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Removal of nitrite interference in the Winkler determination of dissolved oxygen in seawater

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ABSTRACT

Nitrite is a well recognized interference in iodometry. However, while steps for its removal are part of the routine practice in the standard methods for the determination of dissolved oxygen in freshwater and wastewater when the iodometric Winkler method is used, they are not included in any of the widely used standard procedures for seawater analyses. In de-ionized reagent-grade water, artificial seawater and natural surface seawater, the concentration of apparent oxygen increased linearly with increasing concentrations of added nitrite, indicating that the presence of nitrite does lead to an over-estimation. The average ratio of increase in apparent oxygen to nitrite added was 0.4 ± 0.1 mol mol^{-1}. At the widely claimed accuracy and precision in the determination of dissolved oxygen in seawater of ±0.1 to ±0.3%, the interference of nitrite may be safely ignored only when the concentration of nitrite is below about 0.3 μM. At higher concentrations, such as those found at the nitrite maxima and in coastal waters, it should be taken into account. Since nitrite can be easily and readily removed by the addition of azide, such a step should be incorporated into the standard procedures for the determination of dissolved oxygen in seawater.

1. Introduction

Dissolved oxygen data from the oceans have been used at an increasing level of sophistication in recent years for tackling some of the critical oceanographic issues of the day. For example, the deviations of the concentrations of oxygen from their saturation values have been used for estimating net primary production in the oceans (Craig and Hayward, 1987; Platt et al., 1989; Emerson et al., 2001). Inventories of dissolved oxygen in the major ocean basins have been used for constraining the global carbon cycle (Keeling and Garcia, 2002; Plattner et al., 2002). The changes in the concentration of dissolved oxygen in water samples incubated under different defined experimental conditions have been used for the determination of the rates of autotrophic activities and community respiration (Carignan et al., 1998; Chen et al., 2003) and these measurements have profound implications on our understanding of the metabolic balance in the oceans (Duarte and Agustí, 1998; Gattuso et al., 1999; Williams and Bowers, 1999; Duarte et al., 1999; del Giorgio and Duarte, 2002; Karl et al., 2003). The validity of all these studies depends critically on the claimed precision and accuracy, at around ±0.1 to ±0.3% (Pai et al., 1993; Emerson et al., 1995; Labasque et al., 2004), in the determination of dissolved oxygen in seawater. Given an average concentration of dissolved oxygen in surface seawater of 250 μmol kg^{-1}, these precision and accuracy would be equivalent to about ±0.3 to ±0.8 μmol kg^{-1}. Thus, any error at the level of 10^{-1} μmol kg^{-1} would be significant. In fact, a precision as high as ±0.016%, which is equivalent to about ±0.04 μmol kg^{-1}, has been claimed by some investigators (Williams et al., 2004). At this level, even errors of 10^{-2} μmol kg^{-1} are not negligible. As a result, many heretofore neglected or overlooked interferences in the determination of dissolved oxygen in natural waters are now relevant and require a re-examination.

The concentration of dissolved oxygen in seawater has been determined almost exclusively by using methods that are based on the iodometric Winkler reaction scheme. Even when other methods are used, such as electrochemical methods, they are calibrated against these methods (Emerson et al., 2002; Kuss et al., 2006). The chemical reactions involved in the Winkler scheme are:

$$\mathrm{Mn}^{+2} + 2\mathrm{OH}^- \rightarrow \mathrm{Mn(OH)}_2 \qquad (1)$$

$$4\mathrm{Mn(OH)}_2 + \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{Mn(OH)}_3 \qquad (2)$$

$$4\mathrm{Mn(OH)}_3 + 12\mathrm{H}^+ + 4\mathrm{I}^- \rightarrow 2\mathrm{I}_2 + 4\mathrm{Mn}^{+2} + 12\mathrm{H}_2\mathrm{O} \qquad (3)$$

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$$I_2 + I^- \leftrightarrow I_3^- \quad (4)$$

The molecular iodine and tri-iodide ion formed are then quantified either by a titration with thiosulfate (Carpenter, 1965a,b; Strickland and Parsons, 1972) or by spectrophotometry (Pai et al., 1993; Labasque et al., 2004; Reinthaler et al., 2006). In this reaction scheme, any oxidizing chemical species in seawater that may react with iodide under acidic conditions to form molecular iodine will interfere. For example, the oxidation of the excess iodide by oxygen in air under acidic condition has been long recognized and extensive efforts were made to minimize its effect (Carpenter, 1965a). Recently, Wong and Li (2009) pointed out that naturally occurring iodate in seawater also reacts with excess iodide under acidic condition to form tri-iodide and leads to an overestimation in the concentration of dissolved oxygen of up to 0.7 μmol kg^{-1}. Wong et al. (2010) reported that hydrogen peroxide in seawater may result in an additional overestimation of up to 0.5 μmol kg^{-1}.

The interference of nitrite in the Winkler determination of dissolved oxygen has been well recognized in the freshwater and wastewater community (Clesceri et al., 1998) but it has been ignored in the oceanographic community. It was not considered in the original literature when the method was applied to seawater (Carpenter, 1965a,b) and it is not mentioned in the standard methods that are presently in use for the determination of dissolved oxygen in seawater (Strickland and Parsons, 1972; Parsons et al., 1984; Knap et al., 1997; Grasshoff et al., 1999), except in low oxygen water (Broenkow and Cline, 1966), probably as a result of the low concentrations of nitrite in most of the oceans. Here, in view of the level of precision and accuracy at which oxygen data are being used in recent oceanographic studies, the effect of this potential source of error is assessed.

2. Methods

The apparent concentration of dissolved oxygen, which is the sum of the concentration of dissolved oxygen and the oxygen-equivalent of nitrite, was determined by converting both species into a stoichiometrically equivalent amount of molecular iodine and tri-iodide ion by using the classical Winkler reaction scheme (Carpenter, 1965b), and then quantifying the iodine species formed spectrophotometerically by the method of Pai and co-workers (Pai et al., 1993, 1998). The method was standardized using nitrite- and iodate-free artificial seawater or deionized water containing a known amount of added iodate (Wong and Li, 2009) without the addition of azide. The concentration of dissolved oxygen free of the interference of nitrite was determined by using the modified Winkler reaction scheme (Clesceri et al., 1998; Pai et al., 1998) in which nitrite was destroyed prior to the analysis by its reaction with azide. Azide was added by making the NaI-NaOH reagent (Pai et al., 1993) 1% (w/v) with respect to sodium azide (Clesceri et al., 1998; Pai et al., 1998).

The interference of nitrite was determined by measuring the concentration of apparent oxygen in de-ionized reagent-grade water, artificial seawater and surface seawater containing up to 20 μM of added nitrite with and without the addition of azide. The samples were allowed to equilibrate with the laboratory air for at least 2 h in polyethylene bottles before sub-samples were drawn in triplicates for the determination of the concentrations of apparent oxygen. The average precision of triplicate analyses of 12 samples with concentrations ranging between 212 and 303 μmol kg^{-1} was ±0.3 μmol kg^{-1} or about ±0.1% (Wong and Li, 2009). These values are about the same as those claimed in the literature (Pai et al., 1993; Labasque et al., 2004). When multiple sub-samples of artificial seawater and deionized reagent-grade water were exposed to the laboratory air simultaneously for the same amount of time, the resulting bottle to bottle variations in the concentration of apparent oxygen, ±0.2%, were similar to the analytical uncertainty (Wong and Li, 2009), indicating that the variability in the exchange of oxygen between the solution and the atmosphere among the bottles was negligible. Changes in the concentration of apparent oxygen upon the addition of nitrite were the result of the presence of nitrite. The concentrations of added nitrite, 0 to 20 μM, used in the experiments bracketed the concentrations found in the oceans.

3. Results and discussion

3.1. The interference of nitrite

Nitrite reacts with iodide under acidic conditions to form molecular iodine such that:

$$2NO_2^- + 4H^+ + 2I^- \rightarrow I_2 + 2NO + 2H_2O \quad (5)$$

Thus, 1 mol of nitrite leads to the formation of 0.5 mol of molecular iodine, and is therefore stoichiometrically equivalent to the presence of 0.25 mol of dissolved oxygen. However, in the presence of oxygen, a sequence of semi-cyclic reactions may ensue. As a result, the nitric oxide formed can undergo further reactions and regenerate half of the initial nitrite such that:

$$2NO + O_2 \rightarrow 2NO_2 \quad (6)$$

$$2NO_2 + H_2O + \rightarrow NO_2^- + NO_3^- + 2H^+ \quad (7)$$

The nitrite formed may react with iodide to form additional molecular iodine. This sequence of reactions is well known (Kolthoff et al., 1957). If oxygen is freely available so that these cyclic reactions are allowed to run their course, 1 mol of nitrite may give rise to a theoretical maximum of 0.5 mol of apparent oxygen. In the Winkler reactions scheme, nitrite does not react with iodide until the sample is acidified by the addition of sulfuric acid to dissolve $Mn(OH)_3$ as in reaction (3). However, by that time, the oxygen present initially in the sample has already been sequestered as $Mn(OH)_3$ and is no longer available for its reaction with nitric oxide (reaction 6). However, oxygen may be re-introduced into the sample as the oxygen dissolved in the added sulfuric acid and as atmospheric oxygen that may dissolve into the sample during the addition of the acid and the subsequent transfer of the sample for the measurement of its absorbance in the spectrophotometric protocol (Pai et al., 1993) or the subsequent titration in the titrimetric protocol (Strickland and Parson, 1972). The amount of oxygen thus introduced, which becomes available for its reaction with nitric oxide, is likely to vary from analyst to analyst and from sample to sample as the handling of the sample is not stringently controlled in this part of the protocol. As a result, the ratio between the apparent oxygen formed from the presence of nitrite and the concentration of nitrite in the sample may be anywhere between 0.25 and 0.50 mol mol^{-1}. In samples of deionized water, artificial seawater and natural surface seawater that had been equilibrated with air in the laboratory and contained known amounts of added nitrite, the concentration of apparent oxygen increased linearly with increasing concentrations of added nitrite with slopes ranging between 0.29 and 0.44 mol mol^{-1}. The average was 0.35 ± 0.07 mol mol^{-1} (Table 1). Thus, the presence of nitrite does lead to an over-estimation in the determination of oxygen. The range of the slopes fell well within the range that may be attributed to the interference of nitrite according to