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Chemical speciation of iron in seawater using catalytic cathodic stripping voltammetry with ligand competition against salicylaldoxime

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ABSTRACT

The chemical speciation of iron in seawater is typically determined by cathodic stripping voltammetry (CSV) making use of ligand competition between an electroactive ligand added to obtain the CSV signal and the natural ligand to determine the complex stability of the natural species. Different procedures differ in the added ligand that is selected. Recent findings have suggested that several of these procedures suffer from interference by humic substances, which are now known to be ubiquitous in coastal and ocean waters. We re-optimise here CSV of iron speciation using salicylaldoxime (SA) in seawater, finding differences with the pre-existing method, and a different interpretation for the electroactive species. The main findings are that optimum sensitivity is obtained at ~5 × less SA, that the complex responsible for adsorption on the electrode is FeSA, that the $FeSA_2$ species does not adsorb, and that the sensitivity of the method is much improved in the presence of dissolved oxygen (DO) through a catalytic effect (Fe^{II} acts as catalyst for the reduction of DO). The complex stability for complexes of Fe′ with SA (FeSA and $FeSA_2$), in pH 8 seawater, is calibrated over a range of SA concentrations between 1 and 40 μM SA against EDTA and between 1 and 100 μM SA without EDTA. Data fitting of the EDTA data gave $\log K'_{Fe'SA} = 6.50 \pm 0.04$ and $\log B'_{Fe'SA2} = 10.85 \pm 0.08$. The data fits agree with the formation of an electroactive species FeSA which is superseded by a non-electroactive $FeSA_2$ at [SA] > 5 μM. Independent calibration of these stability constants on the basis of the formation of FeSA in competition only with the hydroxide species of Fe^{III}, between 1 and 100 μM SA, without EDTA, gave values of $\log K'_{Fe'SA} = 6.52 \pm 0.01$ and $\log B'_{Fe'SA2} = 10.72 \pm 0.03$. These are the values we propose for the constants as they are independent of any uncertainties in the speciation with EDTA. The similarity of these constants to those determined via calibration against EDTA shows that the speciation of Fe with SA and EDTA is well understood. The re-optimised method is applied to a mixed depth Celtic Sea sample, and two GEOTRACES samples from the Atlantic, at a SA concentration of 5 μM. Ligand concentrations were 1.47 and 1.49 nM in the GEOTRACES water ($\log K'_{Fe'L}$ values of 11.1 and 11.9) and 2.53 nM in the Celtic Sea water ($\log K'_{Fe'L} = 11.5$). Application of the method to ligands added to seawater gave $\log K'_{Fe'L}$ values of 11.6 ± 0.1 for humic acid (Suwannee River) and 12.2 ± 0.3 for a siderophore (desferrioxamine B). Measurement of the rate of dissociation of the complex of Fe with the natural ligand in Celtic seawater gave a value of $k_{FeL} = 0.00133 \pm 0.0002\ s^{-1}$. The half-life of this reaction is 8.7 minutes. This means that a reaction time of 1 h is required after the addition of SA prior to analysis.

1. Introduction

Iron is one of the bioactive elements in the oceans and is essential to marine microorganisms, its uptake causing depletion in ocean surface waters (Martin and Gordon, 1988). This depletion is the reason for limitation of primary productivity in about half of the global oceans (Behrenfeld and Kolber, 1999; Martin et al., 1991; Moore et al., 2002). In spite of being the 4th most abundant element in the earth's crust (Wedepohl, 1995), the oceanic concentration of iron is low (typically <1 nM in deep waters) which is caused by its poor solubility (~0.01 nM as inorganic Fe in pH 8 seawater (Liu and Millero, 2002)) and biological uptake. The poor solubility is the reason that iron tends to be removed from solution in estuarine and coastal waters, and is transported from land to the open ocean largely via the atmosphere rather than from fluvial sources.

It has been demonstrated that organic complexation increases Fe solubility (Kuma et al., 1996; Millero, 1998). For this reason the chemical speciation of iron is fundamental to understanding its marine geochemistry. Iron occurs in seawater in two oxidation states: 2-valent in chemically reducing conditions (Landing and Westerlund, 1988) or when subject to photochemical reactions (Laglera and van den Berg, 2007; Miller and Kester, 1994), whilst the 3-valent, Fe^{III}, is predominant in the presence of oxygen. This work is on Fe^{III}, as it is the predominant species in seawater in the presence of air. All measurements of organic

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speciation of Fe thus far have been in the presence of air (Buck et al., 2012; Croot and Johansson, 2000; Gledhill and van den Berg, 1994; Rue and Bruland, 1995) (apart from the brief detection step which often requires partial oxygen removal) and are therefore for Fe^{III}, apart from a recent method to determine the concentration of organic Fe^{II}-binding ligands (Statham et al., 2012). Organic complexation of Fe is one of the parameters studied as part of the GEOTRACES program and methods for its measurement are still subject to development and intercomparison (Buck et al., 2012). The result of that intercomparison was encouraging (reasonable agreement between methods) but also showed problems (some titrations showed variability).

All Fe^{III} speciation methods make use of cathodic stripping voltammetry (CSV) and the methods can use each of several ligands: 1-nitroso-2-napthol (NN) (Gledhill and van den Berg, 1994), 2-(2-thiazolylazo)-p-cresol (TAC) (Croot and Johansson, 2000), salicylaldoxime (SA) (Rue and Bruland, 1995) and 2,3-dihydroxynaphthalene (DHN) (van den Berg, 2006) have been used successfully. In each case the added ligand forms a complex (FeAL) with Fe^{III} that adsorbs on the mercury electrode. The amount of adsorbed complex is determined by a reducing potential scan using cathodic stripping voltammetry (CSV), and this amount is directly related to the concentration of dissolved FeAL, which in turn is directly related to the concentration of Fe and AL via the sensitivity which is calibrated by means of internal iron standard additions. This is used to obtain the concentration of reactive Fe at a constant concentration of AL.

Competition for iron between AL and natural complexing ligands is the basis for the speciation methods. In each case the free Fe^{III} (that not bound by the natural ligands) is bound by the added ligand and detected. Correction is made for the free Fe^{III} that is bound by the added ligand and which causes equilibria to shift. The procedures vary in that sometimes the sensitivity is increased by adding an oxidant which causes a catalytic effect: NN has been used without oxidant (Gledhill and van den Berg, 1994; Witter et al., 2000), with hydrogen peroxide (van den Berg, 1995) and with bromate (Aldrich and van den Berg, 1998), and DHN with bromate (van den Berg, 2006). Measurements using these ligands can be without oxidant, but then a much longer adsorption time has to be included prior to the voltammetric scan, which may lead to electrode saturation and non-linearity of response: for instance the peak height increases linearly with adsorption time to 8 min for 1.6 nM Cu complexed with SA (Campos and van den Berg, 1994), and up to 30 min for 2.5 nM Fe (Rue and Bruland, 1995). The sensitivity of the method using TAC is sufficient without the need for an added oxidant.

Recent work has suggested that Fe^{III} in seawater is complexed with humic substances (HS) (Laglera and van den Berg, 2009). Fe^{III}-HS in seawater gives a response in CSV which is catalysed by bromate (Laglera et al., 2007). This peak overlaps with that obtained using DHN/bromate, which interferes with the use of this ligand for Fe speciation in the presence of HS. Further work on HS has also shown interference with Fe speciation using TAC and NN, but that SA and DHN (without bromate) can be used (Laglera et al., 2011). On the other hand, TAC was used recently and apparently successfully for Fe speciation in the presence of HS (Batchelli et al., 2010). This is important as HS occurs in all seawater, though the concentration in ocean waters is low. The presence of the HS could be part of the reason for the small differences found between methods tested for the GEOTRACES intercalibration programme (Buck et al., 2012).

The un-catalysed DHN method has poor sensitivity, whilst the un-catalysed SA method has been used successfully in the past, e.g. (Rue and Bruland, 1995). The SA method has problems which have been un-reported and are not understood, and which make it difficult to use. Nevertheless the SA method is being used for Fe speciation (Buck and Bruland, 2007; Buck et al., 2007) with apparently good results. We have re-visited the SA method to resolve the outstanding issues and improve the method.

1.1. Existing Fe speciation method using salicylaldoxime

1.1.1. Equilibration time

The original SA method (Rue and Bruland, 1995) has been modified slightly, and re-calibrated, for estuarine waters (Buck et al., 2007). The Fe added for the complexing ligand titration (0–5 nM Fe) is allowed to equilibrate with the seawater and natural ligands before the SA addition, which was added after a first equilibration period. 1 h equilibration was used after the Fe addition to the seawater (2 h in the Buck version), and a further 10–15 min equilibration after the addition of SA (27.5 μM (Buck et al., 2007; Rue and Bruland, 1995) and 25 μM SA (Buck et al., 2007)). A much longer equilibration period between the added ligand, the iron and the natural ligands is used in the other CLE-CSV methods, which is typically overnight (Croot and Johansson, 2000; Gledhill and van den Berg, 1994; Witter et al., 2000), though then everything is equilibrated simultaneously which can be expected to take longer (because the free iron concentration is lowered by the added ligand) than the sequential equilibration used with SA. The TAC method uses the sequential principle but still equilibrates overnight (Croot and Johansson, 2000).

1.1.2. Removal of dissolved oxygen

The updated SA method (Buck et al., 2007) does not remove dissolved oxygen (DO) during the voltammetric Fe measurement, while the other methods remove DO as it normally interferes with voltammetric measurement.

1.1.3. Decreasing response

The SA method stipulates that just one mercury drop is dispensed (Rue and Bruland, 1995) which is unusual as automated voltammeters normally dispense several before using a fresh one, and the apparatus, or software, may require modification (the software of the Bioanalytical Systems (BAS) voltammeter does not require modification). The use of a single drop was to avoid an apparent decrease in the response when a scan was repeated using the same solution, which was ascribed to adsorption on the mercury drops in the cell (Rue and Bruland, 1995). The drop-size of the systems used for iron speciation can vary by a factor of 8 (Buck et al., 2012), so this aspect is tested in this work. Any decrease due to Fe removal as a result of adsorption on the voltammetric cell is eliminated if a conditioned cell is used. Because of the decreasing response, repeat measurements for Fe-SA on aliquots of a titration are carried out in separate aliquots, whereas other CLE-CSV methods repeat the scans in the same cell. This decreasing response is an inconvenience of the SA method as it affects repeat scans, calibrations and standard additions, and its cause is at least in part resolved here.

A second problem with the existing CSV method using SA is a large variability in the sensitivity between samples from different depths (much lower sensitivity for deeper samples) (Buck et al., 2012). A possible explanation is the presence of surface-active compounds but these probably occur at lower levels in deep waters than in surface waters. Oceanic surfactant concentrations in surface waters are low at <0.02 mg L^{-1} (Croot et al., 2007) suggesting that these are probably not the cause of the difference. Solutions for both problems are suggested in this work. An improved method is developed with much better sensitivity, and the method is re-calibrated over an extensive range of SA concentrations, now allowing measurement at several detection windows, e.g. (Bundy et al., 2014).

1.2. Identity of the adsorptive iron species with SA and effect on calibration

The previous work (Rue and Bruland, 1995) decided on the basis of a literature review that $FeSA_2$ is the species that predominates and therefore adsorbs on the electrode. It is important that this is correct as otherwise the calibration would only be valid at a single calibrated concentration of SA (27.5 μM in this case). The papers cited (Burger and Egyed, 1965; Burger et al., 1965) discuss Fe^{II}-SA species and not