A bespoke chloride sensor for seawater: Simple and fast with a silver electrode

Yanjun Guo, Richard G. Compton

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK

Abstract

Chloride quantification in natural seawater is important in both oceanography and corrosion science. A bespoke electrochemical method was developed for a facile and accurate chloride sensor specifically for use for the high chloride levels encountered in seawater (ca 0.5M). This is based on the voltammetric oxidation of a silver electrode over a well-defined potential range corresponding to AgCl nucleation/formation. The peak current for silver chloride formation varies linearly with chloride concentration in the range 0.484M to 0.624M provided the electrode is suitably activated. In particular, the reduction of dissolved oxygen was found to clean the surface and also to provide a stable peak potential against which other potentials can be referenced if it is wished to use a quasi-reference electrode. Thus, the overall voltammetric scan embraces first the reduction of oxygen followed by silver chloride formation and stripping. Reliable quantification was achieved in synthetic seawater with this methodology. Furthermore, the chloride anion concentration in three different authentic samples of natural seawater was measured accurately giving excellent agreement with independent analysis.

Keywords: Oxygen reduction reaction; chloride quantification; silver chloride; seawater

1. Introduction

Seawater compositions vary as a result of their biological content as well as reflecting local coastal industry and geology. Table 1, in which the number of significant figures presented are those reported in the literature[1], shows the typical inorganic composition of surface seawater per Kg with 35.00g total dissolved salts at 20℃. From which it can be seen that many ions are present with the chloride anion the dominant species.

Table 1. Concentrations of major ions in surface seawater[1]	
Composition	Concentration / mM
Na^+	4.8061×10^{2}
Mg^{2+}	5.413×10
Ca^{2+}	1.052×10
K^+	1.046×10
Sr^{2+}	9.2×10^{-2}
Cl^-	5.5939×10^{2}
SO_4^{2-}	2.8935×10^{1}
HCO_3^-	1.891
CO_3^{2-}	1.89×10^{-1}
Br^-	8.63×10^{-1}
F^-	7.0×10^{-2}
$B(OH)_4^-$	8.39×10^{-2}
$B(OH)_3$	3.42×10^{-1}

Importantly the local chloride concentration in seawater depends on location and season.[2, 3] In turn the chloride level influences the oxidation of toxic containments in marine environment such as Hg^0 and AgNPs.[4-6] At high chloride concentrations, such oxidative dissolution become easier as soluble chloride complexes of Hg(II) and Ag(I) can be formed.[7-9] Further, the marine chloride level is an important factor for electrochemical and atmospheric corrosion in coastal area constructions.[10, 11] The chloride stress affects materials such as steels even inside reinforced concrete structures.[10, 12, 13] Monitoring the specific chloride level in natural seawater systems is of vital importance in both oceanography and corrosion science.

The chloride concentration in seawater has been defined for many years via the term ‘chlorinity’.[14, 15] The definition of chlorinity (Cl, g Kg^{-1}) is the weight in grams of silver that will react with the halides in 328.5233g of seawater.[16] Originally chlorinity was measured to *estimate* the amount of total salts dissolved in seawater. The latter quantity reflects the so-called salinity of the water.[17] Perusal of Table 1 suggests that this is a major approximation! Moreover measurement of salinity, as is now widely undertaken, necessarily neglects the specific chemical effects of chloride, notably in respect of complexation and in corrosion. For neutral solutions, the traditionally used method for measuring chlorinity is the argentometric method (Mohr’s method)[18, 19]; potassium chromate is used to colorimetrically indicate the endpoint of adding silver nitrate. Invented more than a century ago, the method provides good accuracy in skilled hands but uses toxic (and expensive) materials, is time-consuming and is necessarily usually conducted remote from the point of

sampling. Meanwhile, a potentiometric titration method was reported using glass and silver chloride electrodes to detect the end point of the titration of seawater again with silver nitrate solution.[20-22] Potential difference measurements are easier and more precise to determine than colour changes, though both titration methods have the drawbacks of needing large sample volumes and the introduction of toxic chemicals.

Modern approaches to the measurement of chlorinity (Cl, g Kg^{-1}) prefer instrumental rather than wet methods. This comes at the expense of making the approximation that the salinity (S, g Kg^{-1}) reflects the chlorinity. Salinity is found using the polynomial conductivity correlation recommended by UNESCO[23, 24] (Eqn 1).

$$S(‰) = a_0 + a_1K_{15}^{1/2} + a_2K_{15} + a_3K_{15}^{3/2} + a_4K_{15}^{2} + a_5K_{15}^{5/2} \qquad 2 \leq S \text{ (g Kg}^{-1}) \leq 42, \qquad \text{(Eqn 1)}$$

where

$$K_{15} = \frac{conductivity\ of\ Standard\ Seawater\ at\ 15°C \text{ and 1 standard atmosphere}}{conductivity\ of\ KCl\ solution\ (32.4356 g\ KCl\ per\ kg\ solution) at\ 15°C \text{ and 1 standard atmosphere}}$$

and

ao= 0.0080, $a_1 = -0.1692$, $a_2 = 25.3851$, $a_3 = 14.0941$
$a_4 = -7.0261$, $a_5 = 2.7081$, $\sum a_i = 35.0000$

Then in order to find the chlorinity an empirical conversion from salinity is made using the Knudsen equation (Eqn 2).

$$S(\text{g Kg}^{-1}) = 1.80665\ Cl(\text{g Kg}^{-1}) \qquad \text{(Eqn 2)[15]}$$

Therefore the inferred chloride concentration relies on salinity data which in turn requires conductivity measurements which necessarily reflect more the total ion content (Table 1) albeit partly reflecting the different single ion conductivities.[2, 18, 24] Thus ocean salinity indicates approximately the totality of all dissolved salts per Kg seawater.[25] It can be either calculated from the electrical conductivity of sample solutions or measured via a salinometer, an instrument that detects and immediately converts conductivity and temperature of given samples into salinity readings.[26] The conductivity method is portable, but the conversion involves the (extreme) assumption using of potassium chloride (KCl) solutions to approximate seawater[14] and is unable to report specific chloride content.

A new analytical technique which is rapid, simple to use and, if needed, portable with no toxic waste and which directly measures the concentration of chloride is expected to have major impact. Herein we present a fast, robust and facile electrochemical method utilising the silver chloride (AgCl) formation reaction (Eqn 3) on a silver macro electrode to sense the chloride concentration accurately.

$AgCl_{(s)} + e^- \rightleftharpoons Ag + Cl^-$; $E^o = 0.2223V$ (Eqn 3)[27]

$O_2 + e^- \rightleftharpoons O_2^{\cdot-}$; $E^o = -0.284\ V$ (Eqn 4)[27]

$O_2^{\cdot-} \longrightarrow$ Bulk (Diffusion） (Eqn 5)

$O_2^{\cdot-} + H_2O + e^- \rightleftharpoons HO_2^- + OH^-$; E^o=-0.0649V (in alkaline solutions) (Eqn 6)[27]

Amperometric quantification of halides has been previously studied in low analyte concentrations,[28-31] but our new method requires a sample of as little as 3 mL filtered seawater and does not require dilution. It is developed specifically for use in undiluted seawater samples. In the method, the oxygen reduction reaction (ORR, Eqn 4-6)[32] is measured voltammetrically and simultaneously with AgCl formation. As previous reported[32], oxygen reduction on silver electrode in chloride rich neutral solution such as seawater shows clear voltammetric responses, the potentials of which are shown below to be insensitive to salinity or the chloride ion content. The magnitude of the ORR current response gives a measure of the dissolved oxygen content but more importantly the peak potential provides an ‘internal reference electrode’ against which the potential range explored can be reproducibly realised. Furthermore, and critically, potential scanning embracing the ORR reaction is shown to activate the electrode surface and to remove any residual AgCl at the electrode surface. The reported electrochemical method for detecting chloride concentrations thus newly provides essential information for seawater chemistry and corrosion analysis.

2. Experimental

2.1 Chemical reagents

All chemicals were used as received from Sigma Aldrich unless stated otherwise. Natural seawater samples (500mL, filtered) were each supplied by SAMS (Scottish Marine Institute, Argyll, UK), collected from the L4 station (50° 15.00' N, 4° 13.02' W), off the coast of Plymouth (Western Channel Observatory) or collected

from Bermuda 2 km deep in the sea. The spherical citrate-AgNPs ca.100nm diameter (Nanoxact, 0.02mg mL^{-1} silver, 2mM sodium citrate) were purchased from Nanocomposix, USA. For voltammetry analyzing silver chloride peaks in the absence of oxygen, solutions were rigorously degassed with nitrogen gas (N_2, 99.998%, BOC Gases plc, Guildford, UK). The nitrogen flow was sufficiently fast to ensure saturated level of N_2 for voltammetric consistency in each scan with no detectable ORR peaks. For voltammetry analyzing both silver chloride peaks and ORR signals, solutions (3.0mL) were stirred (400rpm) in open to air for 15min to ensure saturation of air each time. All the solutions were prepared using Millipore water with a resistivity of 18.2 MΩ cm at 25°C.

2.2 Electrochemical analysis

All electrochemical measurements were performed in a conventional three-electrode cell consisting of a platinum wire counter electrode, a Ag/AgCl reference electrode (in saturated KCl solution) and a working electrode (WE). A glassy carbon macro-electrode (GC, radius 1.49 mm, BAS, Technical, UK) calibrated as reported in a previous paper[32] or a silver macro-disc electrode (Ag, homemade, radius 1.13 mm) calibrated as described in ESI (Fig S1, ESI Section 1†) were used as working electrodes. Both electrodes were polished using a sequence of 1.0, 0.3 and 0.05micron alumina lapping compounds (Bucher, Germany). Measurements were performed using a μAutolab II potentiostat (Metrohm-Autolab BV, Utrecht, Netherlands) under 25°C. A constant temperature of 25±0.5°C was maintained by a thermostated water bath.

2.3 Chloride detection on a silver macro-electrode

First, cyclic voltammetry at various scan rates was performed to monitor both monolayer and bulk silver chloride formation at a macro silver WE. The experiments were conducted in freshly prepared nitrogen saturated 0.564M sodium chloride (NaCl) solution. The electrode was held at -1.0V for 1min before each scan. The analysed potential range was -0.15V to +0.060V for the monolayer and -0.15V to +0.87V for bulk silver chloride formation and stripping peaks.

Next, the silver chloride peak sensitivity to chloride concentration was studied voltammetrically in air saturated NaCl solutions and seawaters. The method was first undertaken with 0.564M air saturated NaCl at

100 mV s^{-1} scanning from -0.20V to -0.75V then anodically to +0.086V before returning to -0.20V and holding for 1min to remove remaining silver chloride. Second, experiments examined freshly prepared sodium chloride solutions (0.500M to 0.578M) at a scan rate of 20mV s^{-1} using the slightly adjusted potential range of. -0.20V to +0.093V for direct silver chloride formation and -0.75V to +0.093V for silver chloride formation with a simultaneous ORR measurement. Similarly, voltammetric detections of chloride in synthetic seawater and natural seawater were performed at 20mV s^{-1} within potential range of -1.0V and +0.10V. The synthetic seawater of variable salinity (31‰ to 38‰) was prepared using different amounts of sodium chloride following a literature recipe (Table1, ESI Section 2†).[33, 34] Meanwhile, to investigate if scanning to potentials corresponding to the ORR can active the electrode surface, three sets of successive experiments were conducted in air saturated 0.546 M NaCl at 20 mVs^{-1} at a temperature of 20 ℃. Each scan was performed with an air saturated solution *without* electrode mechanical polishing in between. Seven successive scans each started directly from -0.20V and swept towards +0.093V and reversed were conducted in control experiments. Fifteen successive scans each started directly from -0.20V and swept towards +0.093V and reversed followed by a 1min holding at -0.20V to test the single step potential cleaning method. Last, three successive scans each started from -0.20V and swept negative to -1.0V, then reversed to +0.093V and terminated at -0.20V were conducted in the depositions after ORR measurements.

2.4 Chloride detection with silver nanoparticles

Commercial AgNPs with volume of 3.0mL was washed with ultrapure water twice. The solution was centrifuged at 400 rpm for 10 min and 2.0mL of the supernatant was removed and replaced with a further 2.0mL ultrapure water for two repetitions. The final suspension was made up to a total of 3.0 mL to remain the same concentration as that before washing, and the washed AgNPs sample was dispersed by sonication for 1min before drop-casting onto the electrode. Specifically, after polishing the glassy carbon macro-electrode, 7.0μL of washed AgNPs was applied to the electrode surface and dried at 50ºC for 10min. The electrode was then used to detect chloride levels in synthetic seawater with a salinity of 31g Kg^{-1} and 38g Kg^{-1}.

2.5 Chloride titration of natural seawater samples

The so-called argentometric method was performed following a well established procedure[21]. Silver nitrate solution with a concentration of 0.0141M was freshly prepared and standardized with 0.0141M sodium chloride. Natural seawater was diluted 100 times into 50.0 mL and 0.25M potassium chromate (1.0 mL) was added afterwards. The final solution was stirred at 500 rpm and titrated slowly until the pinkish yellow end point.

3. Results and discussion

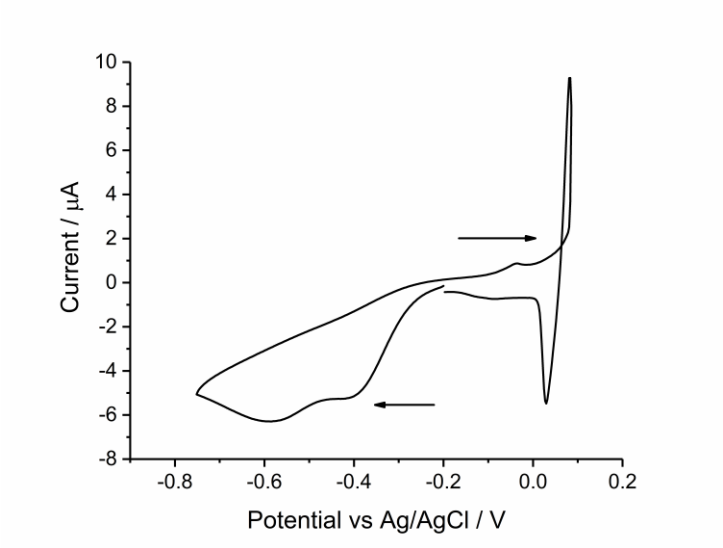

Fig 1. AgCl formation and stripping voltammetry after a scan first embracing ORR at 100mVs^{-1} in air staurated 0.564M NaCl solution at a silver macro-disc electrode r=1.13mm at 25℃, scanning from -0.20V to -0.75V followed by a reverse scan to +0.086V then back to -0.20V.

We explore the possible use of bulk silver chloride formation on silver electrodes for the quantification of chloride at the very high concentration levels present in authentic seawater (see Table 1). The voltammetric basis for our approach is plotted in Fig 1 which shows a voltammetric scan in 0.564M NaCl at 100mV s^{-1} starting at -0.20V, sweeping negative to -0.75V and then anodically to 0.086V before returning to the start voltage. Several voltammetric features are observed. First peak is seen at -0.41V corresponding to the one electron reduction of oxygen to superoxide (recall Eqn 4)

$$O_2 + e^- \rightleftharpoons O_2^{\cdot-} \; ; \; E^\circ = -0.284 \text{ V} \qquad \text{(Eqn 4)[27]}$$

The second reductive peak occurs at a potential of -0.59V and corresponds to further single electron reduction of superoxide to peroxide (recall Eqn 6)

$O_2^{\cdot-} + H_2O + e^- \rightleftharpoons HO_2^- + OH^-$; E°=-0.0649V (in alkaline solutions) (Eqn 6)[27]

On the oxidative scan silver oxidation is seen which consists of two processes. First a “monolayer film” of AgCl (Eqn 3) is formed with a peak potential of -0.036V. Second, a much larger oxidative feature is seen as a result of the formation and partial dissolution of bulk AgCl[35] at 0.083V in Fig 1. Corresponding cathodic, reduction features were seen in the scan following the reversal of the sweep direction leading to stripping peaks which were observed at -0.095V and+0.032V respectively. The monolayer is formed below the thermodynamic potential for the bulk process as expected for an underpotential deposition.[36, 37]

The formation of both forms of AgCl can be further associated with dissolution at high chloride levels.

AgCl + + (n-1) $Cl^- \rightleftharpoons AgCl_n^{-(n-1)}$ (Eqn 8)[35]

where n = 2, 3, 4 [38]

In the following we first address the silver chloride formation peaks in oceanic chloride concentration in more detail prior to exploring their response to variable chloride concentrations in pure sodium chloride solution and synthetic seawater. We then focus on the oxygen reduction peaks stability in synthetic seawater within the common ocean range of chlorinity. Finally, the overall method was assessed with three natural seawater samples.

3.1 Scan rate study of AgCl formation and stripping peaks

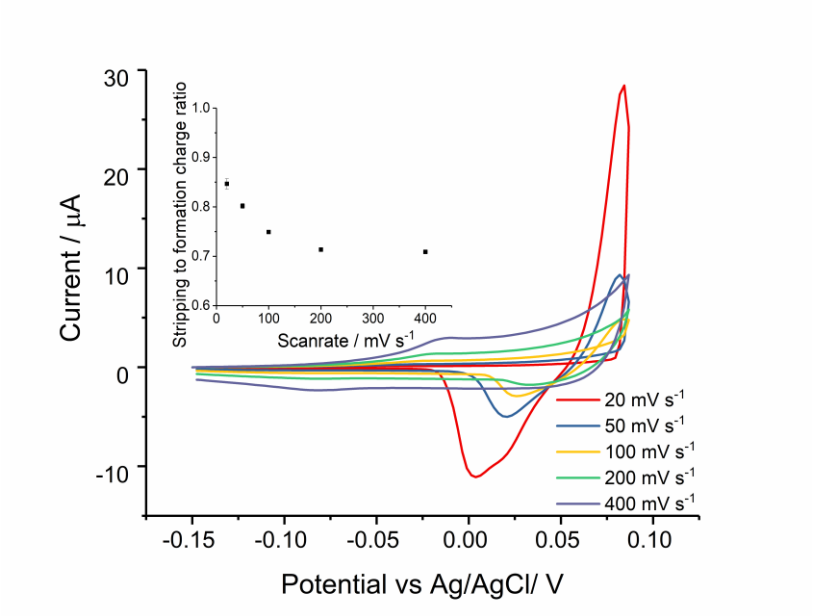

Fig 2. AgCl formation and stripping peak at different scan rates from 20 mVs^{-1} to 400 mVs^{-1} in N_2 saturated 0.564M NaCl solution at a Silver macro-disc electrode r=1.13mm at 25℃. The inlay shows the ratio of the charges in the stripping to deposition peaks as a function of scan rate.

The scan rate dependency of silver chloride peaks on a silver macro-disc electrode was studied at the oceanic chloride concentration (0.564M NaCl) over the range 20mVs^{-1} to 400mVs^{-1} (Fig 2). Each scan consisted of an initial 1min electrochemical cleaning at -1.0V with cyclic voltammetry swept from -0.15V and reversed at 0.087V. The monolayer was formed at -0.013V and reduced at -0.084V with peak current proportional (Fig S2, ESI Section 3) to the scan rate but as expected for the formation of a complete monolayer it did not reflect the bulk chloride concentration of chloride in the range studied[37, 39], although in low halide concentration such pre peak has been used successfully in iodide detection by Malongo *et al.* [31]. Previous work showed the so-called 'monolayer' is in fact formed of silver chloride clusters distributed on the electrode surface rather than a continuous monolayer of AgCl. Prior to formation of the bulk AgCl the clusters expand and merge with each other.[40, 41] The charge passed in the 'monolayer' was found to be 1.2±0.1µC cm^{-2} (SI. Section 2) consistent with the literature.[39] The charge passed in the first peak is tiny compared with that of the overall AgCl formation in peak at +0.084V (637.7 ±82.3 µC cm^{-2} at 20 mV s^{-1}), so does not affect the analysis of the second peak nor does it provide information on solution chloride levels.

The large, bulk AgCl formation feature was observed at higher overpotential. Fig 2 shows that at high scan rates the peak is not seen; rather a largely of pseudo capacity origin signal is observed in the range 200 $mVs^{-1}$to

400mVs^{-1} with the current scaling in direct proportion to the scan rate. However, at progressively lower scan rates from 100mVs^{-1}to 20mVs^{-1}, an anodic nucleation loop started to develop at ca +0.084V on the forward scan associated with an increased signal in the stripping peak on the subsequent cathodic scan. These observations are consistent with those of Pargar *et al*.[42] and confirm that a thicker silver chloride film was built with prolonged reaction time. Mele *et al*[35] developed a detailed mechanism based on progressive nucleation and diffusion-controlled growth in which higher chloride levels promote AgCl formation as well as its subsequent partial dissolution suggesting potential analytical use for chloride determination.[8, 40, 42]

Cathodic stripping signals were observed with decreasing peak potentials from 0.026V at 100mVs^{-1} to 0.0040 at 20mVs^{-1} and shoulder appeared in the latter case at ca. 0.02V which is in agreement with literature.[37, 42] Fig 2 (inlay) shows a plot of the ratio of the charge passed in the silver chloride reduction to that calculated by integrating the oxidation current over the range -0.15V to 0.087V (forward sweep) and 0.087V to 0.055V (reverse sweep) as a function of the scan rate from 20mVs^{-1} to 400mVs^{-1} At low scan rates most of the deposited silver chloride is stripped (ratio approaches unity). The apparent inefficiency of stripping at high scan rates reflects the large capacitance response under these conditions. The slower scan rates ie. 20mVs^{-1} was selected for the following determinations of chloride level focusing on the bulk AgCl deposition / stripping.

3.2 Chloride determination in NaCl solutions

Given the complexity of seawater (Table 1) initial studies aimed at the determination of chloride in seawater focussed first on aqueous NaCl solutions containing concentrations similar to those found in open oceans. The latter range spans the salinity range from 32g Kg^{-1} to 37g Kg^{-1} [41]. This corresponds to a chloride concentration range of 0.500M to 0.578M (Table 2). The following experiments were conducted to determine whether it is possible to distinguish chloride concentrations with silver chloride voltammetric responses.

Table 2 Oceanic chloride concentrations as inferred from salinity values via Eqn 2.

Salinity / g Kg^{-1}	32	33	34	35	37
NaCl / M	0.500	0.515	0.531	0.546	0.578

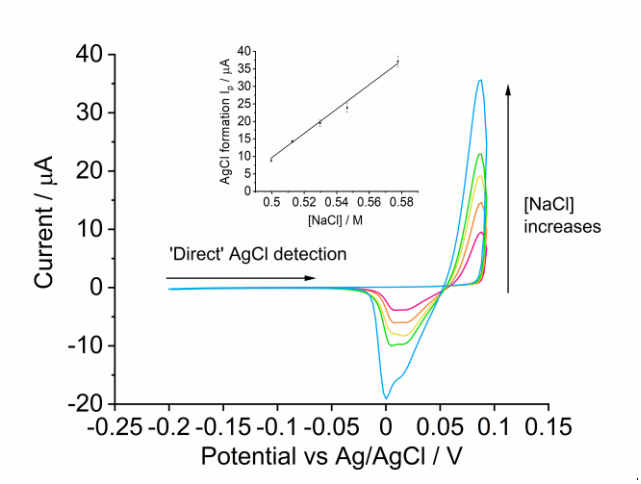

Fig 3. The chloride concentration determination conducted voltammetrically at 20mV s^{-1} in air saturated NaCl solutions (0.500M to 0. 578M) measured at a silver macro-disc electrode. Voltammograms for silver chloride formation started from -0.20V and reversed at +0.093V. Red: 0.500M NaCl; orange: 0.515M NaCl; yellow: 0.531M NaCl; green: 0.546M NaCl and blue: 0.578M NaCl. Inlay: the calibration curve of the silver chloride nucleation peak height against chloride concentration with a regression coefficient R^2 of 0.989 , each data point is the average of a minimum of 3 repeats.

Silver chloride deposition and stripping were performed at 20mV s^{-1} in 0.500M to 0.578M air saturated sodium chloride solutions. Fig 3 shows the study of the deposition / stripping by means of a potential scan from -0.2V to +0.093V followed by sweep reversal to -0.2V. The electrode was held 1min at -0.2V to remove remaining silver chloride.

Initially, an experiment was performed to determine silver chloride peaks parameters as a function of chloride content without oxygen reduction. Fig 3 depicts two large peaks one measured at ca. +0.050V for nucleation and another at ca. 0.00V for cathodic reduction. The broad reduction peak consist of two adjacent peaks at 0.00V and 0.020V. The shoulder in the stripping peak has been discussed by Pargar *et al.*[42] and Birss *et al.*[37], the appearance peak at 0.020V may reflect instantaneous nucleation or silver dissolution, but the cause remains open to debate due to the mechanistic complexity of silver chloride formation. Nevertheless, both nucleation and stripping peak heights increased with increased sodium chloride concentrations. As presented in the inset of Fig 3 a, the bulk AgCl nucleation peak current is linearly dependent on the chloride concentration from 0.500M to 0.578M although the calibration curve does not pass through the origin indicating a threshold concentration is required for the nucleation process.

The overall charge was evaluated for the deposition / stripping process. For the silver chloride nucleation, the integrated range embraced all potentials where oxidative currents flowed; from -0.20V to + 0.093V on the

forward scan and, in the reverse, from + 0.093V to the potential where the oxidative current became zero. In silver chloride reduction, the current was integrated from the potential corresponding to the onset of reductive currents to -0.20V. The integration showed that more than 90% silver chloride formed was removed at each experiments, but the remaining silver chloride can deactivate the surface and prevent reproducible measurements from scan to scan (Fig 4 a). To allow multiple measurements without the need for mechanical cleaning in between, electrochemical cleaning was attempted at -0.20V for 1min after each scan. However this unavoidably increased surface roughness and required prolonged polishing afterwards, but only gave a slight improvement (Fig 4b). We thus sought to discover a more "gentle" method that removes silver chloride residue and 'actives' the silver surface before deposition and attention was turned to the possible use of the oxygen reduction reaction for this purpose whilst noting that an additional advantage of scanning the ORR prior to making analytical measurements using the AgCl features is that it might provide an 'internal reference' potential which would allow the use of a quasi-reference electrode in the analytical measurement by virtue of giving a voltammetric peak(s) against which excursions of a well defined potential range into the AgCl formation region could be made. This has the advantage that the quasi-reference electrode, could be chosen to avoid a liquid junction potential near a conventional reference electrode due to leakage of its electrolyte and / or ingress of seawater and thus a possible shift in the overall voltammogram in addition to any changes resulting from residual AgCl peaks from previous measurements. To avoid such uncertainty, a stable internal reference potential is desirable and the ORR was explored in these contexts with the further possible advantage that dissolved oxygen is invariably present in seawater samples and so the approach would both exploit this whilst simultaneously avoiding the need for outgassing as is commonly undertaken in voltammetry. The peak currents associated with the ORR were also explored to see if they could additionally provide a measure of the dissolved oxygen concentration

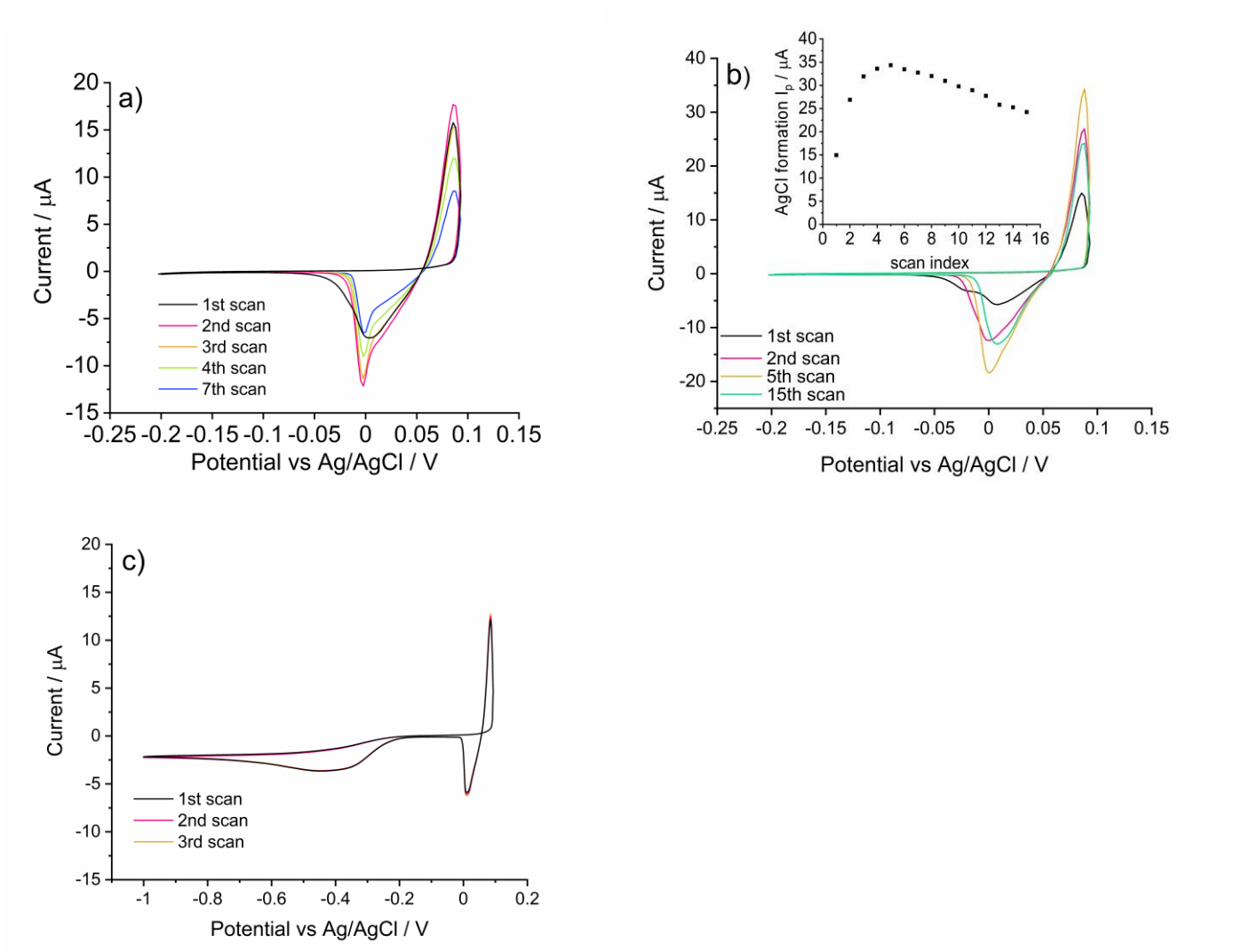

Fig. 4. Silver chloride deposition reproducibility at 20mVs^{-1} at 20°C in 0.546M NaCl air saturated solution. a) Seven successive scans each started from -0.20V to +0.093V and reversed. b) Fifteen successive scans each started from -0.20V to +0.093V and reversed followed by electrochemical cleaning at -0.2V for 1min, inset shows silver chloride formation peak current as a function of the scan index. c) Three successive scans each started from oxygen reduction at -0.20V to -1.0 V and reversed at +0.093V for silver chloride formation.

Accordingly, the oxygen reduction reaction was explored, noting that the oxygen reduction reaction has been studied in chloride rich media and shown to involve two voltammetric features with a first electron transfer at -0.40V forming superoxide and a second at -0.60V forming peroxide.[32] The surface activation with ORR was studied voltammetrically in air saturated 0.546M NaCl at 20mVs^{-1} (Fig 4) with three sets of successive experiments. Each scan was conducted with air saturated solution *without* mechanical polishing of the electrode in between. First a control experiment involving simply the 'direct' formation of AgCl was made in which the voltammetric scan started from -0.20V and swept towards +0.093V at which point it was reversed and a total of seven successive such scans made. Second, the step potential cleaning method was attemped,

starting from a cyclic voltammetry between -0.20V and +0.093V followed by 1min holding at -0.20V and a total of fifteen successive such scans made (Fig 4b). Third a wider potential window was scanned to embrace the ORR. These sweeps started from -0.20V, swept negative to -1.0V, then reversed to +0.093V at which potential the scan again reversed terminating at -0.20V before repeating thrice (Fig 4c). The 'direct' reaction shows large peaks for silver chloride formation (0.088 V) and reduction (ca. 0.00V). Both increased in the second scan but decreased significantly from 15.5µA to 8.4 µA afterwards due to loss of active silver sites. The primary electrochemical cleaning at -0.20V for 1min follows a similar trend with the control experiment but the initial increase in silver chloride peak height was extended from 15µA to 34µA (5^{th} scan) followed by a slower decay to 24µA in 15^{th} scan. In contrast, in the third type of experiment, when oxygen reduction was first conducted prior to the AgCl formation, a remarkable reproducibility was found in both the single broad ORR feature at ca. -0.40V and two sharp silver chloride peaks as shown in Figure 3 which is similar to that seen in concentrated KCl solution albeit with the superoxide and peroxide signals more merged. The application of combined ORR and AgCl reactions are discussed afterwards.

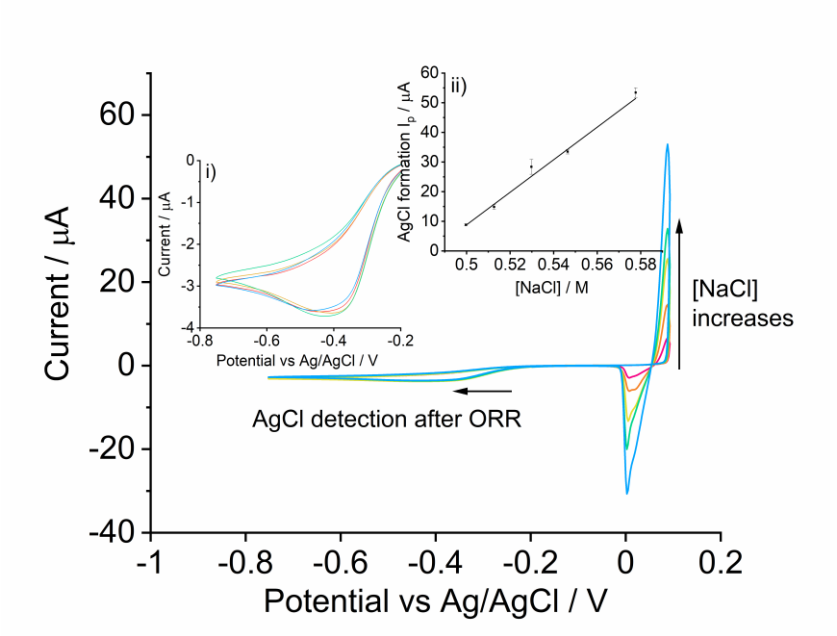

Fig 5. The chloride concentration determination conducted voltammetrically at 20mV s^{-1} in air saturated NaCl solutions (0.500M to 0. 578M) measured at a silver macro-disc electrode. Voltammograms of the first oxygen reduction scanned from -0.20V to -0.75V followed by silver chloride reactions reversed at +0.093V; Red: 0.500M NaCl; orange: 0.515M NaCl; yellow: 0.531M NaCl; green: 0.546M NaCl and blue: 0.578M NaCl. Inlay i) expanded ORR features; ii) the calibration curve of the silver chloride nucleation peak height against chloride concentration with a regression coefficient R^2 of 0.996, each data point is the average of a minimum of 3 repeats.

To investigate practical benefits of scanning through the ORR voltammetric features prior to the AgCl formation/stripping analysis, the voltammetry shown in Fig 5 were performed and compared to 'direct' AgCl formation/stripping in Fig 3. Each voltammogram was conducted at $20mVs^{-1}$, and consisted of initial oxygen reductions induced by scanning from -0.20V to -0.75V followed by a reverse sweep up to the silver chloride reactions at + 0.093V and terminated at -0.20V. The inset of Fig 5 shows single broad ORR peak at ca. -0.40V instead of two adjacent peaks in Fig 1 at -0.40V and -0.60V. This is due to shift in peroxide peak potential from -0.60V at 100mV s^{-1} to a lower overpotential of ca.- 0.45V at 20mV s^{-1}. A previous study of ORR in pure 0.54M KCl solution showed a similar shift in peroxide peak potential from -0.6V at 400 mVs^{-1} to -0.5V at $20mVs^{-1}$ on crystalline silver electrode in contrast to the relative constant peak potential for superoxide formation[32], possibly due the increased superoxide concentration. Regardless of the changes in peroxide formation, the stability of the superoxide feature implies the advantage of introducing ORR in oceanic chlorinity detections as an internal reference potential.

Meanwhile, Fig 5 shows silver chloride features after oxygen reduction. From -0.20V to +0.093V. Only bulk silver chloride peaks were observed at potentials identical to 'direct' deposition / stripping measurements in Fig 5, but the nucleation peak is much higher in current than seen in the 'direct' measured signals at the same chloride level. Fig 5 inlay ii) shows a linear calibration curve of silver chloride nucleation peak current against the chloride concentration from 0.500M to 0.578M. Particularly, the overall 'sensitivity' was improved from 10μA to ca.35μA in Fig 3 to 10μA to ca.55μA in Fig 5. The significant enhanced sensitivity to chloride concentrations shows the second advantage of introducing ORR for the silver surface activation.

In summary, the methodology for chloride measurement in pure solution can be improved by first voltammetrically scanning the oxygen reduction reactions before making the silver chloride deposition /stripping measurements at $20mVs^{-1}$ and has been validated in pure sodium chloride solutions within the oceanic chlorinity range using the bulk deposition peak current to determine chloride concentrations. We next apply the method in synthetic seawater.

3.3 Chloride level determination in synthetic seawater

In the previous section we established an approach for the accurate electrochemical determination of high chloride concentrations in excess of 0.500M. The next objective is to apply this method to synthetic seawater with a composition within the oceanic salinity range. In order to obtain accurate correlations, synthetic seawater of eight levels of chloride concentrations were studied. The detection range was also extended to salinity values from 31g Kg^{-1} to 38g Kg^{-1} in addition to the usually encountered range of 32g Kg^{-1} to 37g Kg^{-1}. The total chloride concentrations studied thus ranged from 0.484M to 0. 593M and were made using varying amounts of sodium chloride to the otherwise standard recipe (ESI, Table 1).[33, 34]

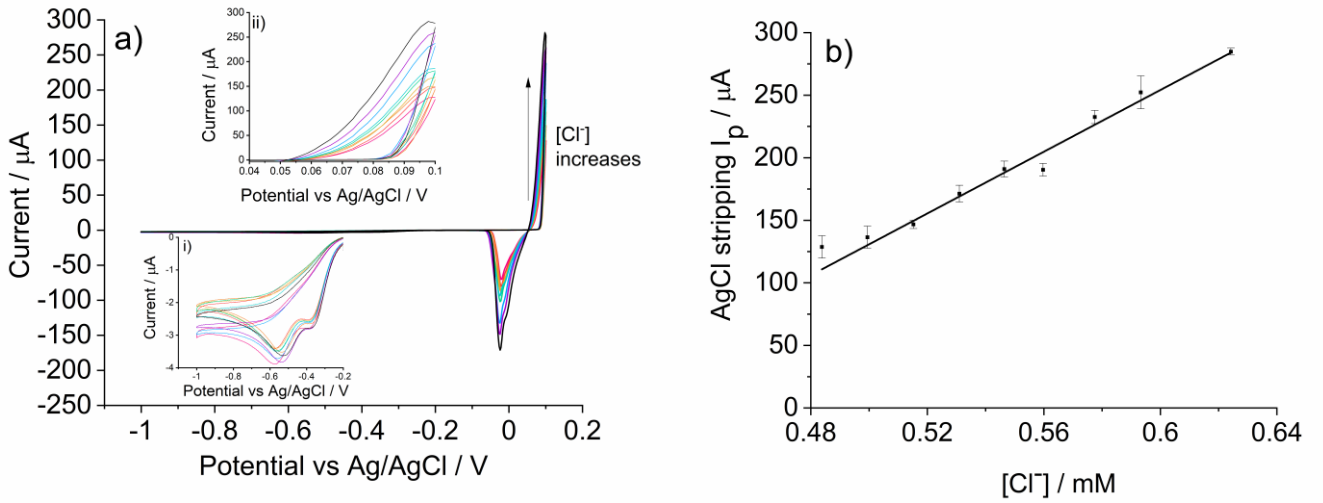

Fig 6. The chloride concentration determination conducted at 20mVs^{-1} in air saturated synthetic seawater (0.484M to 0.624M) measured at a silver macro-disc electrode. a) Voltammograms consist of first oxygen reduction from -0.20V to -1.0V followed by silver chloride reactions reversed at +0.1V; inlay i) expanded ORR features; ii) expanded silver chloride nucleation peaks; b) the calibration curve of the silver chloride nucleation peak height against chloride concentrations with a regression coefficient R^2 of 0.989, each data point consists of 4 repeats.

The electroanalytical responses of silver chloride at 20mVs^{-1} were explored in air saturated synthetic seawater. The potential range was extended into -1.0V to +0.1V. Fig 6 shows the voltammogram which consists of oxygen reduction and silver chloride deposition / reduction, scanned first from -0.20V to -1.0V then scanned positively to +0.1V and returned to -0.20V.

First the ORR features were analysed as providing a possible internal reference potential. Fig 6 a inset i) shows two clear separated diffusional peaks during two single-electron transfer reactions of oxygen at ca. -0.40V and

-0.60V. The first peak refers to the formation of superoxide the potential of which was used as an internal reference. The second peak relates to further reaction to produce peroxide According to the summarised data in ESI Section 4†, Fig S3, the superoxide peak potential and current are almost constant at -0.39±0.01V and 2.51±0.08μA over the chloride concentration (0.484M to 0.624M). Closely similar superoxide redox potentials were reported in other media by Baxendale *et al.[43]* (−0.395V *vs.* Ag/AgCl) and Koppenol *et al.* [44](-0.385±0.02V *vs.* Ag/AgCl). The constant value of superoxide peak potential confirms the viability of using the superoxide peak as an internal reagent free reference potential in air saturated seawater. Meanwhile, the constant superoxide peak current is consistent with the findings of Debelius *et al.*[45] who determined oxygen solubility in brine with salinity of 30.77g Kg^{-1} (212.7uM) and 37.77g Kg^{-1} (203.2 uM) experimentally. The overall difference in current is as little as 4% detected voltammetrically.

Next, silver chloride formation / reduction features were analysed. Both peaks increased clearly along with the chloride increase (Fig 6 a), similar to the trend observed in pure sodium chloride measurements. The peak height of the AgCl formation varied linearly with chloride concentration from 0.484M to 0.624M. The calibration curve is plotted in Fig 6 b. The methodology with extended potential range of -1.0V to +0.1V shows increased sensitivity of chloride detection from 0.36mA M^{-1} in Fig 5 to 1.13mA M^{-1} in Fig 6 even in present of other sea salts.

Meanwhile, Toh *et al.*[46] quantified chloride ions in synthetic sweat using silver nanoparticles modified electrodes. Thus attempts were made to similar use silver nanoparticles to detect chloride ions in synthetic seawater. 1.0 nmole equivalent of silver in the form of washed AgNPs (diameter of 100nm) was drop casted on a glassy carbon electrode. Cyclic voltammograms were swept at 20mV s^{-1} from -0.40V to +0.90V and reversed in three different nitrogen saturated solutions; first 0.1M KNO_3 solution in the control experiment then two synthetic seawater solutions with 0.484M Cl^- and 0.593M Cl^-(data not shown). In 0.1M KNO_3, a broad peak at +0.50V was observed corresponding to oxidation of metallic silver. In synthetic seawater solutions, two peaks were observed at ca. +0.11V and -0.040V corresponding to silver chloride formation and stripping. By increasing media chloride concentration from 0.484M to 0.593M, the silver chloride formation peak was shifted from +0.11V to +0.10 V with a slight peak current decrease. Similarly the broad stripping

peak was shifted from -0.040V to -0.033V. Despite a decreased overpotential with increased chloride concentration seen for both oxidation and reduction features, for the whole detection range the peak potential shifted as little as 0.010V. This is consistent with expectation based on the Nernst equation - the range of chloride ions encountered in seawater is too small to be accessed via a peak potential measurement and so quantification of chloride ions using AgNPs was not successful and further experiments focussed on the method developed above using a silver electrode.

3.4 Chloride level determination in natural seawater

To examine the feasibility of real seawater chloride determination, batches of Scottish, Plymouth and Bermuda seawater were tested using the newly developed method. The chloride concentrations of the authentic samples were tested with the well established argentometric method.[21] First 0.0141M silver nitrate was standardised with sodium chloride solution of the same concentration. Next, 1.0mL of natural seawater was diluted into 100.0mL then 1.0mL of 0.25M potassium chromate solution was added. Silver nitrate was slowly dropped into the seawater sample until the pinkish yellow end point was realized. With three repeats, the estimation of the chloride concentration by titration in the Scottish, Plymouth and Bermuda seawater sample were found to be 0.563 ± 0.001M, 0.582 ± 0.001M and 0.619 ± 0.001 M respectively.

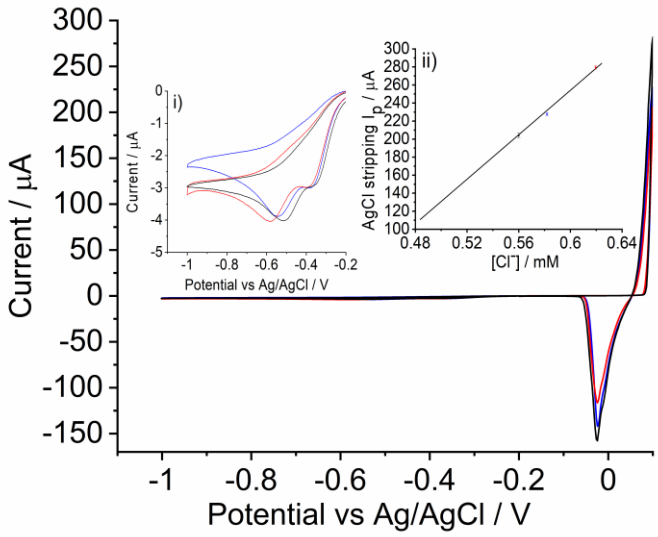

Fig 7. The chloride concentration determination conducted at 20mV s^{-1} in air saturated authentic seawater samples measured at a silver macro-disc electrode. Black: natural seawater from Scotland, [Cl^-] = 0.563M , blue: natural seawater from Plymouth, [Cl^-] = 0.562M; Red: natural seawater from Bermuda. Inlay i) expanded ORR feature, ii) black line: the calibration plot of peak height of nucleation peak against the concentration of

chloride from synthetic seawater data; black scatter: Scottish seawater sample; blue scatter: Plymouth seawater sample; red scatter: Bermuda seawater sample, each data point consists of three repeats.

Next, a cyclic voltammogram was conducted in air saturated natural seawater starting from -0.20V to -1.0V with reversal to +0.10V before finally being returned to -0.20V at the end of the scan. The experiment was repeated three times. Fig 7 shows the recorded voltammograms for three natural seawater samples.The voltammetric peaks of both oxygen reductions and silver chloride deposition and stripping signals are consistent with each other based on their identical dissolved oxygen concentrations and higher chloride concentration in Plymouth and the extreme salty Bermuda deep seawater. The latter either reflects the depth of sampling or evaporation during transport of the sample For the ORR features, two large peaks were as expected and discussed above, observed for each sample at -0.39V and ca. -0. 55V. The peak potential for superoxide formation matches the experimental results in pure sodium chloride and synthetic seawater so that the peak can be used as an internal reference. Meanwhile the concentration of chloride in natural seawaters were calculated via the calibration curve shown in inset ii) using the silver chloride formation peak current. For both seawater samples, with 204±3μA (Scotland), 228±2μA (Plymouth) and 280±2μA (Bermuda) in peak height, the expected chloride concentration is 0.561±0.003M (Scotland), 0.581±0.002M (Plymouth) and 0.624±0.003M (Bermuda) in excellent agreement with the titration result (black, red and blue scatters of inlay ii)). In this way the developed method was validated in authentic seawater

Conclusions

This paper presents a simple and facile chloride detection system for the use in media of high chloride concentration and was specifically developed for the use in seawater in which chloride is the major component and presents over a narrow range of high concentrations of ca. 0.5M which challenges potentiometric methods. The method uses the currents flowing during the nucleation / growth of AgCl on a bulk silver electrode over a well-defined potential range as a measure of the chloride concentration. In order to realise reproducibly clean electrodes and to facilitate the use of quasi-reference electrodes a prior sweep is used to clean the electrode and permit reproducible measurements even without mechanical cleaning. The method was developed using authentic samples of seawater from Scotland, Plymouth and Bermuda respectively with validation against an independent method.

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References

[1] M.E.Q. Pilson, An Introduction to the Chemistry of the Sea, 2 ed., Cambridge University Press, Cambridge, 2012.
[2] E.L. Lewis, The practical salinity scale of 1978 and its antecedents, IEEE J. Oceanic. Eng. 5(4) (1982) 350-357.
[3] G.S.E. Lagerloef, C.T. Swift, D.M.L. Vine, Sea surface salinity: The next remote sensing challenge., Oceanography (Wash D C) 8(2) (1995) 44-50.
[4] M. Yamamoto, Stimulation of elemental mercury oxidation in the presence of chloride ion in aquatic environments, Chemosphere 32(6) (1996) 1217-1224.
[5] A. Gupta, M. Maynes, S. Silver, Effects of halides on plasmid-mediated silver resistance in Escherichia coli, Appl. Environ. Microbiol. 64(12) (1998) 5042-5045.
[6] C. Batchelor-McAuley, K. Tschulik, C.C.M. Neumann, E. Laborda, R.G. Compton, Why are Silver Nanoparticles More Toxic Than Bulk Silver? Towards Understanding the Dissolution and Toxicity of Silver Nanoparticles, Int. J. Electrochem. Sci. 9(3) (2014) 1132-1138.
[7] K.W. Bruland, M.C. Lohan, 6.02 - Controls of Trace Metals in Seawater, in: H.D. Holland, K.K. Turekian (Eds.), Treatise on Geochemistry, Pergamon, Oxford, 2003, pp. 23-47.
[8] C. Levard, S. Mitra, T. Yang, A.D. Jew, A.R. Badireddy, G.V. Lowry, G.E. Brown, Effect of Chloride on the Dissolution Rate of Silver Nanoparticles and Toxicity to E. coli, Environ. Sci. Technol 47(11) (2013) 5738-5745.
[9] F.M.M. Morel, A.M.L. Kraepiel, M. Amyot, THE CHEMICAL CYCLE AND BIOACCUMULATION OF MERCURY, Annu. Rev. Ecol. Evol. Syst 29(1) (1998) 543-566.
[10] U. Angst, B. Elsener, C.K. Larsen, Ø. Vennesland, Critical chloride content in reinforced concrete — A review, Cement and Concrete Research 39(12) (2009) 1122-1138.
[11] J. Alcántara, D.d.l. Fuente, B. Chico, J. Simancas, I. Díaz, M. Morcillo, Marine Atmospheric Corrosion of Carbon Steel: A Review, Materials 10(4) (2017) 406.
[12] K.Y. Ann, H.-W. Song, Chloride threshold level for corrosion of steel in concrete, Corros. Sci. 49(11) (2007) 4113-4133.
[13] V. Marcos-Meson, A. Michel, A. Solgaard, G. Fischer, C. Edvardsen, T.L. Skovhus, Corrosion resistance of steel fibre reinforced concrete - A literature review, Cem. Concr. Res. 103 (2018) 1-20.
[14] F.J. Millero, R. Feistel, D.G. Wright, T.J. McDougall, The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale, Deep Sea Research Part I: Oceanographic Research Papers 55(1) (2008) 50-72.
[15] W.J. Wallace, The development of the chlorinity/salinity concept in oceanography, Elsevier Scientific Pub. Co, Amsterdam, New York, 1974.
[16] J. LYMAN, REDEFINITION OF SALINITY AND CHLORINITY, 14(6) (1969) 928-929.
[17] R.H. Stewart, Introduction to physical oceanography, University Press of Florida, United States, 2009.
[18] K. Grasshoff, A. Wenck, A Modern Version of the Mohr-Knudsen Titration for the Chlorinity of Sea Water, ICES Journal of Marine Science 34(3) (1972) 522-528.
[19] T.-K. Hong, M.-H. Kim, M.-Z. Czae, Determination of Chlorinity of Water without the Use of Chromate Indicator, International Journal of Analytical Chemistry 2010 (2010) 602939.
[20] W.S. REEBURGH, J.H. CARPENTER, DETERMINATION OF CHLORINITY USING A DIFFERENTIAL POTENTIOMETRIC END POINTY1, 9(4) (1964) 589-591.
[21] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewate, 20th ed., APHA American Public Health Association, USA, 1998.
[22] H.H. Willard, J. Merritt, L L, J.A. Dean, J. Settle, F A, Instrumental methods of analysis, 7th edition, Florence, KY (US); Wadsworth Publishing Company1988.
[23] UNESCO, Tenth report of the joint panel on oceanographic tables and standards, UNESCO Technical Papers in Marine Science 36 (1981) 24.
[24] E.L. Lewis, R.G. Perkin, The Practical Salinity Scale 1978 - Conversion of Existing Data, Deep Sea Res. Part A Oceanogr. Res. Pap. 28(4) (1981) 307-328.
[25] D.G. Wright, R. Pawlowicz, T.J. McDougall, R. Feistel, G.M. Marion, Absolute Salinity, "Density Salinity" and the Reference-Composition Salinity Scale: present and future use in the seawater standard TEOS-10, Ocean Sci. 7(1) (2011) 1-26.
[26] E. Lewis, The practical salinity scale 1978 and its antecedents, IEEE J. Oceanic. Eng. 5(1) (1980) 3-8.
[27] A.J. Bard, R. Parsons, J. Jordan, P. International Union of, C. Applied, Standard potentials in aqueous solution, M. Dekker, New York, 1985.
[28] K. Arai, F. Kusu, N. Noguchi, K. Takamura, H. Osawa, Selective Determination of Chloride and Bromide Ions in Serum by Cyclic Voltammetry, Analytical Biochemistry 240(1) (1996) 109-113.
[29] X. Qin, H. Wang, Z. Miao, X. Wang, Y. Fang, Q. Chen, X. Shao, Synthesis of silver nanowires and their applications in the electrochemical detection of halide, Talanta 84(3) (2011) 673-678.
[30] J. Bujes-Garrido, D. Izquierdo-Bote, A. Heras, A. Colina, M.J. Arcos-Martínez, Determination of halides using Ag nanoparticles-modified disposable electrodes. A first approach to a wearable sensor for quantification of chloride ions, Analytica Chimica Acta 1012 (2018) 42-48.
[31] T.K. Malongo, S. Patris, P. Macours, F. Cotton, J. Nsangu, J.-M. Kauffmann, Highly sensitive determination of iodide by ion chromatography with amperometric detection at a silver-based carbon paste electrode, Talanta 76(3) (2008) 540-547.
[32] Y.J. Guo, M.J. Yang, R.C. Xie, R.G. Compton, The oxygen reduction reaction at silver electrodes in high chloride media and the implications for silver nanoparticle toxicity, Chem. Sci. 12(1) (2021) 397-406.
[33] F.M.M. Morel, J.G. Rueter, D.M. Anderson, R.R.L. Guillard, AQUIL: A CHEMICALLY DEFINED PHYTOPLANKTON CULTURE MEDIUM FOR TRACE METAL STUDIES12, J. Phycol. 15(2) (1979) 135-141.
[34] N.M. Price, G.I. Harrison, J.G. Hering, R.J. Hudson, P.M.V. Nirel, B. Palenik, F.M.M. Morel, Preparation and Chemistry of the Artificial Algal Culture Medium Aquil, Biological Oceanography 6(5-6) (1989) 443-461.
[35] M.F.L. de Mele, R.C. Salvarezza, V.D. Vasquez Moll, H.A. Videla, A.J. Arvia, Kinetics and Mechanism of Silver Chloride Electroformation during the Localized Electrodissolution of Silver in Solutions Containing Sodium Chloride, J. Electrochem. Soc. 133(4) (1986) 746-752.
[36] H. Ha, J. Payer, The Effect of Silver Chloride Formation on the Kinetics of Silver Dissolution in Chloride Solution, Electrochimica acta 56(7) (2011) 2781-2791.
[37] V.I. Birss, C.K. Smith, The anodic behavior of silver in chloride solutions—I. The formation and reduction of thin silver chloride films, Electrochim. Acta. 32(2) (1987) 259-268.
[38] R.D. Giles, The anodic behaviour of silver single crystal electrodes in concentrated chloride solutions, J. Electroanal. Chem. Interf. Electrochem. 27(1) (1970) 11-19.

[39] S. Jaya, T.P. Rao, G.P. Rao, Mono-and multilayer formation studies of silver chloride on silver electrodes from chloride-containing solutions, J. Appl. Electrochem. 17(3) (1987) 635-640.
[40] X. Jin, J. Lu, P. Liu, H. Tong, The electrochemical formation and reduction of a thick AgCl deposition layer on a silver substrate, J. Electroanal. Chem. 542 (2003) 85-96.
[41] H. Ha, J. Payer, The Effect of Silver Chloride Formation on the Kinetics of Silver Dissolution in Chloride Solution, Electrochim Acta 56(7) (2011) 2781-2791.
[42] F. Pargar, H. Kolev, D.A. Koleva, K. van Breugel, Microstructure, surface chemistry and electrochemical response of Ag|AgCl sensors in alkaline media, J. Mater. Sci. 53(10) (2018) 7527-7550.
[43] J.H. Baxendale, M.D. Ward, P. Wardman, Heats of ionization of HO2 and OH in aqueous solution, J. Chem. Soc. Faraday Trans. 67(0) (1971) 2532-2537.
[44] W.H. Koppenol, D.M. Stanbury, P.L. Bounds, Electrode potentials of partially reduced oxygen species, from dioxygen to water, Free Radic. Biol. Med. 49(3) (2010) 317-322.
[45] B. Debelius, A. Gómez-Parra, J.M. Forja, Oxygen solubility in evaporated seawater as a function of temperature and salinity, Hydrobiologia 632(1) (2009) 157-165.
[46] H.S. Toh, C. Batchelor-McAuley, K. Tschulik, R.G. Compton, Electrochemical detection of chloride levels in sweat using silver nanoparticles: a basis for the preliminary screening for cystic fibrosis, Analyst 138(15) (2013) 4292-4297.