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A new spectrophotometric method to quantify dissolved manganese in marine pore waters

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ABSTRACT

This study explores the use of Cadmium (II) *meso*-Tetrakis(4-sulfophenyl) porphyrin complex (Cd-TSPP) as an indicator for the spectrophotometric determination of dissolved manganese (II) in pore waters from marine sediments. Both single absorbance and second derivative based methods were evaluated with a multifunctional plate reader. Cd-TSPP has a maximum absorbance at 433 nm in solution, but the core Cd(II) ion in the complex can be quickly replaced by Mn(II) at pH 4–8 to form a new Mn porphyrin complex (Mn-TSPP) with maximum absorbance at 469 nm. The absorbance of Mn-TSPP at 469 nm and its second derivative spectra at the same wavelength show excellent linear relationships with Mn(II) concentrations ($R^2 = 0.997$ and $R^2 = 0.999$, respectively) in the 0–37.5 μM range for 200 μL samples. The detection limits using single absorbance and the second derivative are 0.4 and 0.3 μM Mn(II), respectively. A correction subtracting reference absorbance at 490 nm from 469 nm signal was required in the single absorbance approach in order to eliminate the effect of baseline fluctuations. In contrast, the second derivative approach shows higher selectivity, accuracy and precision for Mn(II) determination in pore water. The reaction is not affected by pH (4–8) or salinity but is temperature sensitive in the range of 10–45 °C with an activation energy of 22.12 kJ mol^{-1}. No interferences from metal ions such as Pb(II), Cu(II), Fe(II), Zn(II) etc. were found. The proposed method, which is rapid and suitable for small size samples, was successfully applied to the determination of Mn(II) in pore water.

1. Introduction

Manganese is a key redox reactive element in marine environments, particularly sedimentary deposits. In the oxic zones of marine sediment, manganese is commonly present as solid phase Mn(IV) and Mn(III) oxides and oxyhydroxides (Post, 1999). Oxidized manganese can be readily reduced to more soluble Mn(II) in anoxic regions by electron donors such as organic matter, and rapidly reoxidized during subsequent transport and re-exposure to oxidants. Thus, cyclic manganese redox reactions are closely coupled to multiple biogeochemical and physical processes, for example, the degradation of organic matter, oxidation of reduced metabolites, and consumption of oxygen (Takamatsu et al., 1985; Sundby et al., 1986; Burdige et al., 1992; Canfield et al., 1993; Aller, 1994; Luther et al., 1997; Hulth et al., 1999; Thamdrup, 2000). The quantification of dissolved Mn(II) concentrations and distributions is an essential aspect of understanding redox reaction–transport processes in sedimentary deposits.

Several viable analytical techniques have been reported for Mn(II) determination, including atomic absorption spectroscopy (Porta et al., 1991), electroanalytical chemistry (Ma et al., 2008), and spectrophotometric methods (Chiswell et al., 1990). Spectrophotometric methods are particularly useful due to simplicity, sensitivity, stability, comparative low cost and suitability for both automation and field research. Various reagents and sensing schemes have been proposed for colorimetric measurements of manganese in natural environments by using permanganate and formaldoxime, the latter being the most used method since the 1960s (Chiswell et al., 1990). Here, we examine the use of the porphyrin complex: cadmium (II) *meso*-Tetrakis(4-sulfophenyl) porphyrin, as an alternative basis for spectrophotometric determination of dissolved Mn(II).

Porphyrins show high sensitivity and selectivity as indicators for metal ion determinations. Typically, the reaction of free phorphyrins with metals is slow and thus difficult to incorporate directly into an analytical scheme. However, substitution reactions of dissolved metal ions with metalloporphyrins containing large complexed ions (e.g. Hg^{2+}, Pb^{2+} or Cd^{2+}) can be fast. Of critical importance is that in the process of exchanging the metal ion core of metalloporphyrin complexes, absorption spectra change (Biesaga et al., 2000). Both porphyrins and metalloporphyrins show intense absorption and molar absorptivities in the Soret band (400–500 nm), a metal specific property which is highly useful for optical quantification of metalloporphyrins, and which can be further optimized for analytical applications by use of derivative spectrophotometry (e.g. Ishii et al., 1982b).

Successive formation of metalloporphyrin from metal-free porphyrin (MP) reacting with a divalent metal ion (M^{2+}) and the substitution

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of a second metal (Mb^{2+}) into the metalloporphyrin nucleus can be generally depicted by Eqs. (1) and (2):

$$M^{2+} + H_2P \leftrightarrow MP + 2H^+ \quad (1)$$

$$MP + Mb^{2+} \rightarrow MbP + M^{2+} \quad (2)$$

Many studies have characterized the formation of metalloporphyrins (e.g. Shamim and Hambright, 1980; Tabata, 1987; Kilian and Pyrzynska, 2003; Gharib et al., 2009) and have demonstrated that metal ions typically form a 1:1 complex with porphyrins, excepting Na, Li and K ions which form complexes in a 2:1 ratio with the metal ions projecting slightly out of the macrocyclic plane (Biesaga et al., 2000). A second special case is complexation with large metal ions like mercury, lead and cadmium which are bound just on the central surface of the porphyrin. The resulting deformation of the porphyrin nucleus makes it possible for rapid substitution reactions with other smaller divalent metal ions, forming complexes with spectroscopic properties specific to the substituting metal and thus potential target analytes (Tanaka, 1983).

Several porphyrins and metalloporphyrins have been used in different analytical schemes involving spectrophotometric, potentiometric, capillary electrophoresis and HPLC techniques to measure a wide range of divalent metal ions in plant and water samples (Ishii et al., 1982a; Xu et al., 1991; Okutani et al., 1994; Almeda et al., 2009). In particular, the most commonly used porphyrins for manganese ions determination are meso-Tetrakis(3-bromo-4-sulfophenyl) porphyrin (*m*-$BrTPPS_4$), *meso*-Tetrakis(4-sulfophenyl) porphyrin, *meso*-Tetrakis (4-carboxyphenyl) porphyrin [T(4-CP)P] and its cadmium complex (Cd-T(4-CP)P) (Ishii et al., 1982a; Ishii and Kohata, 1987; Biesaga et al., 2000).

Given that *meso*-Tetrakis(4-sulfophenyl) porphyrin has been successfully used in determination of metal ions in both terrestrial and fresh water samples, and the highly convenient isolation of the absorbance peak associated with the manganese complex versus other metalloporphyrin spectra inside the Soret band, we further investigated the suitability of its cadmium complex (Cd-TSPP) as a new indicator for rapid spectrophotometric quantification of dissolved manganese in pore water from marine sediments. Because modern multichannel plate readers permit rapid acquisition of continuous spectra on multiple samples, we also evaluated the efficacy of the second derivative technique and adaptation of the spectrophotometric Mn^{2+} method to common 96-well microplates. The effects of pH, temperature, salinity and potential interferences from foreign divalent ions on the measurement were studied and conditions were optimized. The second derivative approach provides for substantial improvements in the selectivity and sensitivity in measurement relative to single wavelength absorbance methods. The Cd-TSPP method has been successfully applied for Mn^{2+} measurements in real pore water samples, allowing measurement of hundreds of samples within a half hour.

2. Experimental

2.1. Equipment and reagents

A POLARstar Omega multifunctional plate reader with UV/VIS absorbance spectra capabilities was used to perform both kinetic and endpoint measurements at specific wavelengths (469 and 490 nm) and obtain wavelength scans (250–700 nm). Reaction and measurement temperature (25 ± 0.1 °C) was monitored and controlled using the incubation mode of this equipment, and a 4 second double orbital (400 rpm) shaking sequence was performed before each measurement to avoid possible variation between replicates due to mixing processes inside wells, as previously described in the literature (Weiss et al., 2002). The number of Xenon lamp flashes per measurement was fixed at 50 to increase signal stability.

Atomic absorption measurements were carried out using a Graphite Furnace/Flame Perkin Elmer A Analyst 800 Atomic Absorption Spectrometer equipped with an automated motorized atomizer and a hollow cathode lamp for manganese. The graphite furnace mode was selected for all measurements with a sample injection volume of 20 μL, and each sample was measured three times.

The 5,10,15,20-Tetrakis(4-sulfonatophenyl) porphyrin (TSPP) was obtained from SIGMA-Aldrich (88074) and a 0.48 mM stock solution was prepared by dissolving 245.5 mg TSPP in 500 ml of 0.01 M sodium hydroxide solution. Cadmium porphyrin (Cd-TSPP) complex solutions were prepared according to the method reported by Kilian and Pyrzynska (2003). Briefly, cadmium ion was mixed with TSPP at a molar ratio of 4:1 (Cd^{2+}/TSPP) in a 250 ml amber flask. The reaction was carried out in the dark, and the concentrations of reactant TSPP and product Cd-TSPP were spectrophotometrically determined at 412 nm ($\varepsilon = 3.47 \times 10^5$; Inamo et al., 1997) and 433 nm, respectively. The reaction was stopped when the TSPP absorption peak at 412 nm disappeared. All Cd-TSPP working solutions were prepared the day before use. The stock solutions used to study interference from other metal ions: Fe(II), Pb(II),Cu(II) and Zn(II), were treated with hydroxylamine hydrochloride (0.32 M in each well) as reductant. Reductant addition assured stable oxidation states for interference evaluations. All pH adjustments were carried out using the total [H^+] scale.

2.2. Procedures

A clear polystyrene microplate with optical glass bottom (Whatman) was used for measurements of Mn^{2+}. 200 μL samples with different Mn^{2+} concentrations (pH 4–8) were transferred into each microplate well (maximum capacity 370 μL), and then 50 μL of 0.24 mmol/L Cd-TSPP solution was added. The mixture was allowed to stand for 15 min at room temperature and the absorbances of each well at 469 nm and at 490 nm (reference) were then measured. The absorbance difference ($\Delta A_{469-490} = A_{469} - A_{490}$) and the second derivative at 469 nm (described below) were used to construct calibrations and perform measurements. For the studies of pH effect and foreign ion interferences, 0.32 M of hydroxylamine hydrochloride in each well was used to ensure that the oxidation state of redox metal ions was stable and also consistent with that under anoxic conditions (the latter important for possible in situ applications).

Pore water samples used for precision and accuracy study were obtained from surface marine sediments (0 – 1 cm) which were collected in July 2010 from Flax Pond, Great Peconic Bay and West Meadow Beach, Long Island, NY, respectively. Pore water was separated by centrifugation of sediment. These pore water samples were stirred, oxygenated and filtered through 0.2 μm pore polysulfone filters and spiked with a specific amount of Mn^{2+} standard prior to the determination.

Marine sediment samples used for Mn^{2+} determinations were obtained from Great Peconic Bay in July 2010 and Long Island Sound in Nov. 2007 and stored at 15 °C. Pore water samples were separated by centrifugation of sediment, filtered through 0.2 μm pore polysulfone filters and acidified to pH 2 with HCl (trace metal grade) before storage. Sample pH was adjusted to 4 using NaOH solution immediately before analysis. 200 μL subsamples diluted in distilled water (dilution factor: 1.5) were used to ensure absorbance in the 0–1 range and a final total volume of 250 μL per well after adding 50 μL of indicator.

2.3. Second derivative determination

Application of the second derivative approach in spectrophotometric determinations of Mn(II) using Cd-TSPP was tested. The