *et al.*⁷⁸ varied the pH of a Cu-en buffer ($\text{Cu}_{\text{total}} = 1$ mM, en = 11–16 mM), and showed that a CuISE (Beckman 39612) responded linearly (99.2% Nernstian slope) in the range $3 < p\text{Cu} < 19$. The concentration of Cu^{2+} was calculated from known stability constants. Hoyer⁷⁹ obtained Nernstian response (Radiometer F1112) in the range $9 < p\text{Cu} < 16$ in solutions buffered with histidine, glycine, diethylenetriamine, tris(2-aminoethyl)amine and en. Significantly, he obtained the same results even in the presence of chloride (0.5 M) and at much lower concentrations of total copper (2–900 μM). Belli and Zirino⁷⁶ also obtained Nernstian response for a CuISE (Orion 94–29) in Cu-en buffers, in the presence of chloride, over the range $3 < p\text{Cu} < 10$.

De Marco⁶⁰ showed that the response of an Orion 94–29 electrode in Cu-en buffers containing chloride (0.6 M) was not only Nernstian but the calibration line from $p\text{Cu}$ 8 to 15 was collinear with the calibration line for copper in chloride-free standards covering the range $p\text{Cu}$ 1 to 7. Similar results were also obtained by Belli and Zirino.⁷⁶ This implies that, in solutions of comparable ionic strength, there is a direct correspondence between the concentrations of copper in chloride-free standards at high concentrations of copper, and with concentrations of copper calculated from measured CuISE responses in buffered systems in the presence of chloride. XPS measure-

ments of a membrane exposed to a Cu-en buffer detected nitrogen on the surface implying that some en and/or its Cu(II) complexes had become adsorbed. However, this has no effect on either the slope or the E^0 value of the electrode presumably because the adsorbed and charged forms of en (*i.e.*, H_2en^{2+} , Hen^+ , $Cu(en)_2^{2+}$ and $Cu(en)^{2+}$) assist with the desorption of AgCl, usually formed in unbuffered media, through peptization.⁷⁵

This is not the case for the Radiometer F1112 electrode where the calibration line from $11 < pCu < 16$ in Cu-en buffers containing chloride (0.6 M) has a Nernstian slope but is offset from the calibration line from $1 < pCu < 5$ in chloride-free solution.⁶⁰ This leads to an effective sub-Nernstian response of about 15 mV/decade in the range $9 < pCu < 11$ and is one of the other reasons that we consider this electrode to be unsuitable for the analysis of seawater.

Electrode E^0 Values

De Marco⁶⁰ has shown that a CuISE (calibrated in Cu-en buffers) immersed in a Cu-glycine buffer ($Cu_{total} = 3$ nM, $NaCl = 0.3$ M), gave a response in agreement with the calculated Cu_{free} . This implies that the E^0 values, and slopes, are the same in saline glycine buffers, saline en buffers and in unbuffered systems in the absence of chloride.

This does not appear to be the case for seawater acidified to pH 2. De Marco *et al.*³⁴ have shown good agreement between values of Cu_{total} determined by DPASV and graphite furnace atomic absorption spectrometry (GFAAS) and by measurement with a CuISE, provided the Cu was determined by standard addition potentiometry.⁷⁷ In the latter case, it was assumed that acidification had destroyed any organic complexes of copper in the seawater and a Nernstian (31.6 mV/decade) response was obtained. However, the potential readings were much lower than expected on the basis of measurements in Cu-en buffers³⁴ and this is probably attributable to occlusion and adsorption of Cu into and onto precipitated organic matter at pH 2. Alternatively, the naturally occurring organic compounds had adsorbed on to the membrane surface at pH 2 (XPS identified carboxylic acid functional groups) giving rise to a negative shift in E^0 . When the sample was acidified to pH 2 and UV photooxidised, Cu was not removed by occlusion and/or adsorption into or onto precipitated organic matter, no membrane adsorption occurred and CuISE values, calibrated against Cu-en buffers, agreed with values obtained by GFAAS.³⁴ Precipitation and adsorption phenomena of naturally occurring compounds should be less important at pH 8, and the similarity of ISE data for Nafion-coated and bare membranes suggest that any such effects are negligible in seawater.⁶⁰

An XPS study of the jalpaite membrane,⁷⁵ aged in raw and acidified seawater, showed that the membrane surface composition changed slowly

from jalpaite (*i.e.*, $\text{Cu}_{0.45}\text{Ag}_{1.55}\text{S}$) to a mixture of copper deficient sulfide (*i.e.*, $\text{Cu}_{0.45-2x}\text{Ag}_{1.55}\text{S}_{1-x}$) along with AgCl and AgI. This process led to a gradual alteration of the electrode slope and E^0 which degraded the reproducibility of the ISE measurements. De Marco *et al.*,³⁴ however, demonstrated that the sensor surface and electrode calibration factors both stabilised after 24 hours exposure to seawater. Subsequently, conditioning of the ISE in seawater for 24 hours improved the electrode reproducibility and its response rate. Together, these factors helped to minimise the contamination of samples through corrosion of the ISE membrane. In fact, De Marco *et al.*³⁴ used DPASV to show that only about 0.3–0.8 nM of Cu was released into UV-photoxidised seawater during ISE analysis.

Beneficial Effects of Natural Organic Ligands

It is generally believed that the organic ligands of seawater alter the response of the CuISE and it has been suggested^{38,39} that a comparison of ISE response data in natural seawater against a calibration curve obtained in Cu buffers (*e.g.*, Cu-en) is prone to error because of the influence of different ligands on the ISE behaviour. However, this hypothesis is not supported by any structural or mechanistic studies of the CuISE membrane in media of this type. Consequently, the present authors have undertaken a detailed XPS and EIS (Electrochemical Impedance Spectroscopy) study of the jalpaite surface in natural seawater.

XPS analyses of jalpaite surfaces exposed to saline Cu-en buffer and natural seawater for 2 days revealed that the ligands (*i.e.*, en and humic/fulvic acids) were adsorbed onto the membrane, and this suppressed the formation of AgCl which usually gives rise to a classical chloride interference above 10^{-7} M total Cu (*i.e.*, super-Nernstian response).⁷⁵ It has been proposed⁷⁵ that amelioration of AgCl poisoning is due to promotion of nucleation and peptization of AgCl through the adsorption of surface active ligands (*e.g.*, H_2en^{2+} , Hen^+ , RCOO^- , *etc.*). Whatever the reason, this behaviour alleviates the chloride interference that normally shifts the ISE potential to negative values and gives rise to a super-Nernstian response.^{52,48}

A preliminary EIS study of the corrosion of jalpaite in UV-oxidised seawater showed that the corrosion resistance was trebled when the seawater was spiked with 1 mg/L of commercial humic acid.⁸⁰ This finding is consistent with a 3-fold reduction in the corrosion rate of jalpaite in the presence of adsorbed humic acid (XPS has detected the presence of carboxylic acids⁷⁵). Since De Marco *et al.*³⁴ have shown that 0.3–0.8 nM total Cu is released into UV-oxidised seawater (100 mL) over the duration of an ISE determination (*i.e.*, approximately 5 minutes), the lower corrosion rate in the presence of humic acid infers a Cu release of 0.1–0.26 nM total Cu. This represents a low level of background contamination for coastal and estuarine samples

that normally contain 1–10 nM total Cu. Contamination of the sample by dissolution of the membrane can be reduced to a negligible level by incorporating the CuISE in a flow injection analyser and we are currently investigating such a system.

The suppression of the corrosion rate of jalpaite in the presence of adsorbed humic acid is not unexpected. Long chain carboxylic acids are used widely as corrosion inhibitors, and it is proposed that these compounds function by physically blocking the cathodic and anodic sites of the corroding surface.^{81–84} Consequently, the natural organic compounds of seawater (*i.e.*, humic and fulvic acids) are behaving as corrosion inhibitors, and this significantly reduces the level of Cu contamination arising from corrosion of the jalpaite membrane.

In summary, the XPS and EIS data demonstrate that the organic compounds in seawater exert a beneficial effect on the behaviour of the jalpaite CuISE. The adsorption of organic matter suppresses both the formation of AgCl and the corrosion rate of jalpaite, and this leads to reliable ISE behaviour in natural seawater (*i.e.*, Nernstian response and low levels of Cu contamination).

Nafion-coating of ISE membranes has been proposed as a means of decreasing the dissolution of the membrane,⁶⁵ and eliminating the interference of halide ions^{60,64} since Donnan exclusion prevents these anions from contacting the surface. For the analysis of seawater, our results above indicate that this is not necessary for the Orion 94–29 electrode. Indeed, we consider Nafion-coating to be disadvantageous since the coating only lasts a day or so and increases the response time of the electrode.⁶⁴

However, Nafion-coating of an ISE should presumably also act as a barrier to naturally occurring organic compounds that would be expected to be anionic at the pH of seawater and so prevent the adsorption of such compounds on to the membrane surface. Hoyer and Loftager⁶⁴ showed that coating a CuISE with Nafion did not cause any significant change in E^0 in chloride-free media and De Marco⁶⁰ showed that the calculated value of $p\text{Cu}$ in seawater, using an Orion 94–29 electrode calibrated against Cu-en buffers, was essentially the same for a bare electrode (12.6) and after Nafion-coating (12.4). This implies that the electrode E^0 is unaffected by the presence of naturally occurring organic matter at pH 8 and that the electrode is therefore giving a reliable estimate of $p\text{Cu}$ in natural seawater. At pH 2, there is evidence that the adsorption of natural organic matter from seawater may change the E^0 value of the electrode but not the electrode slope.^{34,75} In this case, the CuISE can still be used, provided that the electrode is calibrated by the method of standard addition.^{34,75}

CONCLUSIONS

The results presented here indicate that the CuISE may be able to determine both $p\text{Cu}_{\text{total}}$ and $p\text{Cu}_{\text{free}}$ in seawater. While environmental quality guidelines are based on the former, it is widely accepted that the latter would be of far more value in determining the state of the environment as well as providing invaluable information on the uptake of copper by marine organisms. Moreover, by measuring $p\text{Cu}_{\text{free}}$ as a function of $p\text{Cu}_{\text{total}}$ we would be in a much better position to evaluate how a marine system would respond to changes in the input of copper as a result of various options proposed by environmental managers. The results presented in this paper suggest that this may be achievable in the near future.

Acknowledgments. – The authors thank M. E. Hughes (Chemistry Department, University of Tasmania) for assistance with the XPS work. Financial assistance from the Australian Research Council is gratefully acknowledged. We also thank Al Zirino, Ruth Eriksen and Dana Kester for valuable comments and discussions during the preparation of this manuscript.

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SAŽETAK**Mjerenja bakra u morskoj vodi: primjenljivost ionsko selektivnih elektroda**

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Uobičajeno je mišljenje da je ion-selektivna elektroda za bakar (CuISE) neprikladna za mjerenje u morskoj vodi zbog niza efekata koji uključuju: smetnje zbog kloridnih iona, elektrodni pomak, sub- i super-Nernstov odziv, onečišćenje uzorka i manjak osjetljivosti. Iako su svi ti efekti nedvojbeno opaženi, postoje također primjeri koji upućuju na to da CuISE može dati Nernstov odziv, 29 mV po dekadi, u otopinama soli sve do vrlo niskih koncentracija slobodnih bakrovih iona.

Primjena eksperimentalnih tehnika za ispitivanje promjena na površinama membrane, kao i upotreba »čistih« tehnika koje su postale standardne za ispitivanje tragova metala pri vrlo niskim koncentracijama, omogućile su bolje razumijevanje procesa koji dovode do navedenih problema.

Uz pregled literature, autori navode da se CuISE mogu rabiti za pouzdana mjerenja specijacije bakra u vodama mora i ušća.