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The Biogeochemistry of Iodine in Seawater

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THE BIOGEOCHEMISTRY OF IODINE IN SEAWATER

by

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ABSTRACT

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Iodate and iodide are the two major species of iodine in seawater. In comparison to iodate, iodide is thermodynamically unstable in oxic seawater. The conversion (or reduction) of iodate to iodide may be mediated via biological activities. Since biological activities vary with the season, the conversion of iodate to iodide may also vary seasonally. The conversion (or oxidation) of iodide to iodate is thermodynamically feasible, but the mechanism is poorly known. Hydrogen peroxide, which is ubiquitous in surface seawater, may oxidize iodide to iodate.

Water samples were collected in the middle and lower Chesapeake Bay in different seasons between 1990 and 1992. The concentrations of iodate, iodide, and total iodine were determined by polarography or voltammetry. In the surface water iodate was the dominant form of inorganic iodine in the winter while iodide was the dominant species most of the rest of the year. Dissolved organic iodine was mainly found in the spring. In the deep water iodate was present in significant concentrations in the winter. Iodide was the dominant species

in the other three seasons; organic iodine was very minor. In the deep water iodate might be removed to the sediment under oxidizing conditions in the winter. The sediment might act as a source of iodide under reducing conditions in the summer. This evidence indicated that the speciation of iodine varied in different seasons in a coastal marine environment such as the Chesapeake Bay. Furthermore, the Chesapeake Bay might act as a geochemical reactor which reduces iodate in the Bay and transports iodide to the oceans.

The reaction between H_2O_2 and iodide was investigated by adding them in artificial seawater and monitoring the variations in the concentrations of H_2O_2 and iodide. At neutral conditions (pH 7 to 9), H_2O_2 oxidized iodide, probably to molecular iodine or hypoiodite. The disappearance of H_2O_2 was first order with respect to iodide and H_2O_2, respectively. The reaction rate increased with increasing temperature and increasing salinity, but it was independent of pH within pH 7 to 9. At millimole levels of H_2O_2, molecular iodine (or hypoiodite) was immediately reduced back to iodide. The net result was a quasi-catalytic decomposition of H_2O_2 in the presence of iodide. The direct oxidation of iodide to iodate was not observed. By extrapolating the results to oceanic conditions (i.e. at sub-μM levels of H_2O_2), molecular iodine (or hypoiodite) may be reduced to iodide by H_2O_2, form organic iodine and be converted back to iodide, or further disproportionate to form iodate and iodide. The last possibility may explain the oxidation of iodide to iodate in seawater.

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TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (cont'd)

LIST OF FIGURES (cont'd)

CHAPTER ONE

GENERAL INTRODUCTION

I-1 INTRODUCTION

One of the major challenges in chemical oceanography is to understand and quantify the processes that may control or affect the chemical speciation of the elements in seawater (Broecker and Peng, 1982; Chester, 1990; Libes, 1992). A classical approach is to use thermodynamic information to predict elemental speciation (e.g. Sillen, 1961; Breck, 1972; 1974; Liss *et al.*, 1973; Turner *et al.*, 1981), based on the assumptions that seawater is a closed system and that the element has reached a thermodynamic equilibrium with the prevailing chemical conditions of the environment. However, this approach has been shown to be inadequate for accounting for the chemical speciation of many elements. This inadequacy is especially conspicuous in the case of some of trace elements where the required assumptions are frequently violated (e.g. Stumm and Morgan, 1981; Morel, 1983). Seawater may not behave as a closed system since it can receive energy from the sun and it is subject to a continuous exchange of material and energy with the other major geochemical reservoirs, such as the atmosphere and the lithosphere, of the

earth (e.g. Chester, 1990; Cooper *et al.*, 1987; Mopper and Zhou, 1990; Thompson and Zafiriou, 1983). The kinetics of the geochemical reactions may be slow enough so that some elements in seawater may never have reached a thermodynamic equilibrium in their geochemical history while others may not be able to reestablish a thermodynamic equilibrium once the equilibrium state has been disturbed. Nevertheless, the thermodynamic approach is still a useful frame of reference for understanding the chemical speciation of the elements in seawater. It provides insights on the direction of the reactions that an element may be involved in since the energetic tendency is for the element to strive to reach the equilibrium state (Chester, 1990; Libes, 1992). Thus, in order to understand the chemical speciation of an element, efforts have to be made to identify the processes which may drive its speciation away from this frame of reference, that is, thermodynamic equilibrium, and to quantify the factors which may control the rates of these reactions. Then, the relative importance of these processes may be evaluated since it is unlikely that all the processes are equally significant in controlling the speciation of the specific element.

The speciation of iodine in seawater is often cited as an example for testing the applicability of the thermodynamic approach in predicting the elemental speciation in seawater (Sillen, 1961; Breck, 1972; 1974; Liss *et al.*, 1973). Iodine is one of the most abundant minor elements in seawater and it is present in several different chemical species (Tsunogai,

1971; Tsunogai and Henmi, 1971; Wong and Brewer, 1974; 1976). The distribution of iodine in seawater is relatively well known. Dissolved inorganic iodine is found in two forms: iodide and iodate. Their concentrations in surface seawater usually range between 0.1 and 0.2 μM for iodide and 0.3 and 0.4 μM for iodate. Based on the thermodynamic information, however, the ratio of the concentration of iodate to that of iodide in oxygenated seawater has been predicted to be $10^{13.5}$ (Sillen, 1961). This value is orders of magnitude higher than the observed values in surface waters. It is widely accepted that the ratio of iodate to iodide in surface seawater cannot be predicted by using chemical thermodynamics alone (Wong and Brewer, 1977; Stumm and Morgan, 1981). Other processes, and especially biological processes, may be the dominating controlling factor of the speciation of iodine in seawater (Tsunogai and Sase, 1969; Elderfield and Truesdale, 1980; Wong, 1991). The objective of this work is to further elucidate the processes that may control the distribution of the different species of iodine in seawater.

I-2 QUESTIONS AND APPROACHES

It is generally accepted that iodate is reduced to form iodide in surface seawater and the conversion of iodate to iodide is mediated by biological activities (Tsunogai and Sase, 1969; Tsunogai and Henmi, 1971; Elderfield and Truesdale, 1980). Many questions concerning the details of this mechanism for the conversions of iodate to iodide remain.

One of these questions addressed in this study is:

ARE THERE SEASONAL VARIATIONS IN THE SPECIATION OF IODINE IN SEAWATER, GIVEN THAT BIOLOGICAL ACTIVITIES MAY VARY WITH SEASON ?

The seasonal variations in the speciation of iodine in seawater have been studied by several investigators (Truesdale, 1978; Jickells *et al.*, 1988; Rebello *et al.*, 1990). The results were inconsistent. While no seasonal variation in the speciation of iodine (measured as total iodine and iodate) was observed in the Menai Straits and the Irish Sea (Truesdale, 1978), significant variations were observed in the Sargasso Sea and the Bermuda inshore waters (Jickells *et al.*, 1988).

Another question addressed in this study is:

CAN IODIDE BE OXIDIZED IN SEA WATER BY HYDROGEN PEROXIDE ?

Once iodide is formed in the surface oceans, eventually, it must be oxidized back to iodate, since (1) iodate is the thermodynamically stable form of iodine in seawater (Sillen, 1961; Wong, 1980; Turner *et al.*, 1981), and (2) the standing crop of iodide in the oceans (including both the surface water and the deep water) is only about 5% of that of iodate (Wong, 1991). If iodide is not converted back to iodate, over time, the majority of the standing crop of iodine would be in the form of iodide.

The oxidation of iodide by hydrogen peroxide, which is rather ubiquitous in surface seawater (e.g. Zika *et al.*,

1985a; 1985b), is thermodynamically feasible under mildly basic condition (Liebhafsky and Mohammad, 1933). Because the concentration of hydrogen peroxide in surface seawater, which ranges from 0.1 to 0.3 μM, is far greater than the concentrations of other strong trace oxidants, such as hydroxyl radical (Mopper and Zhou, 1990), hydrogen peroxide may be the principal oxidant for oxidizing iodide in surface seawater. The concentration of molybdenum in seawater is about 0.1 μM (Riley and Taylor, 1972) which is close to that of iodide. In analytical chemistry, molybdenum is used as a catalytic reagent for the reaction between hydrogen peroxide and iodide (e.g. Kieber and Helz, 1986). In seawater, the reaction between hydrogen peroxide and iodide may still be catalyzed by molybdenum.

The following hypotheses were formulated to address the first question raised:

(1) As a result of the seasonal variations in biological activities, there are seasonal variations in the speciation of iodine (iodide and iodate) in seawater.

(2) Seasonal variations in the speciation of iodine are more pronounced in estuarine waters than that in open ocean waters, since biological activities in estuarine waters are greater than those in open ocean waters.

Water samples were collected from the mid and lower Chesapeake Bay in different seasons between 1990 and 1992, and their

concentrations of iodide, iodate and total iodine were determined. The results are presented in Chapter Three: "Seasonal variations in the speciation of iodine in the Chesapeake Bay".

Concerning the oxidation of iodide by hydrogen peroxide, it was hypothesized that:

(3) Iodide is oxidized in seawater by hydrogen peroxide.

(4) The rate of oxidation of iodide by hydrogen peroxide is affected by the concentration of iodide and molybdate, temperature, salinity, and pH.

The concentration of hydrogen peroxide ranges from tens of μM in rainwater to sub-μM in seawater. The dynamic range of the widely used analytical method (e.g. Zika *et al.*, 1985a; Cooper *et al.*, 1987) is within a sub-μM level. Furthermore, hydrogen peroxide must be analyzed immediately after the samples are collected (Cooper and Lean, 1989). Improvements on the analytical methods for the determination of hydrogen peroxide in natural waters have been made as part of this study and the results are presented in Chapter Two: "The determination of hydrogen peroxide in aqueous solutions". The effects of temperature, salinity, pH, and molybdate on the kinetics of the reaction between hydrogen peroxide and iodide were investigated. The results are presented in Chapter Four: "The kinetics of the reaction between iodide and hydrogen peroxide".

I-3 A BRIEF REVIEW OF THE BIOGEOCHEMISTRY OF IODINE IN SEAWATER

The occurrence and geochemical cycling of iodine in seawater

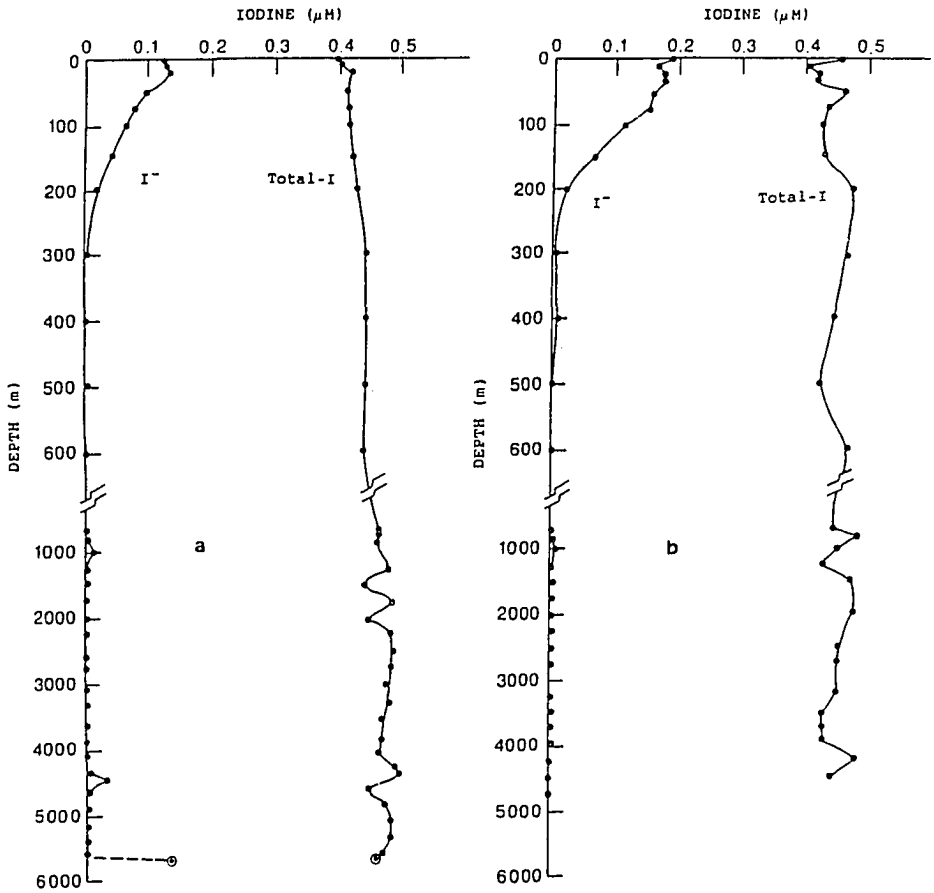
Iodine (atomic number 53, atomic mass 126.91) is one of the halogen elements (F, Cl, Br, and I) of Group VII in the periodic table. The concentration of total dissolved iodine in seawater is about 0.5 μM. Iodine is the third most abundant minor element in seawater after lithium (25 μM) and rubidium (1.4 μM) (Wong, 1991).

Iodine species was first measured in seawater by Pfaff in 1825 (Brewer, 1975). Since then, its biogeochemistry in seawater has been studied by a number of investigators (e.g. Barkley and Thompson, 1960; Tsunogai, 1971; Tsunogai and Henmi, 1971; Liss *et al.*, 1973; Wong and Brewer, 1974; 1977; Truesdale, 1975; 1978; Jickells *et al.*, 1988). Marine macroalgae may release halogenated organic compounds to seawater (Gschwend *et al.*, 1985). The presence of organic iodine has been reported by Lovelock (1975); Truesdale (1975); Singh *et al.* (1983); and Manley and Dastoor (1987). The concentration of organic iodine is about 5% or less of that of dissolved inorganic iodine in the open oceans. The concentration of particulate iodine is less than 1% of the concentration of dissolved inorganic iodine (Wong *et al.*, 1976; Jickells *et al.*, 1990). Thus, "total iodine" is often not distinguished from dissolved inorganic iodine in the open oceans. However, in some estuarine waters, 15 to 70% of total

dissolved iodine has been reported to be dissolved organic iodine (Smith and Butler, 1979; Luther *et al.*, 1991). The concentration of total dissolved iodine is slightly lower in surface water than in deep water where it is relatively uniformly distributed with only minor differences found among different water masses (Tsunogai, 1971; Elderfield and Truesdale, 1980).

Dissolved inorganic iodine in seawater is found in two forms: iodide and iodate. The concentrations of iodide and iodate vary significantly with depth. The concentration of iodide is 0.1 to 0.2 μM in the surface waters (Fig. I-3-1). It decreases with depth and it is close to or below the detection limit (several nM) at depths below the euphotic zone (Tsunogai and Henmi, 1971; Wong and Brewer, 1976). The concentration of iodate is approximately the difference between total iodine and iodide. It is about 0.3 to 0.4 μM in the surface water and about 0.5 μM in the deep water. The vertical distribution of iodate is approximately the mirror-image of that of iodide. Spatially, in surface seawater, higher concentrations of iodide have been found in the equatorial area (Tsunogai and Henmi, 1971) and in some coastal areas (Tsunogai and Henmi, 1971; Truesdale, 1978). Tsunogai and Henmi (1971) suggested that the higher concentrations of iodide in the equatorial area may be the result of higher biological activities.

Several versions of the cycling of the iodine species among the different geochemical reservoirs have been constructed (Miyake and Tsunogai, 1963; Tsunogai, 1971). The



Vertical profiles of iodine species in the central North Pacific Ocean. (a) DE-7, 30°00'N, 159°51'W; (b) DE-8, 24°05'N, 159°20'W.

Fig. I-3-1

The vertical distribution of iodine species in seawater (From: Nakayama *et al.*, 1989).

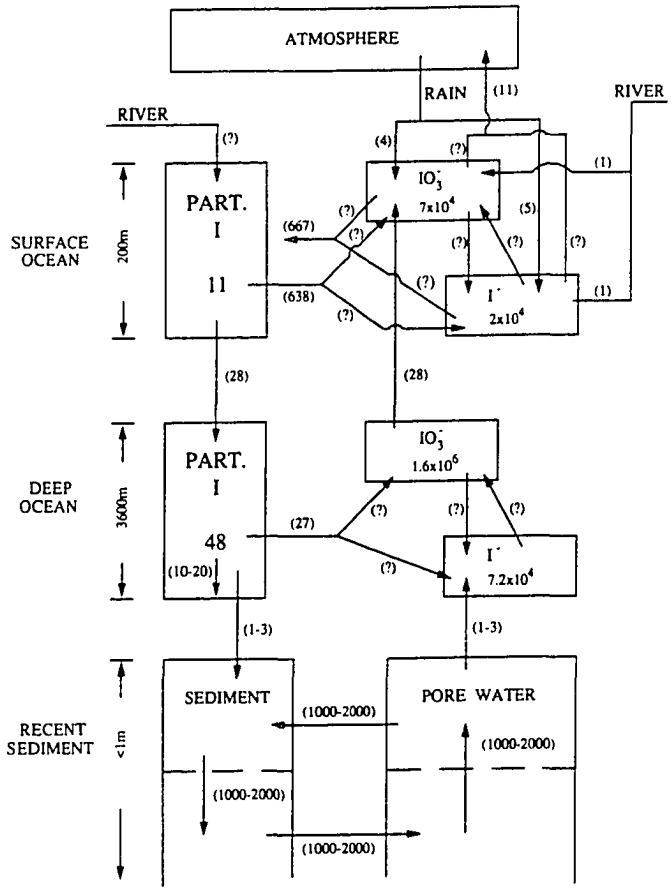
most recent version by Wong (1991) is given in Fig. I-3-2. The standing crops of iodine in individual geochemical reservoirs are relatively well known. In the surface water, the standing crop of iodide is about 30% of that of iodate. However, the standing crop of iodide in the whole water column is only about 5% of that of iodate.

The thermodynamic stability of iodine in seawater

If seawater reaches a thermodynamic equilibrium, the ratio of the concentration of iodate to that of iodide in the oxygenated seawater may be predicted by using thermodynamic principles. Based on Sillen's model (Sillen, 1961), the pE of seawater, if it is solely controlled by the redox couple of O_2/H_2O which is in equilibrium with atmospheric oxygen, is 12.5 at a pH of 8.1 and a temperature of 25°C. The ratio of iodate to iodide in seawater will then be $10^{13.5}$ (Sillen, 1961; Wong, 1980; Turner *et al.*, 1981). Thus, the conversion of iodate to iodide in oxygenated seawater is thermodynamically unfavorable. It was reported that iodine exists almost exclusively in the form of iodate in the deep seawater, but about one third of iodine exists in the form of iodide in the surface water (Tsunogai, 1971). The thermodynamic prediction about the speciation of iodine is approximately valid in the deep seawater but not in the surface water.

The production of iodide in surface seawater

Several mechanisms have been proposed to account for the



A tentative marine geochemical cycle of iodine. Figures in the boxes denote standing crops in the geochemical reservoirs in micromole per square meter. Figures in parentheses denote fluxes in micromole per square meter per year. (?) denotes fluxes poorly known.

Fig. I-3-2

The cycling of iodine species in seawater

(From: Wong, 1991).

presence of iodide in the surface waters: (1) iodide is formed by the biologically mediated enzymatic reduction of iodate (Tsunogai and Sase, 1969); (2) in coastal waters, iodide may be formed by the reduction of iodate by terrestrial reducing substances brought in by continental runoff (Truesdale, 1978); and (3) iodide may be transported to the interior ocean from the coastal oceans by advective processes (Smith and Butler, 1979; Wong and Zhang, 1991).

Iodide might be produced from the reduction of iodate via the mediation of biological activities (Tsunogai and Sase, 1969). This mechanism is supported by indirect and direct evidence. Iodine is much more concentrated in seaweeds with respect to the concentration of iodine in seawater (Mairh *et al.*, 1989). Iodide is mainly found existing in the euphotic zone (Fig. I-3-1). The vertical distribution of total dissolved iodine shows the behavior of nutrient-like elements. In fact, a close linear relationship has been found between nutrients (PO_4^{3-}) and total dissolved iodine (Elderfield and Truesdale, 1980). Nitrate reductase may reduce iodate to iodide (Tsunogai and Sase, 1969). Some diatoms may mediate the reduction of iodate to iodide by assimilation and excretion (Butler et al., 1981; Udomkit and Dunstan, 1991).

The concentrations of iodate in some coastal waters have been found to be slightly lower than those in open ocean waters (Truesdale, 1978). It was suspected that iodate might be reduced by terrestrial reducing substances which were brought into the coastal water by the continental runoff

(Truesdale, 1978). However, it should be remembered that since biological activities in coastal waters are much higher than those in open ocean waters, it might be difficult to differentiate between these two mechanisms for the reduction of iodate in coastal waters.

Recent studies have shown that in a number of estuaries, such as the Chesapeake Bay and the Winyah Bay, and in the inner shelf of a shelf sea such as the South Atlantic Bight, iodide may become the predominant or even the exclusive species of dissolved iodine (Ullman *et al.*, 1988; Luther *et al.*, 1991). It was postulated that, if this phenomenon can be generalized to the world oceans, iodide in the marginal seas may be added to the interior ocean by mixing. Thus, physical transport may account for a part of iodide found in the surface seawater of the interior ocean (Wong and Zhang, 1991).

I-4 A BRIEF REVIEW OF BIOGEOCHEMISTRY OF H_2O_2 IN SEAWATER

Hydrogen peroxide is involved in photochemical and biological processes in the surface oceans (e.g. Cooper and Zika, 1983; Moffett and Zafiriou, 1990; Palenik *et al.*, 1987; Palenik and Morel, 1988). These reactions which involve hydrogen peroxide also play a significant role in controlling the speciation of several redox-sensitive elements, such as Cu, Fe, Mn and Cr (e.g. Moffett and Zika, 1987; Pettine and Millero, 1990). In the atmosphere, hydrogen peroxide is one of the constituents of smog (e.g. Bufalini *et al.*, 1972) and it contributes to the formation of acid rain (e.g. Penkett *et*

al., 1979; Calvert *et al.*, 1985). As a result, the atmospheric and aquatic chemistry of hydrogen peroxide has been investigated extensively in recent years (e.g. Lee *et al.*, 1986; Cooper *et al.*, 1987; Fridovich, 1978; Petasne and Zika, 1987; Szymczak and Waite, 1988; Yoshizumi *et al.*, 1984).

The distribution of hydrogen peroxide in seawater

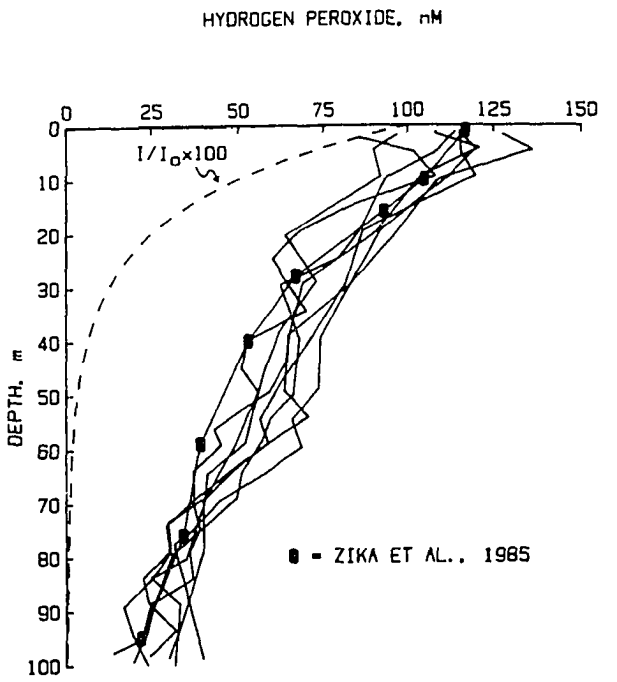
The presence of hydrogen peroxide in seawater was first detected in samples collected from the Gulf of Mexico (Van Baalen and Marler, 1966). Subsequent measurements from other parts of the world oceans (Table I-4-1) have shown that its concentration ranges from less than 5 nM to 300 nM in surface waters (e.g. Zika *et al.*, 1985a; 1985b; Johnson *et al.*, 1989). In depth profiles, a concentration-maximum is usually found in the surface water and the concentration decreases exponentially with depth, reaching undetectable level at the bottom of the euphotic zone (Fig. I-4-1). Diel variations in the concentration of hydrogen peroxide in surface waters have also been reported. The concentration reaches a minimum in the early morning and then increases to a maximum in the mid to late afternoon (Zika *et al.*, 1985a; Johnson *et al.*, 1989; Palenik and Morel, 1988).

The thermodynamics of hydrogen peroxide

Hydrogen peroxide is an intermediate in the reduction of oxygen to water where oxygen may be reduced successively to superoxide anion radical, hydrogen peroxide, hydroxyl radical

Table I-4-1: Hydrogen peroxide in the seawater

Place	Range (nM)	Reference
Narragansett Bay	25 - 115	Miller & Kester, 1988
Gulf of Mexico	28 - 372	Van Baalen & Marler, 1966
Gulf of Mexico	120 - 160	Moffett & Zika, 1983
Gulf of Mexico	100 - 300	Zika *et al.*, 1985a
Gulf of Mexico	70 - 110	Cooper *et al.*, 1987
Atlantic Ocean	60	Cooper *et al.*, 1987
Sargasso Sea	130 - 160	Palenik & Morel, 1988
Sargasso Sea	139	Miller & Kester, 1988
Mediterranean Sea	80 - 130	Johnson *et al.*, 1989
Peru upwelling area	8 - 50	Zika *et al.*, 1985b



Hydrogen peroxide concentration profiles vs depth measured at Stas 27, 28, and 31–35. These stations are located away from the influence of the frontal region. Each profile consists of 17 data points, each of which is usually the average of two or more measurements. Individual points are not shown for clarity. The profile measured by ZIKA *et al.* (1985a) at Sta. 1′ in oligotrophic waters of the Gulf of Mexico is shown for comparison. The dashed line is the ratio of the light intensity at depth to the surface intensity, expressed as a percentage, for a diffuse attenuation coefficient of $-0.07\ m^{-1}$. This was a typical value for the area.

Fig. I-4-1

The vertical distribution of hydrogen peroxide in seawater (From Johnson *et al.*, 1989).

and, finally, water (Fig. I-4-2). Hydrogen peroxide is the most stable species among these intermediates. Its concentration in surface seawater, reaching 300 nM, is the highest among these intermediates. Hydroxyl radical has also been measured in seawater (Zhou and Mopper, 1990; Mopper and Zhou, 1990), but its concentration is far below that of hydrogen peroxide.

The standard reduction potential of the redox couple of O_2/H_2O is 1.23 V:

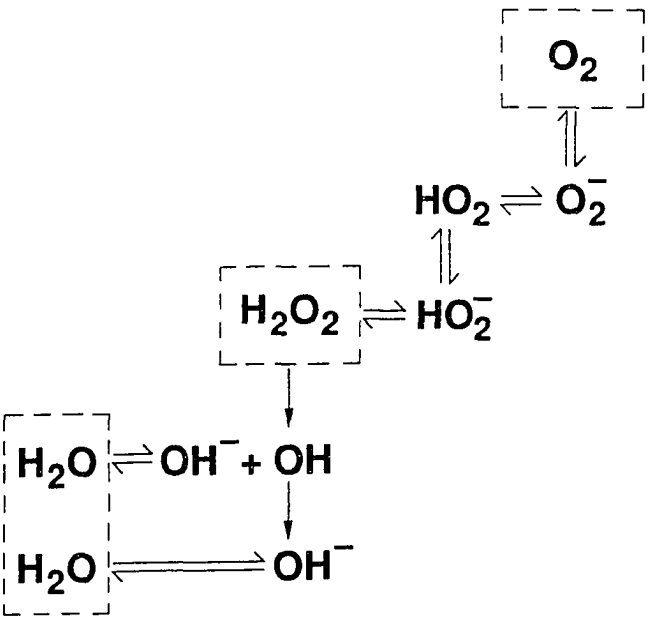
$$O_2 + 4H^+ + 4e = 2H_2O, \qquad E^\circ = 1.23 \text{ V}.$$

Thermodynamically, hydrogen peroxide can receive two electrons and act as an oxidant with respect to the redox couple O_2/H_2O in aqueous solutions, since the standard reduction potential of the redox couple of H_2O_2/H_2O is 1.78 V:

$$H_2O_2 + 2H^+ + 2e = 2H_2O, \qquad E^\circ = 1.78 \text{ V}.$$

However, it may also act as a reductant, also with respect to the redox couple O_2/H_2O, since hydrogen peroxide may lose two electrons to form oxygen and the standard reduction potential of the redox couple of O_2/H_2O_2 is 0.70 V:

$$O_2 + 2H^+ + 2e = H_2O_2, \qquad E^\circ = 0.70 \text{ V}.$$



Charge transfer and proton transfer reactions in the reduction of O_2 to H_2O, showing the intermediates involved. Electron transfer reactions are vertical; proton transfer reactions are horizontal.

Fig. I-4-2

The reduction of oxygen to water

(From Moffett and Zafiriou, 1990).

The sources and sinks of hydrogen peroxide in seawater

The sources and sinks of hydrogen peroxide in seawater are depicted in Fig. I-4-3. The sources consist of *in situ* photochemical production (Zika, 1980; Cooper and Zika, 1983; Petasne and Zika, 1987; Johnson *et al.*, 1989), biological production (Palenik *et al.*, 1987; Palenik and Morel, 1988), and dry or wet atmospheric deposition (Thompson and Zafiriou, 1983; Cooper *et al.*, 1987). The most important source is *in situ* photochemical production through the following reactions:

$$\text{Org} + \text{photon} = \text{Org}^{+\cdot} + e^{-}(aq)$$

$$e^{-}(aq) + O_2 = O_2^{-\cdot}$$

$$2O_2^{-\cdot} + 2H^{+} = H_2O_2 + O_2.$$

In this series of reactions, humic material in the photic zone, or Org, may be photochemically oxidized. In the process, hydrated electrons are generated. Hydrated electrons can reduce oxygen to the superoxide anion, $O_2^{-\cdot}$, which may subsequently disproportionate to form hydrogen peroxide (Zafiriou, 1977; Zika, 1980; Draper and Crosby, 1983). This mechanism may explain the formation of hydrogen peroxide in ground water (Cooper and Zika, 1983), fresh water (Cooper and Zika, 1983), coastal water (Petasne and Zika, 1987), and seawater upon their incubation under sunlight (Johnson *et al.*, 1989; Moffett and Zafiriou, 1990). The rate of production is directly related to the concentration of total dissolved organic carbon (Cooper and Zika, 1983) and the light intensity

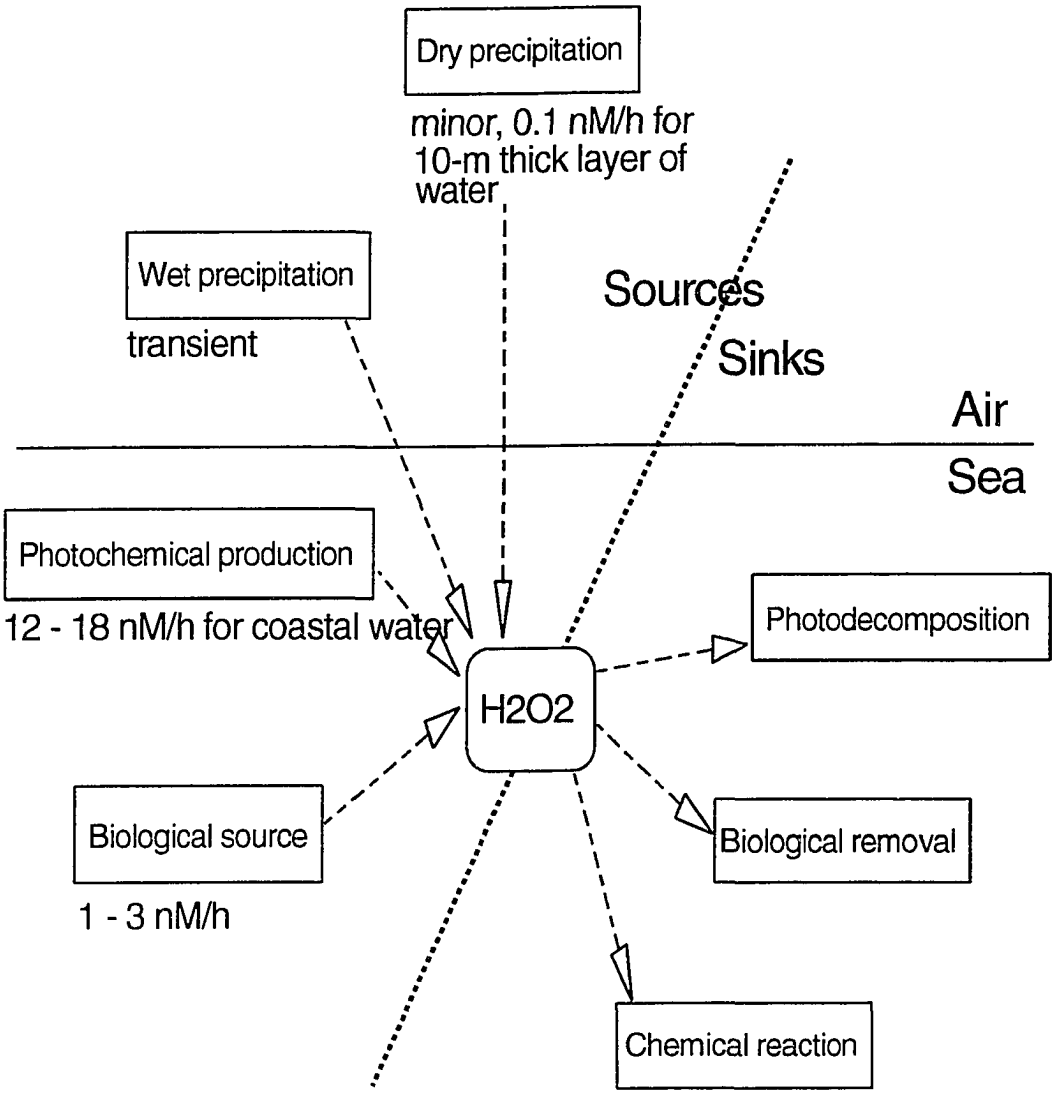


Fig. I-4-3

The sources and sinks of hydrogen peroxide in seawater

(Cooper and Zika, 1983; Petasne and Zika, 1987; Johnson *et al.*, 1989). Cooper and Zika (1983) suggested that the net rate of photochemical production of hydrogen peroxide in a sample of fresh water may be expressed as:

$$P = k\,[TOC];$$

where

P: Net rate of photochemical production of hydrogen peroxide, in nM/h;

[TOC]: Concentration of total dissolved organic carbon for a sample of water that has been filtered through a 0.22 μm polycarbonate membrane filter, in mgC l^{-1};

k: Rate constant which is equal to 6.9 (nM h^{-1})/(mgC l^{-1}) for a sample of fresh water under full sunlight at midday in June in Miami (latitude, 25°44').

If this relationship can be extrapolated to the photochemical production of hydrogen peroxide in seawater, the rate of production will be 11 nM h^{-1} in coastal waters with a concentration of total dissolved organic carbon of 1.6 mgC l^{-1}, and 4 nM h^{-1} in the open ocean water with 0.6 mgC l^{-1} of total dissolved organic carbon. This estimation is in agreement with the results obtained by the incubation of seawater under sunlight (Johnson *et al.*, 1989).

Hydrogen peroxide can be produced at the rate of 1 to 3 nM h^{-1} by organisms (Palenik *et al.*, 1987; Palenik and Morel,

1988). The dry atmospheric depositional flux supplies 0.84 μmol $m^{-2}h^{-1}$ of hydrogen peroxide to surface water (Thompson and Zafiriou, 1983), which is equivalent to 0.08 nM h^{-1} for a 10-meter thick layer of water. Thus, relative to photochemical production, biological production and dry atmospheric deposition are only minor sources of hydrogen peroxide to coastal waters (Fig. I-4-3). However, in the oligotrophic open ocean waters where the concentration of dissolved organic carbon is lower than that in coastal waters (Zika *et al.*, 1985b), the sources of biological production and dry atmospheric deposition may be significant.

While the sources for hydrogen peroxide in seawater are relatively well known, the mechanisms for its removal are not as well understood. Diel variations in the concentrations of hydrogen peroxide have been observed (Palenik and Morel, 1988; Zika *et al.*, 1985a). In stored surface seawater, hydrogen peroxide disappears with a lifetime on the order of days (Zika *et al.*, 1985a; Johnson *et al.*, 1989). Some of the possible sinks for hydrogen peroxide are *in situ* photodecomposition (Moffett and Zafiriou, 1990), biologically mediated decomposition (Zepp *et al.*, 1987; Cooper *et al.*, 1988), and chemical reactions with trace elements and dissolved organic material (Zika *et al.*, 1985a) (Fig. I-4-3). However, direct evidence supporting these mechanisms is still very limited.

CHAPTER TWO

THE DETERMINATION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS

II-1 INTRODUCTION

Hydrogen peroxide has been found in various kinds of natural waters. Its concentrations range from less than 5 nM to 300 nM in surface seawater (e.g. Zika *et al.*, 1985a; Johnson *et al.*, 1989) and from several μM to tens of μM in rainwater (Zika *et al.*, 1982; Kelly *et al.*, 1985; Cooper *et al.*, 1987; Cooper and Lean, 1989). Hydrogen peroxide is involved in photochemical reactions in rainwater (e.g. Cooper and Zika, 1983) and photochemical and biological reactions in surface seawater (Moffett and Zafiriou, 1990; Palenik *et al.*, 1987; Palenik and Morel, 1988). It plays an important role in controlling the speciation of several redox sensitive elements in the surface oceans (Moffett and Zika, 1987; Pettine and Millero, 1990). It is one of the components of smog in the atmosphere (Bufalini *et al.*, 1972). It is also partially responsible for the formation of acid rain (Penkett *et al.*, 1979; Calvert *et al.*, 1985). As a result, the biogeochemistry of hydrogen peroxide has been investigated extensively in recent years by atmospheric as well as aquatic scientists (Lee

et al., 1986; Cooper *et al.*, 1987; Fridovich, 1978; Petasne and Zika, 1987; Szymczak and Waite, 1988; Yoshizumi *et al.*, 1984).

A number of analytical methods, such as those based on iodometric titration (Kieber and Helz, 1986), mass spectrometry (Moffett and Zafiriou, 1990), spectrophotometry (Cohen and Purcell, 1967), chemiluminescence (Kok *et al.*, 1978), and fluorometry (Zika *et al.*, 1985a), have been reported for the determination of hydrogen peroxide in aqueous solution. However, few of these methods have been evaluated for the determination of hydrogen peroxide in natural waters (Frew *et al.*, 1983). The method that has been used most widely for this purpose is the fluorometric method based on the catalytic oxidation of scopoletin by hydrogen peroxide in the presence of the enzyme horseradish peroxidase and the resulting fluorescence quenching of scopoletin (Van Baalen and Marler, 1966; Zika *et al.*, 1985a; Holm *et al.*, 1987; Cooper *et al.*, 1987; Szymczak and Waite, 1988). One of the major analytical advantages of this method is its superior detection limit, which has been reported to be less than 5 nM (Zika *et al.*, 1985). However, the samples must be analyzed immediately once they are collected. Serious errors would result if the storage period exceeds one hour (Holm *et al.*, 1987; Cooper and Lean, 1989) possibly as a result of the instability of hydrogen peroxide. Furthermore, since the concentration of hydrogen peroxide in some natural waters, such as rain water, usually exceeds 1 μM, the superior detection limit of the

scopoletin-fluorometric method may become an inconvenience. Thus, samples of rain water must be diluted before hydrogen peroxide can be measured with this method, since the linear range of the method is only from 10 nM to 250 nM (Cooper and Lean, 1989). The detection limit might also not be an important issue in laboratory experiments in which higher concentrations of hydrogen peroxide (e.g. several μM) may be used. On the other hand, the necessity for analyzing the samples once they are collected is a rather stringent limitation. In many cases, the ability to store samples for later analysis is highly desirable for logistic reasons. For example, the samples collected from coastal waters by using a small boat usually cannot be analyzed on site. They must be returned to a land-based laboratory for the determination of hydrogen peroxide. In other cases, a small number of samples may be generated periodically over an extended period of time. It would be desirable if the samples may be allowed to accumulate and then analyzed later on as a single batch.

The objectives of this work are to develop methods for the determination of hydrogen peroxide that (1) may measure higher concentration directly without any dilution, (2) do not require on-site analyses and/or (3) can be applied to natural waters. Three methods have been studied: a square wave voltammetric method, a spectrophotometric method based on leuco crystal violet and a fluorometric method based on scopoletin and horseradish peroxidase. The results are presented here.

II-2 THE DETERMINATION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS BY SQUARE WAVE VOLTAMMETRY

ABSTRACT

A method has been designed for the direct determination of hydrogen peroxide in aqueous solutions by square wave voltammetry. Peak current is linearly related to concentration up to at least 600 μM. The relationship is not affected by the pH of the sample between pH 4 and 12 and minimally affected by salinity from distilled deionized water to full strength seawater. The detection limit of the method is about 2 μM. The precisions are about ±1.8%, ±0.7%, and ±0.8%, respectively at 6.4, 24.4 and 319 μM of hydrogen peroxide. This method is more rapid, more sensitive and has a much larger dynamic range than the traditional method by dc or differential pulse polarography. The lower detection limit allows this method to be applied to the determination of hydrogen peroxide in rainwater.

INTRODUCTION

Hydrogen peroxide may be electrochemically reduced to the hydroxyl ion in a neutral or alkaline solution:

$$H_2O_2 + 2\ e = 2\ OH^- .$$

This electrode reaction is irreversible. Its half-wave potential is approximately -1.0 V *vs* SCE (Milner, 1957). Based on this reaction, hydrogen peroxide in aqueous solutions has been determined by d.c. polarography (Ricciuti *et al.*, 1955) and by differential pulse polarography (Boto and Williams, 1976). In the latter mode, the relationship between the peak current and the concentration of hydrogen peroxide is linear over the range of 5 to 20 μM (Boto and Williams, 1976). A compound which can be determined by differential pulse polarography potentially may also be determined by square wave voltammetry (Christie *et al.*, 1977; Turner *et al.*, 1977). If this analytical approach is feasible, the latter method will be preferred since it can be orders of magnitude more rapid, it may be more sensitive and may provide a greater dynamic range than the former method. Thus, this possibility was explored in this study.

EXPERIMENTAL

Reagents

All chemicals used were of the ACS reagent-grade.

Standard solution of hydrogen peroxide (approximately 0.01 M): One ml of a 30% (w/w) solution of hydrogen peroxide was diluted to 1000 ml. This solution was standardized iodometrically by using iodate as the primary standard.

Solution of sodium chloride (0.38 M) - potassium bromide (1 mM) - sodium bicarbonate (5 mM): Sodium chloride (21.9 g), potassium bromide (0.12 g) and sodium bicarbonate (0.42 g) were dissolved in about 800 ml of distilled de-ionized water. The pH of the solution was adjusted to 8.0 with 1 M HCl and/or 1 M NaOH. It was then diluted to 1 liter. The composition of this solution is similar but not identical to that of seawater which is about 0.5 M in sodium chloride, 0.8 mM in Br^-, 2 mM in HCO_3^- and 10 mM in K^+.

Solution of sodium dihydrogen phosphate (1 M) - sodium citrate (1 M) (Ionic strength adjuster): Sodium dihydrogen phosphate (30.0 g) and sodium citrate (64.5 g) were dissolved in 200 ml of distilled de-ionized water. The pH was adjusted to 7.0 with 1 M HCl and/or 1 M NaOH. The solution was diluted to 250 ml.

Natural waters

Surface seawater (salinity = 36.6; pH = 8.0) was collected in the Sargasso Sea (8/1990. 32°00.0′ N; 75°00.0′ W). Estuarine water (salinity = 23.4; pH = 8.0) was collected from the lower Chesapeake Bay (2/1993. Bay mouth, 37°01.8′ N; 76°08.6′ W). Lake water (pH = 7.3) was collected from the Lake Whitehurst in Norfolk, VA (2/1993). Rain water (pH =

4.7) was collected in the ODU campus in Norfolk, VA (7/1992, 2/1993).

Apparatus

An EG&G/PAR Model 384B-4 polarographic analyzer system, equipped with a PAR Model 303A static mercury dropping electrode (SMDE) in the hanging mercury drop electrode (HMDE) mode, a Model 305 stirrer and a Houston Instrument DMP-40 series digital plotter, was used throughout this work. A platinum wire and a standard calomel electrode were used as the auxiliary electrode and the reference electrode respectively.

The pH was measured with an Orion Model 701A digital ionalyzer and a Corning deep vessel combination electrode.

Procedure

Pipette a 5-ml aliquot of the sample into a polarographic cell. Add 0.5 ml of ionic strength adjustor. Position the cell in the SMDE. Purge the sample with argon for 4 minutes to remove any dissolved oxygen in the sample. Blanket the sample with a positive pressure of argon gas to prevent oxygen from re-dissolving into the sample. Analyze the sample under the following conditions: mode, SWV (Square Wave Voltammetry); initial potential, -0.4; final potential, -1.6 V (The final potential can be adjusted to have a proper print-out of the voltammogram. For example, the final potential can be set to -1.5 V when the concentration of hydrogen peroxide is expected

to be less than 30 μM); reference electrode, standard calomel electrode; frequency, 120 Hz; scan increment, 10 mV; pulse height, 80 mV; drop size, medium for concentrations of H_2O_2 higher than 30 μM, large for concentrations of H_2O_2 below 30 μM. Construct a calibration curve by measuring the peak currents of hydrogen peroxide in distilled de-ionized water at various known concentrations. After each spike of the standard solution of hydrogen peroxide, purge the sample with argon for 2 minutes. Estimate the concentration of hydrogen peroxide in the sample from the calibration curve.

RESULTS AND DISCUSSION

Optimization of voltammetric parameters - frequency, scan increment, and pulse height

The dependence of peak current on frequency, scan increment, and pulse height was determined in the NaCl-KBr-$NaHCO_3$ solution containing 95 μM of added hydrogen peroxide. At a fixed scan increment (10 mV) and a pulse height (100 mV), the peak current of hydrogen peroxide was 802 nA at a frequency of 20 Hz and it increased approximately linearly with increasing frequency at about 1.93%/Hz between 20 to 80 Hz (Fig. II-2-1). Between 80 and 120 Hz, peak current still increased significantly with frequency. However, the rate of increase was slightly reduced. A frequency of 120 Hz which is the highest frequency available from the instrument was chosen as the standard condition for the method. Further increase in

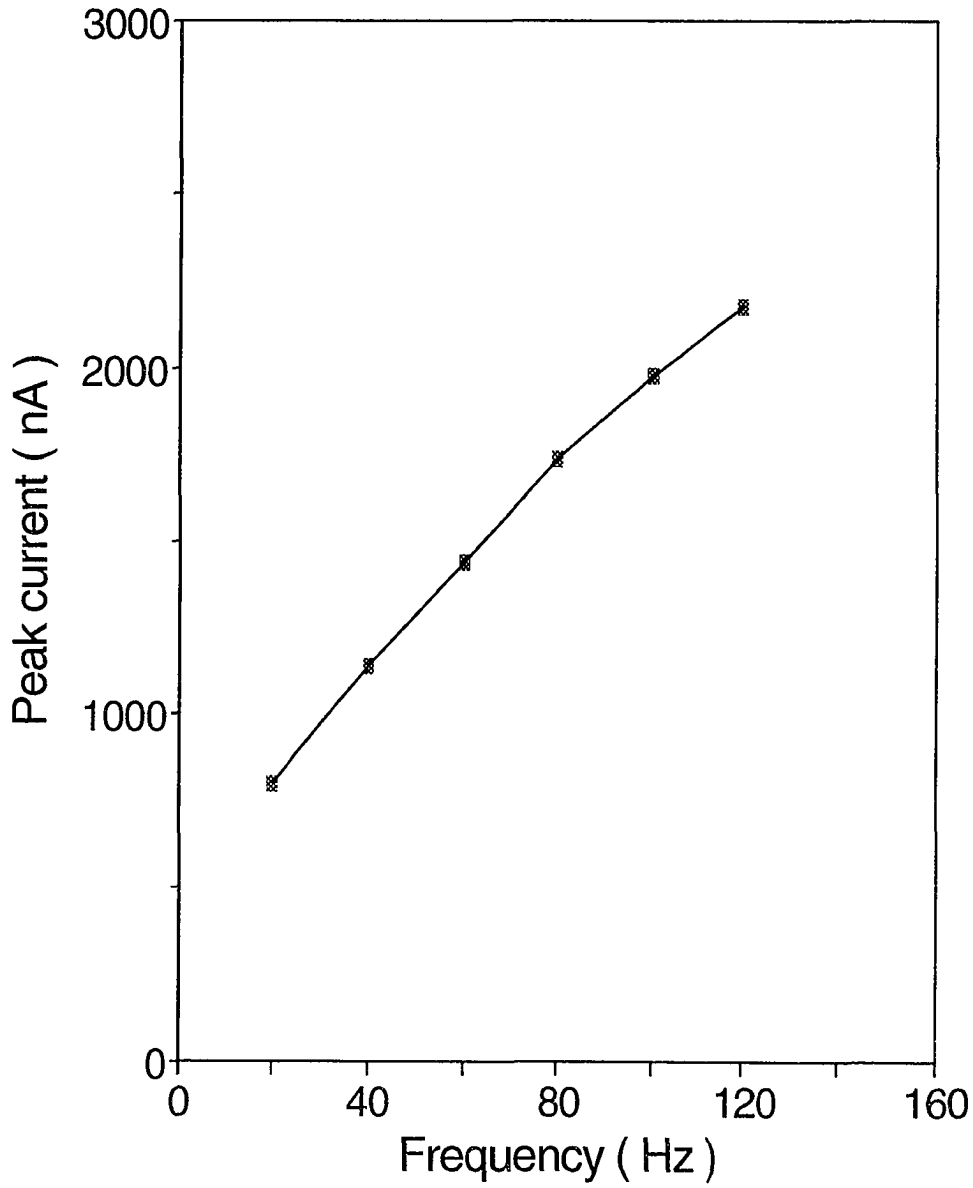


Fig. II-2-1

The variation of the peak current of hydrogen peroxide with frequency. Scan increment = 10 mV. Pulse height = 100 mV. $[H_2O_2]$ = 95 μM.

frequency is not recommended since it may distort the relationship between peak current and concentration (Christie *et al.*, 1977; Turner *et al.*, 1977).

The dependence of peak current on scan increment was determined at a frequency of 120 Hz and a pulse height of 100 mV. The peak current was 1014 nA at 2 mV of scan increment and it increased systematically with increasing scan increment at a rate of 14.4%/mV within the range of values, 2 to 10 mV, tested (Fig. II-2-2). This behavior is in agreement with the theory of square wave voltammetry (Christie *et al.*, 1977; Turner *et al.*, 1977). A scan increment of 10 mV was selected for the recommended standard condition. At this scan increment, the peak current is maximized, the time required for the completion of a scan is minimized while the resolution of the current peak is not noticeably compromised. The recommended frequency and scan increment gives an effective scan rate of 1200 mV/s. This rate is several hundred times faster than the typical scan rate used in differential pulse polarography. As a result, a scan may be completed within a second rather than in several minutes.

The dependence of peak current on pulse height was determined at a frequency of 120 Hz and a scan increment of 10 mV. The peak current was 572 nA at 20 mV of pulse height and it increased approximately linearly with increasing pulse height between 20 and 80 mV at a rate of 3.65%/mV (Fig. II-2-3). At higher values, the increase in peak current with increasing pulse height diminished significantly and the

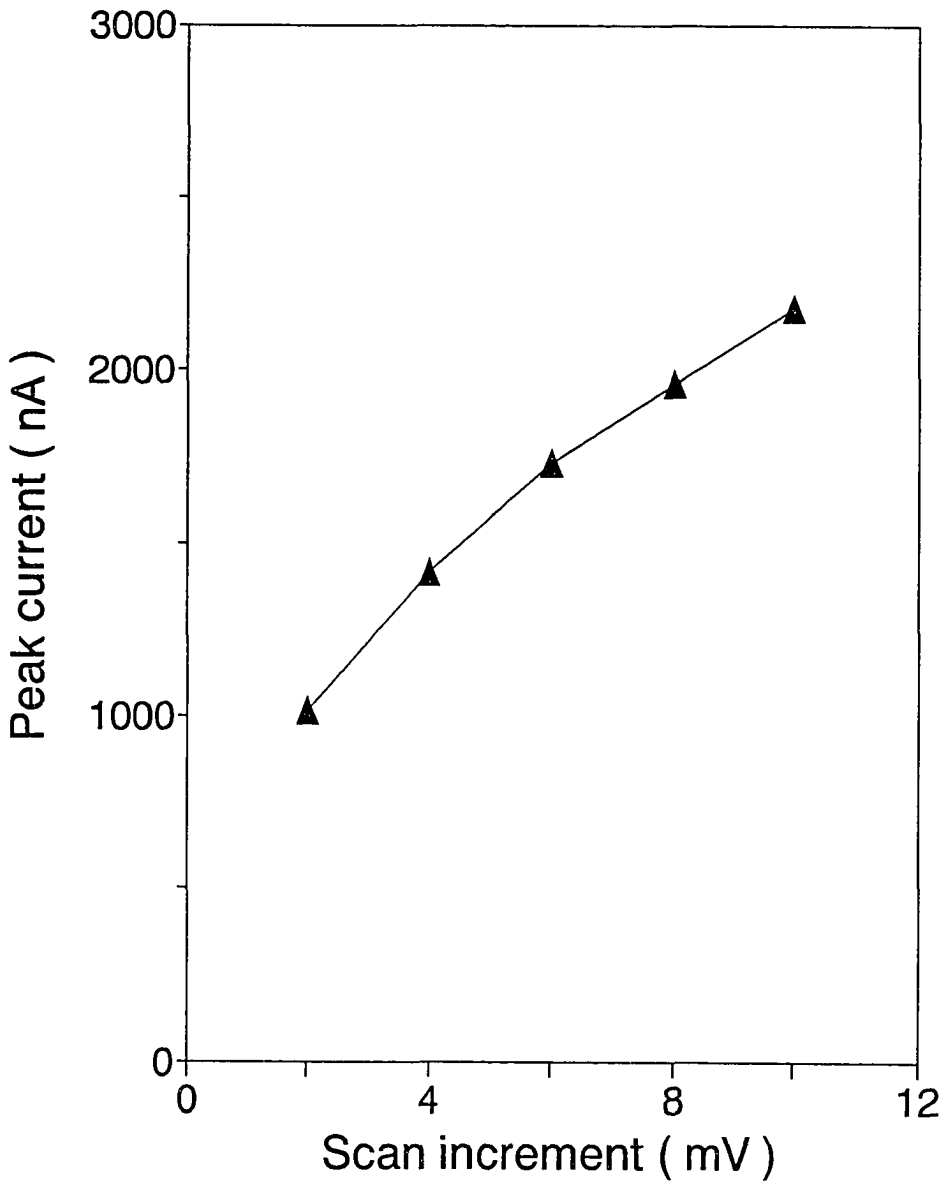


Fig. II-2-2

The variation of the peak current of hydrogen peroxide with scan increment. Frequency = 120 Hz. Pulse height = 100 mV. $[H_2O_2]$ = 95 μM.

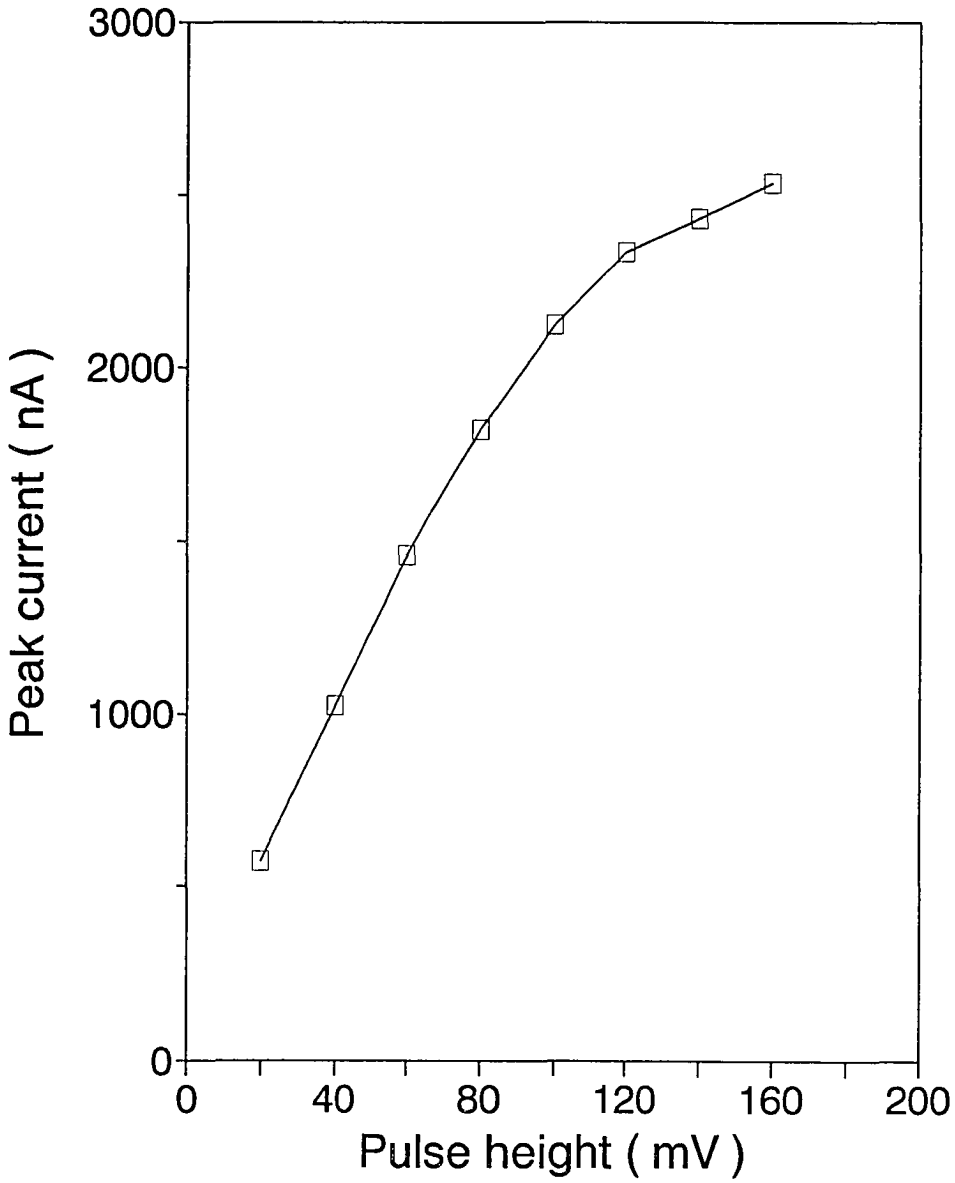


Fig. II-2-3

The variation of the peak current of hydrogen peroxide with pulse height. Frequency = 120 Hz. Scan increment = 10 mV. $[H_2O_2]$ = 95 μM.

current peak broadened as is usually observed in pulse voltammetry (Christie *et al.*, 1977). In order to maximize the peak current and minimize the distortion of the peak shape, a pulse height of 80 mV was chosen for the recommended standard condition.

pH effect

Shown in Fig. II-2-4 are the variations in peak current with pH in the NaCl-KBr-$NaHCO_3$ solution containing 0 to 457 μM of added hydrogen peroxide between pH 2 and 13.7. The pH of the solution was adjusted to the desired value by the addition of 1 M HCl or 1 M NaOH. The peak current remained at the maximum value between pH 4.3 and 11.7 at all concentrations of hydrogen peroxide. At lower and higher pH, the peak current was depressed significantly. Between pH 2 and 11.7, peak current was linearly related to the concentration of hydrogen peroxide (Fig. II-2-5). In all cases, the correlation coefficient of the linear least square relationship exceeded 0.99 and the intercept of the linear relationship was indistinguishable from zero (Table II-2-1). Since the pH of most natural waters falls between 4 and 12, this method should be applicable to most natural waters even without making any pH adjustment. Proper maintenance of the pH of the sample to within this optimal range is further assured by adding the phosphate-citrate ionic strength adjuster, which can also act as a pH buffer, to the sample.

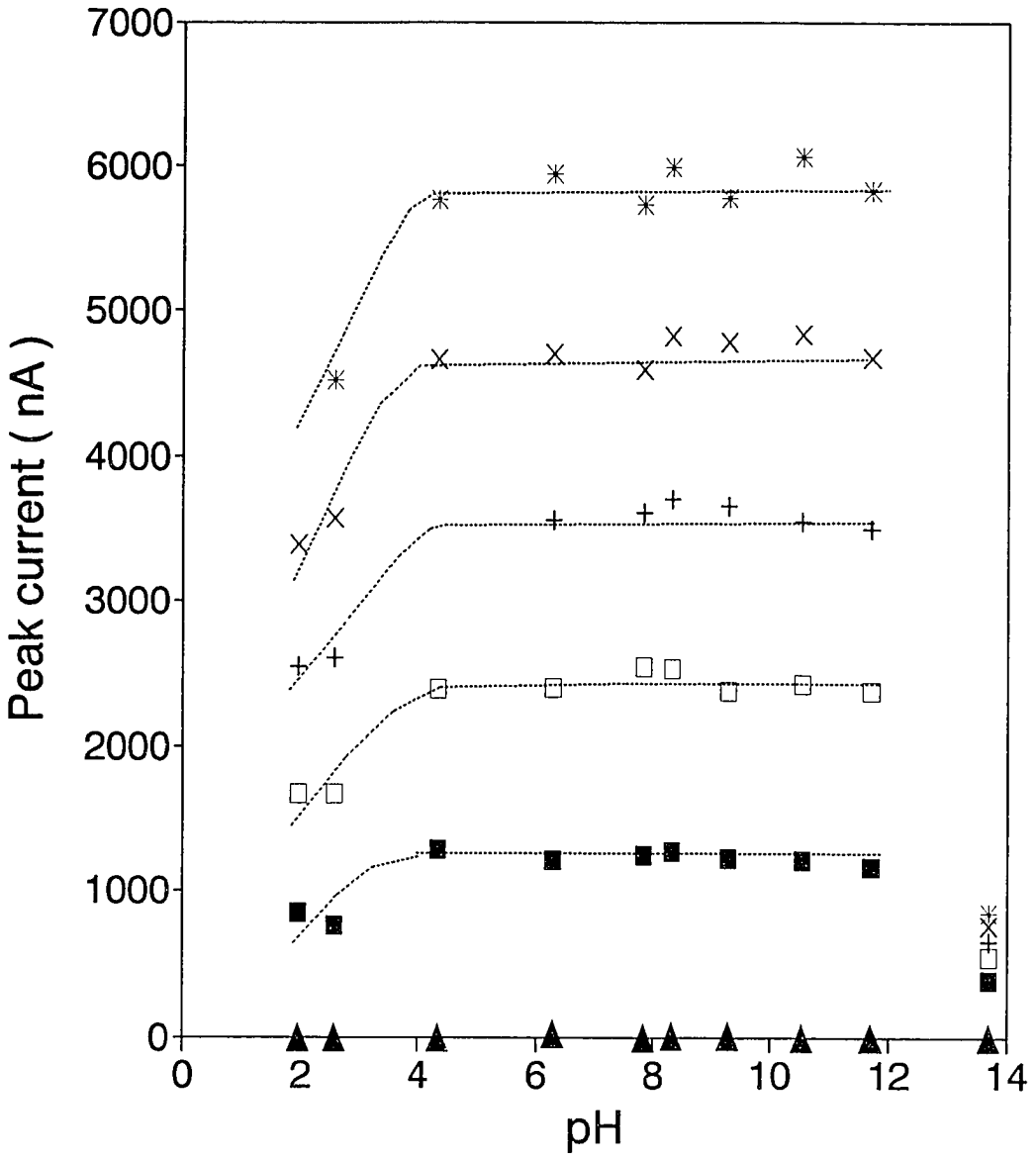


Fig. II-2-4

The variation of the peak current of H_2O_2 with pH in solutions of NaCl-KBr-$NaHCO_3$. The pH 13.7 solution was a solution of 0.5 N NaOH. The concentrations of hydrogen peroxide were: 0 (▲); 95 (■); 188 (□); 280 (+); 369 (×); and 457 μM (*).

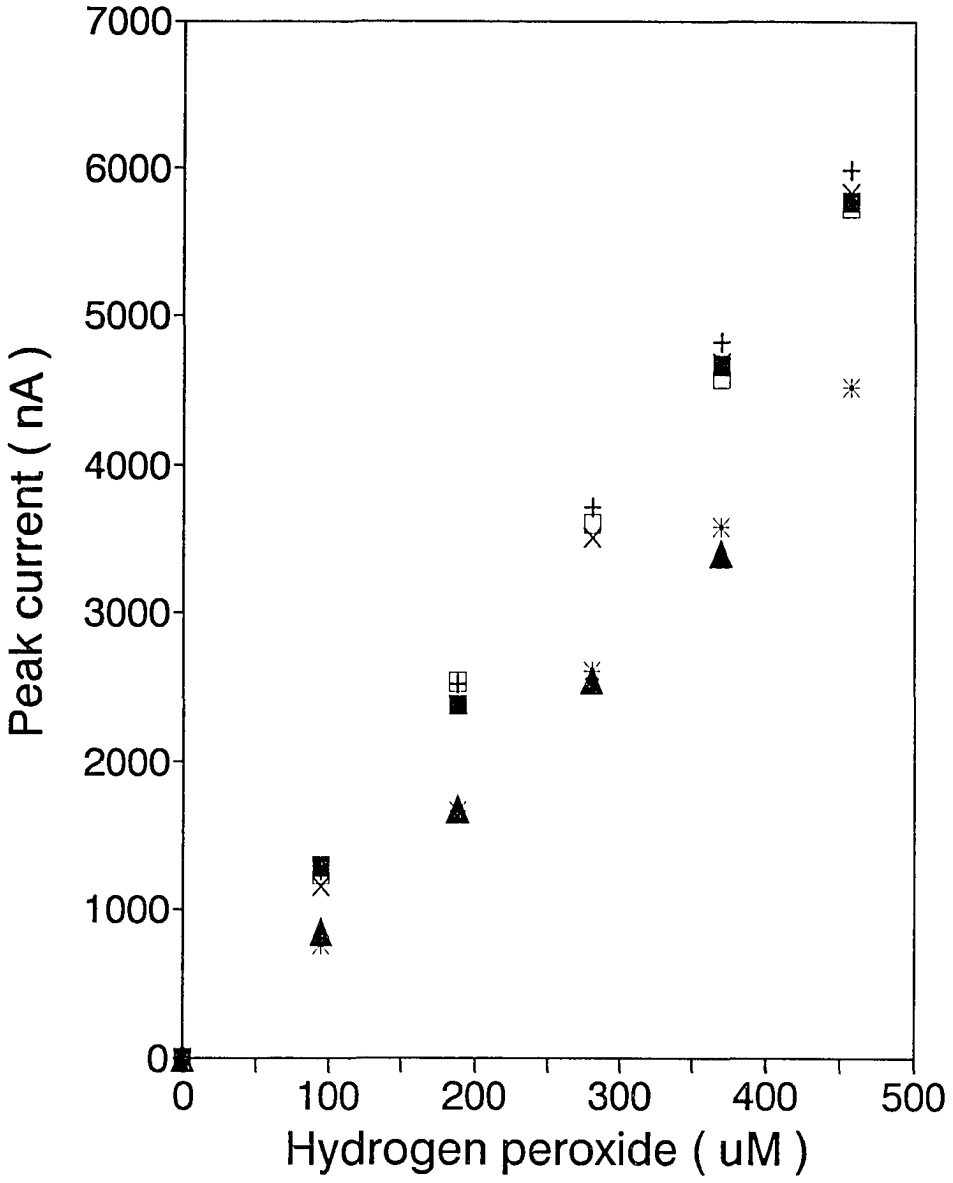


Fig. II-2-5

The peak current of H_2O_2 in solutions of NaCl-KBr-$NaHCO_3$ at different pH.

pH 2.0 (▲); 2.6 (*); 4.3 (■); 7.8 (□); 8.3 (+); and 11.7 (×).

Table II-2-1: The constants of the least-square lines for the relationship of the peak current to the concentration of hydrogen peroxide at different pH

pH	Intercept	σ(*)	Slope	σ(*)	r^2 (**)	$[H_2O_2]$
2.0	-23	29	9.2	0.1	0.9996	Up to 369 μM
2.6	-127	99	10.0	0.3	0.9973	Up to 457 μM
4.3	34	39	12.6	0.1	0.9998	"
6.3	-16	44	12.9	0.1	0.9997	"
7.8	71	86	12.4	0.2	0.9987	"
8.3	34	30	13.0	0.1	0.9999	"
9.3	16	61	12.8	0.2	0.9994	"
10.5	-48	69	13.2	0.2	0.9993	"
11.4	-50	93	12.7	0.2	0.9986	"
11.7	-32	32	12.8	0.1	0.9998	"

(*) σ = One standard deviation.

(**) n = 6 but n = 5 at pH 2.0 and at pH 4.3.

Medium effect

The relationship between peak current and the concentration of hydrogen peroxide, as determined by the recommended procedure, in distilled de-ionized water, rain water, lake water, estuarine water, open ocean water and the NaCl-KBr-$NaHCO_3$ solution is shown in Fig. II-2-6. The peak currents of the samples were measured after 0.5 ml of the ionic strength adjustor had been added to the samples. In all cases, peak current increased linearly with concentration below 20 μM with correlation coefficients exceeding 0.98 and the intercepts of the linear lines were again indistinguishable from zero (Table II-2-2). Thus, this method may be applied to natural waters with a wide variety of ionic strength/composition.

Sensitivity, dynamic range and precision

The sensitivity of the method is given by the slope of the linear regression line relating peak current and the concentration of hydrogen peroxide. The sensitivity of the method was pH-dependent. Between pH 4.3 and 11.7, the slope varied between 12.4 and 13.2 nA/μM, with an average of 12.8±0.2 nA/μM. Below pH 4, although a linear relationship between peak current and concentration continued to hold, the slope decreased significantly to 9.2 nA/μM. Thus, while the method may still be valid at these lower pH values, the sensitivity of the method will be reduced. At pH 13.7, in a 0.5 M NaOH solution, the linear relationship broke down.

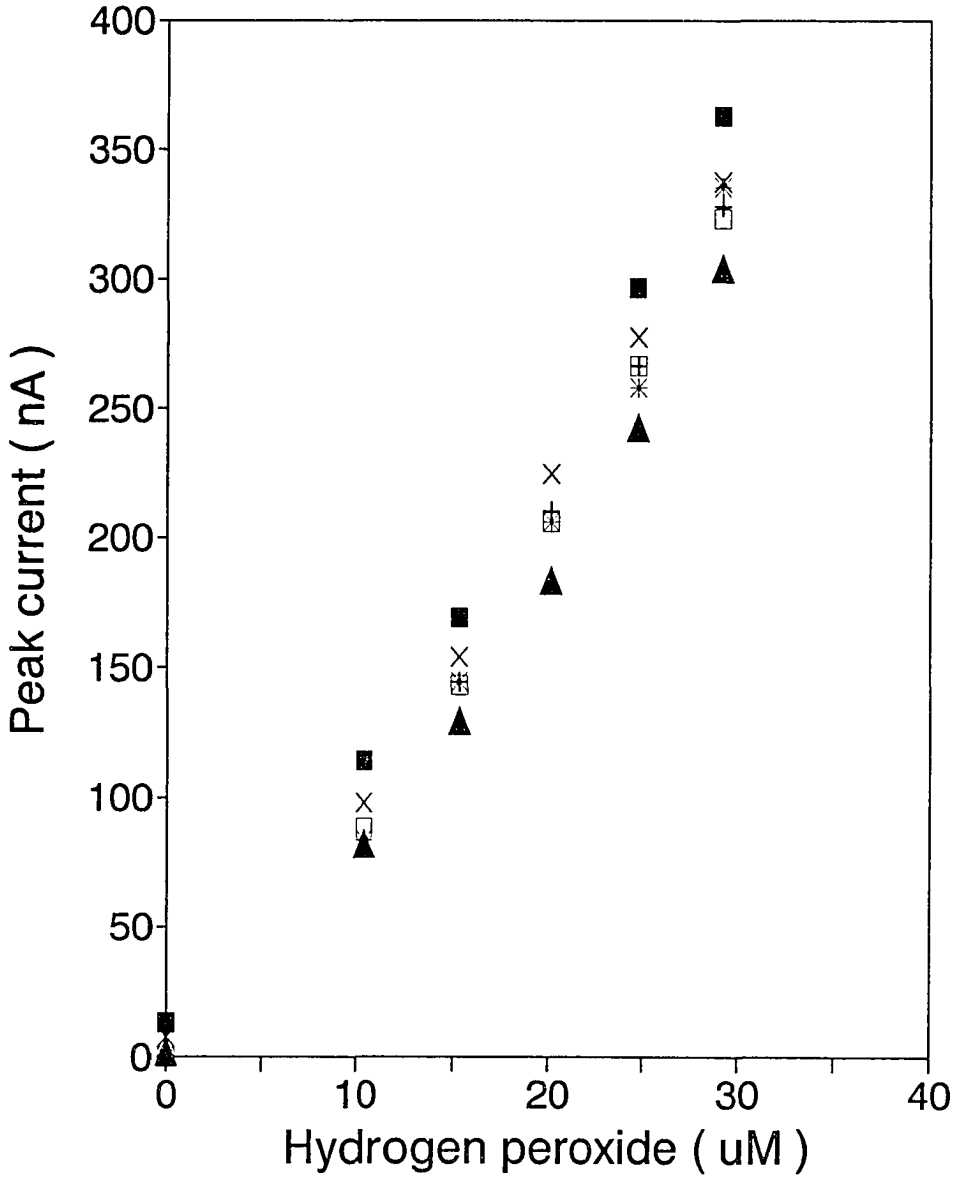


Fig. II-2-6

The variation of the peak current of hydrogen peroxide with its concentration in distilled de-ionized water (+), rain water (□), lake water (×), estuarine water (▲), seawater (■) and solution of NaCl-KBr-$NaHCO_3$ (*).

Table II-2-2: The constants of the least-square lines for the relationship of the peak current to the concentration of hydrogen peroxide in different medium

Medium	Intercept	σ(*)	Slope	σ(*)	r^2 (**)	$[H_2O_2]$
DDW	-8	15	10.3	1.0	0.9808	Up to 20 μM
Rain	-6	12	10.1	0.8	0.9876	"
L.W.	-3	9	8.9	0.6	0.9914	"
E.W.	0	14	10.5	1.0	0.9838	"
S.W	12	3	10.1	0.3	0.9990	Up to 15 μM
NaCl	-8	14	10.1	0.9	0.9833	Up to 20 μM

DDW: Distilled de-ionized water.

Rain: Rain water.

L.W.: Lake water.

E.W.: Estuarine water.

S.W.: Seawater.

NaCl: Solution of NaCl-KBr-$NaHCO_3$

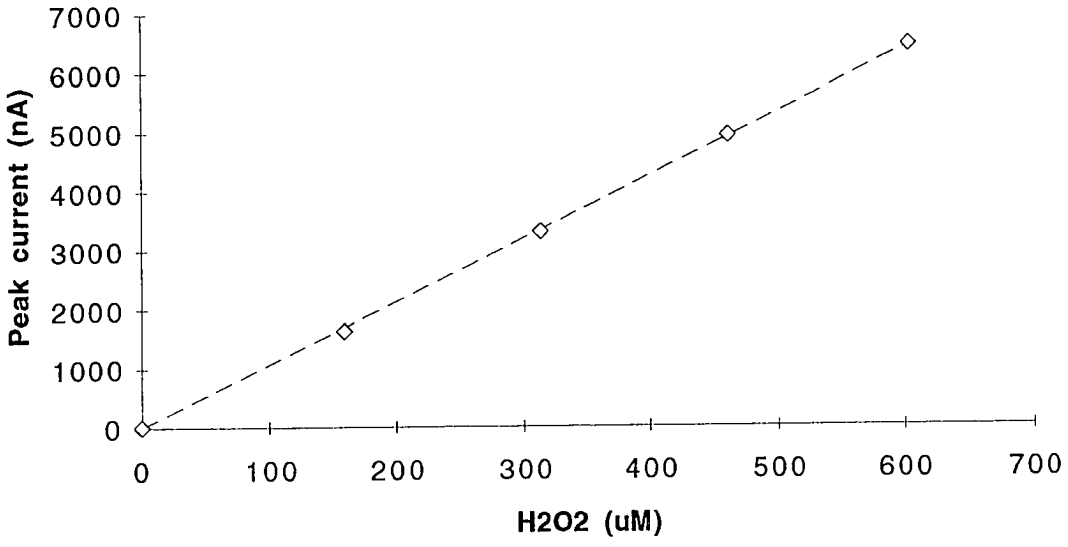
(*) σ = One standard deviation.

(**) n = 4 but n = 3 for seawater.

The sensitivity of the method varied slightly with the medium of the sample. The slope of the linear regression lines, at 8.9 nA/μM, was the lowest in the lake water (Table II-2-2). The low sensitivity probably was caused by the high concentration of dissolved organic material in the lake water.

The sensitivity of the method was also dependent on the size of the hanging mercury drop. It decreased from 24 nA/μM to 11 nA/μM as the drop-size was reduced from "large" to "medium" as set by the manufacturer of the polarographic analyzer system. Thus, in order to maximize the sensitivity and minimize the detection limit, the "large" drop-size was chosen as the recommended standard condition at concentrations below 30 μM. Above 30 μM, the "medium" drop-size was used. Boto and Williams (1976) reported that the sensitivity of the determination of hydrogen peroxide by differential pulse polarography was 6 nA/μM. Under the recommended standard conditions, the sensitivity of the square wave voltammetric method will be significantly higher even when the "medium" drop-size is used.

The peak current was linearly related to the concentration of hydrogen peroxide up to 600 μM (Fig. II-2-7), the highest concentration studied. Shown in Fig. II-2-8 is the voltammogram of hydrogen peroxide obtained in distilled de-ionized water treated with ionic strength adjuster when the drop size was set to "large". The concentration of hydrogen peroxide in a sample (distilled de-ionized water treated with ionic strength adjuster) containing 2.6 μM of hydrogen



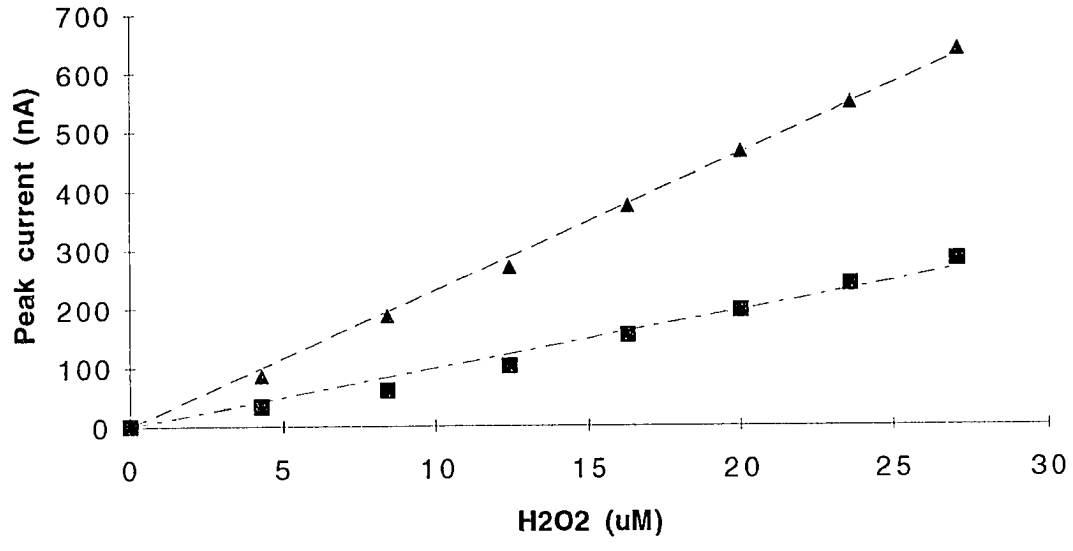


Fig. II-2-7

Standard curves of the peak current *vs* the concentration of hydrogen peroxide.

A: 0 - 600 μM.

B: 0 - 30 μM (large drop (▲) and medium drop (■)).

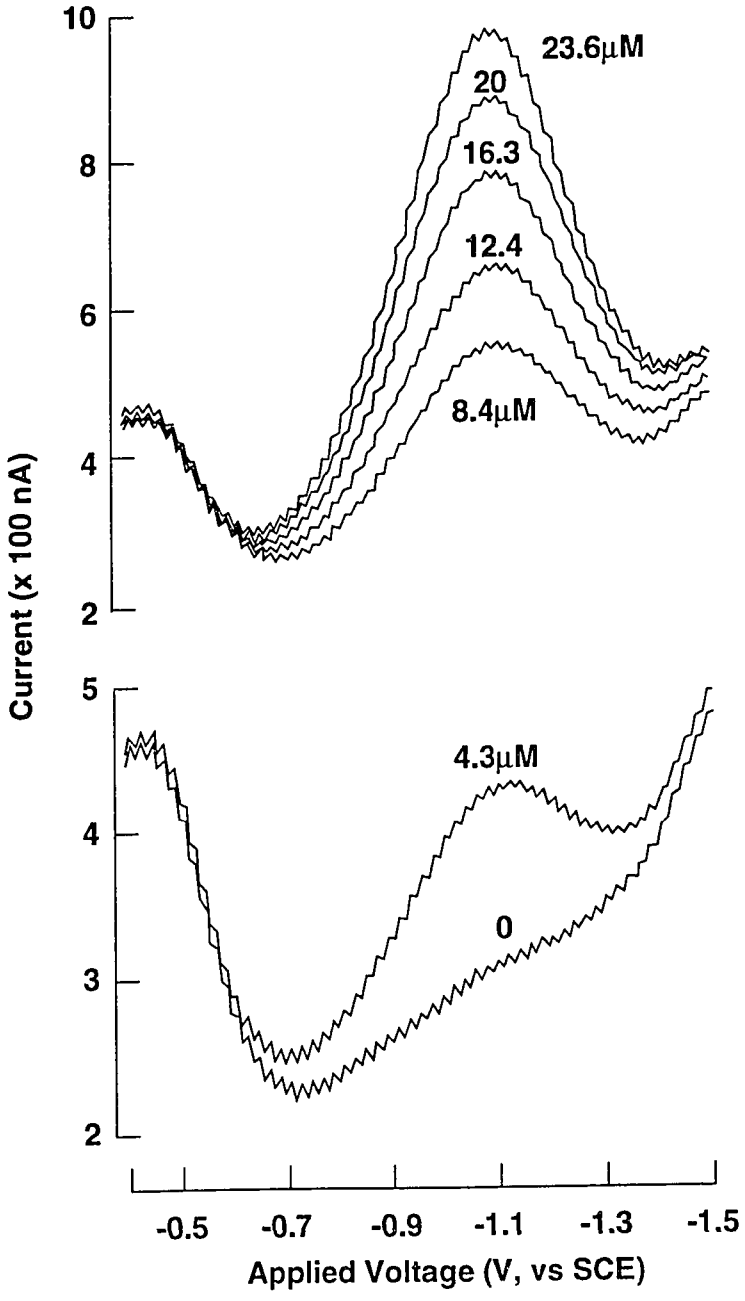


Fig. II-2-8

The voltammogram of hydrogen peroxide. The concentrations of hydrogen peroxide were 0, 4.3, 8.4, 12.4, 16.3, 20.0 and 23.6 μM, respectively.

peroxide was repeatedly measured. The detection limit, which is defined as three times of the standard deviation of the average concentration of this sample, was 2 μM. Thus, hydrogen peroxide may be measured by square wave voltammetry between 2 and, at least, 600 μM. This dynamic range is much larger than that of 5 to 20 μM of differential pulse polarography (Boto and Williams, 1976). The detection limit of this method, 2 μM, is low enough so that it may be applicable to the determination of hydrogen peroxide in rainwater since the concentration of rainwater usually lies between several μM to several tens of μM (e.g. Zika *et al.*, 1982; Cooper *et al.*, 1987; Cooper and Lean, 1989).

The precision of the square wave voltammetric determination of hydrogen peroxide has been determined at 3 concentrations of added hydrogen peroxide. At 6.4, 24.4 And 319 μM, the precisions were about ±1.8%, ±0.7% And ±0.8%, respectively.

Hydrogen peroxide in rainwater

The concentrations of hydrogen peroxide in 3 samples of rainwater collected between July, 1992 and February, 1993 were determined by the proposed method. The measurements were made immediately upon the collection of the samples. The concentrations of hydrogen peroxide in these samples ranged 3.2 to 18.1 μM (Table II-2-3). This range of concentrations is within the range of reported concentrations of hydrogen peroxide in rainwater (e.g. Zika *et al.*, 1982; Cooper *et al.*,

Table II-2-3: The concentrations of hydrogen peroxide in rain water

Date	Time	Rainfall (cm)	H_2O_2 (μM)	σ(*)
7/18/92	1700-1730	1.3	18.1	0.4 (n = 2)
2/11/93	2200-0400	0.5	3.2	0.4 (n = 4)
2/21/93	0900-1100	0.3	9.8	0.1 (n = 3)

(*) σ: One standard deviation.

1987; Cooper and Lean, 1989). These samples were analyzed repeatedly and the standard deviation of these analyses ranged from ±0.1 to ±0.4 μM.

CONCLUSIONS

Hydrogen peroxide in aquatic phases can be determined by square wave voltammetry quantitatively from 2 μM to at least 600 μM. The precision is better than 2% in most cases. The determination of hydrogen peroxide is not affected by pH from 4 to 12 and is minimally affected by salinity from distilled deionized water to full strength seawater. This method can be applied to natural waters with a wide variety of ionic strength/composition.

II-3 SPECTROPHOTOMETRIC DETERMINATION OF H_2O_2 IN NATURAL WATERS WITH LEUCO CRYSTAL VIOLET

ABSTRACT

H_2O_2 in natural waters, including seawater, may be determined at sub-μM concentrations by measuring the absorbance of crystal violet, formed by the enzymatically catalyzed oxidation of leuco crystal violet by H_2O_2 in the presence of horseradish peroxidase, at 592 nm. The detection limit of the method can reach 0.02 μM. The precision of the method is about ±7% at a concentration of 0.3 μM. The results obtained by this method and by a widely used fluorometric method agreed with each other well.

INTRODUCTION

An accurate, selective, and sensitive spectrophotometric method has been used for the determination of hydrogen peroxide (Mottola *et al.*, 1970). In the presence of the enzyme horseradish peroxidase (HRP), leuco crystal violet (4,4′,4″-methylidynetris (N,N-dimethylaniline) or LCV) may be oxidized by hydrogen peroxide to form crystal violet ({4-{bis[p-(dimethylamino)phenyl]methylene}-2,5-cyclohexadien-1-ylidine} dimethylammonium ion or CV^+). CV^+ absorbs strongly at 596 nm. Relative to the concentration of hydrogen peroxide consumed in the reaction, the molar absorptivity is 75,000 M^{-1} H_2O_2 cm^{-1} (Mottola *et al.*, 1970). Thus, by measuring the absorbance of the CV^+ formed, Mottola *et al.* (1970) reported that hydrogen peroxide in aqueous solutions may be determined in concentrations ranging from 1.8 to 15 μM. However, based on this reported molar absorptivity, this method may have a much lower detection limit so that it may be adequate for the determination of the lower, sub-μM, concentrations of hydrogen peroxide in many kinds of natural waters, including most surface seawater. For example, at the reported molar absorptivity, even 10 nM of hydrogen peroxide should give a detectable absorbance of 0.007 if a 10-cm cell is used. The work of Mottola *et al.* (1970) only dealt with pure aqueous solutions of hydrogen peroxide at the more elevated concentrations. The possibility of applying this method for the determination of hydrogen peroxide in natural waters is explored here.

EXPERIMENTAL

Reagents

All chemicals used were of ACS reagent-grade.

Standard solution of hydrogen peroxide (about 0.01 M): One ml of a 30% (w/w) solution of H_2O_2 was diluted to 1000 ml. This solution was standardized iodometrically by using iodate as the primary standard.

pH 4 buffer (0.5 M potassium di-hydrogen phosphate): KH_2PO_4 (68.0 g) was dissolved in 490 ml of distilled de-ionized water. The pH was adjusted to 4.0-4.1 with concentrated H_3PO_4 (85%). The solution was diluted to 500 ml.

Leuco crystal violet (LCV: 1 mM): Leuco crystal violet (EASTMAN KODAK CO., Cat. #3651, MW = 373.54) (0.374 g) was dissolved in 1 liter of 0.06 M HCl. This reagent was stored in the dark at room temperature. It is stable for at least 0.5 years.

Horseradish peroxidase (HRP): Horseradish peroxidase (SIGMA, P-8250, 200 purpurogallin units/mg) (10 mg) was dissolved in 10 ml of distilled de-ionized water.

Seawater

Surface seawater (salinity = 33 psu) was collected with a polyethylene bucket from Oceanfront, Virginia Beach, VA (5/1989) and from the lower Chesapeake Bay (salinity = 23 psu. 2/1993. 37°01.8′ N, 76°08.6′ W). Coastal water (salinity = 28) was collected with a polyethylene bucket from Oceanview,

Norfolk, VA (6/1991). The water was filtered through glass fiber filter (1 μm nominal) and it was stored in the laboratory at room temperature.

Apparatus

A Beckman UV5230 double beam spectrophotometer was used.

The pH was measured with an Orion Model 701A digital ionalyzer.

Procedure

Pipet a 40-ml aliquot of the sample to a 50-ml volumetric flask. Add 4 ml of the pH 4 buffer and 0.5 ml of the 1 mM LCV. Mix the solution and then add 0.1 ml of the HRP solution. Dilute to mark, mix the solution. Measure its absorbance at 592 nm with a 10-cm cell with distilled de-ionized water as the reference. Prepare a "H_2O_2-free" seawater by mixing 500 ml of seawater with 0.5 g of powdered MnO_2 for 2 hours and then filtering the seawater through a 0.45 μm filter (Milipore, Type HA). Construct a calibration curve with the "H_2O_2-free" seawater with various known amounts of added hydrogen peroxide.

RESULTS AND DISCUSSION

Effect of pH

Crystal violet undergoes consecutive protonation as pH decreases (Cigen, 1958) according to the equilibria:

$$CV^{+} + H^{+} = HCV^{2+} \quad , \quad pK = 2.39;$$

$$HCV^{2+} + H^{+} = H_2CV^{3+} \quad , \quad pK = 0.91.$$

The absorption spectra of these different protonated forms of crystal violet are not identical. The absorption of CV^{+} at its absorption maximum at 592 nm is used for the determination of hydrogen peroxide. The equilibrium constants suggest that CV^{+} should be the predominant species at pH values higher than 3. However, as pH increases, the excess LCV in the sample will precipitate and give rise to a turbidity blank. Thus, the pH of the final solution must be carefully controlled to insure that, on the one hand, CV^{+} predominates, and, on the other hand, LCV does not precipitate (Mottola *et al.*, 1970). In order to ascertain the optimal pH for the method, the pH of a sample of surface seawater or distilled de-ionized water was adjusted to values between 2 and 7.1 with 1 M HCl and/or 1 M NaOH in the presence or absence of 0.4 μM of added hydrogen peroxide. Then, LCV and HRP were added as described in "procedure" and the spectrum of the solution between 400 and 700 nm was recorded. The results are shown in Fig. II-3-1. Below pH 3, in the presence of H_2O_2 in both seawater and distilled de-ionized water, the absorbance was less than 0.05 throughout the entire range of wavelengths and there was no discernible absorption peak. At pH 3, an absorption maximum at 590 nm became conspicuous. There were also two shoulders at 550 and 640 nm. Above pH 3, the absorbance at the absorption maximum at 592 nm increased while the absorbance at

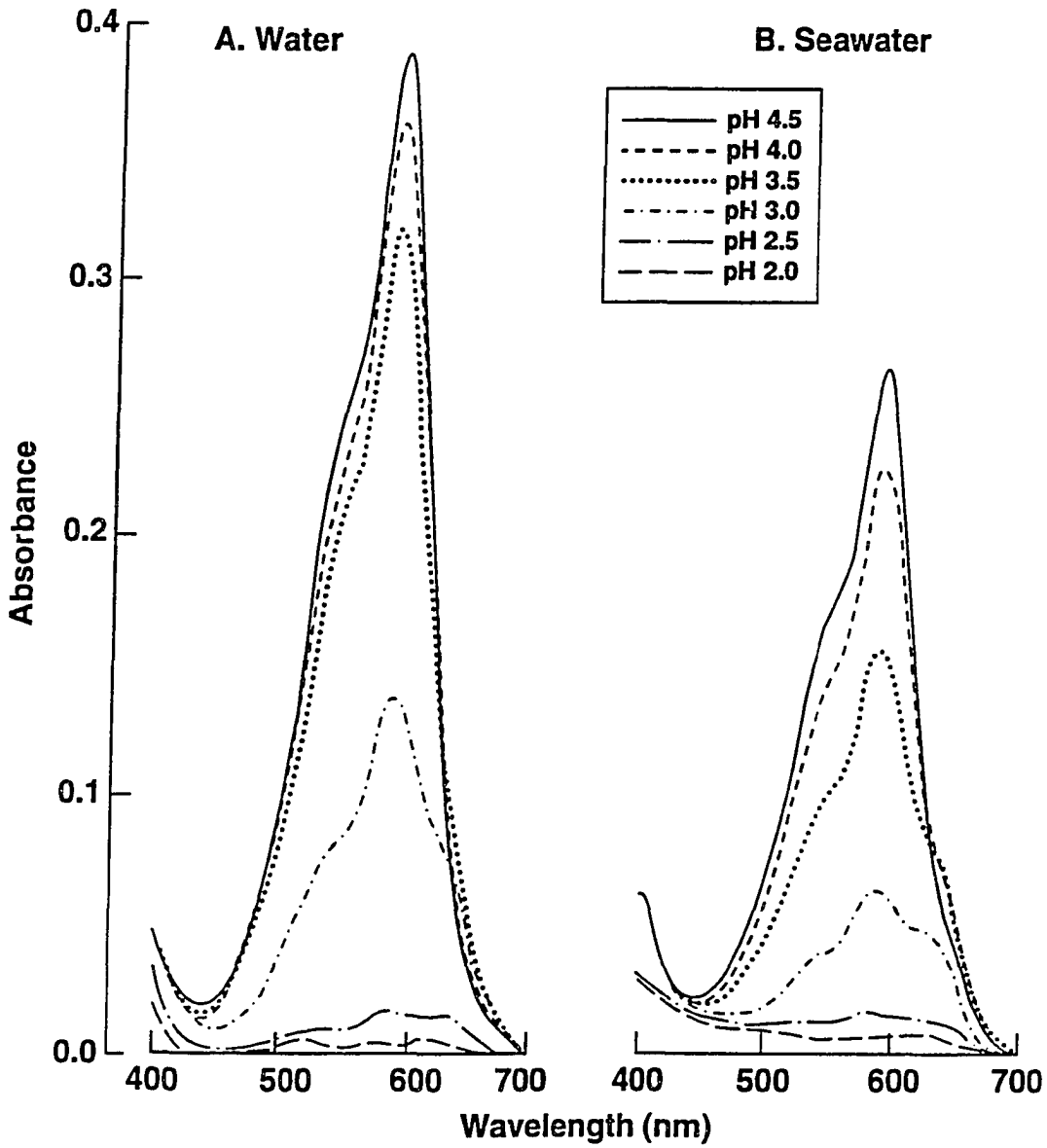


Fig. II-3-1
Spectra of CV^+ in distilled de-ionized water (A) and in seawater (B). In the order of increasing absorbance, the pH was 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5, respectively.

the shoulder at 640 nm decreased. The shoulder at 640 nm became undiscernible while the shoulder at 550 nm remained present at pH above 4. Thus, the absorbance at 592 nm was negligible below pH 2.5 (Fig. II-3-2). It increased rapidly between pH 2.5 and 3.5 in distilled de-ionized water and between 2.5 and 4 in seawater. At higher pH, up to pH 4.5, the absorbance increased more gradually. The lack of a well defined absorption spectrum below pH 3 suggests that H_2O_2 does not react with LCV to form crystal violet and/or that, if crystal violet is formed, HCV^{2+} and H_2CV^{3+} are the dominating species and they do not absorb strongly at these wavelengths. As pH increases, the oxidation of LCV by H_2O_2 proceeded and CV^+ became the dominant species. As a result, its absorption maximum at 592 nm became the dominant feature in the absorption spectrum. Even in the absence of H_2O_2, an absorbance at 592 nm became detectable at pH 4.7 as a result of the precipitation of LCV. The solution became noticeably turbid at pH above 5 as the absorbance increased sharply (Fig. II-3-3). Thus, the optimal pH should be between 4 and 4.5 as suggested in previous studies (Black and Whittle, 1967; Mottola *et al.*, 1970; Lambert *et al.*, 1975). With the recommended procedure, the final pH of the sample was 4.3 to 4.4.

Stability of CV^+

After CV^+ was formed in a sample of seawater, its absorbance at 592 nm was followed over time for 5 days. In

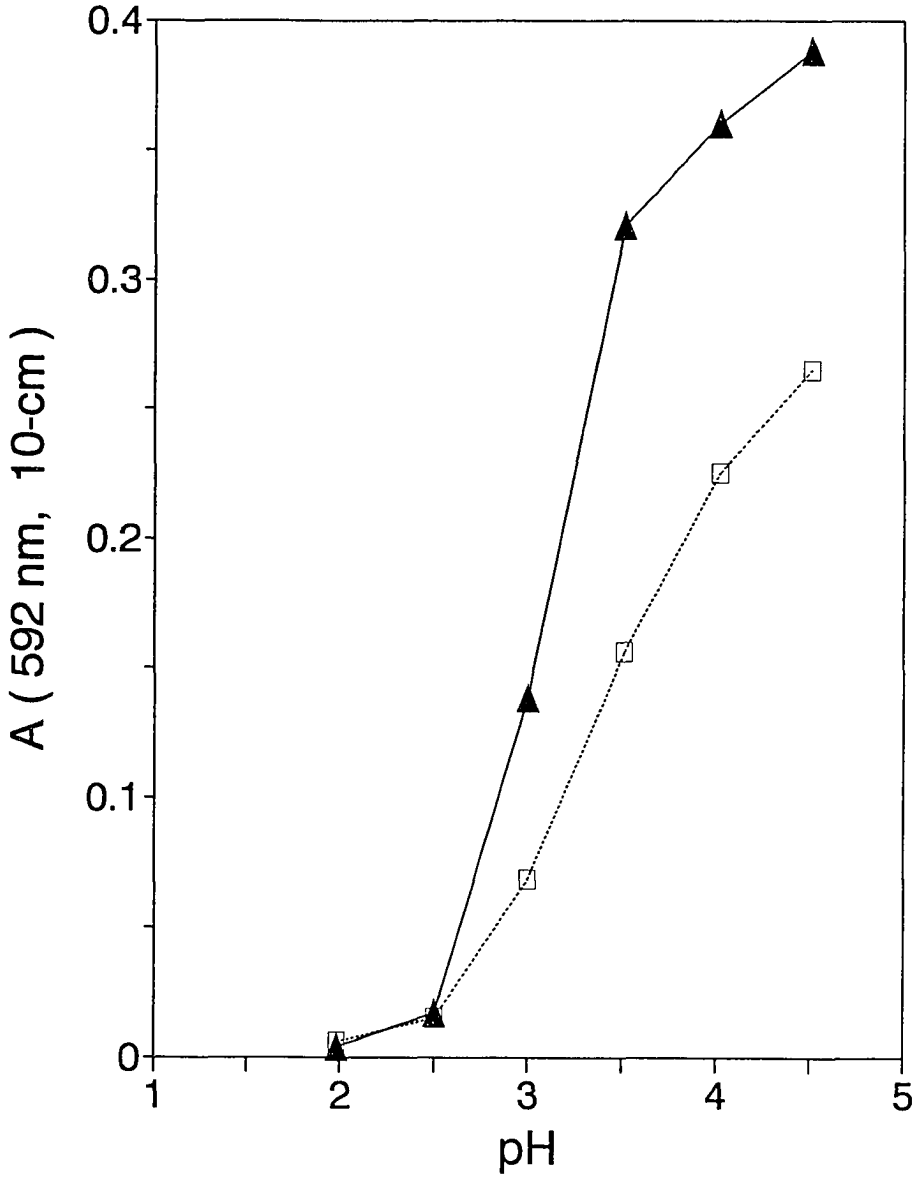


Fig. II-3-2

The absorbance of crystal violet (CV^+) at different pH. The initial concentration of H_2O_2 was 0.4 μM.

Seawater (□). Distilled de-ionized water (▲).

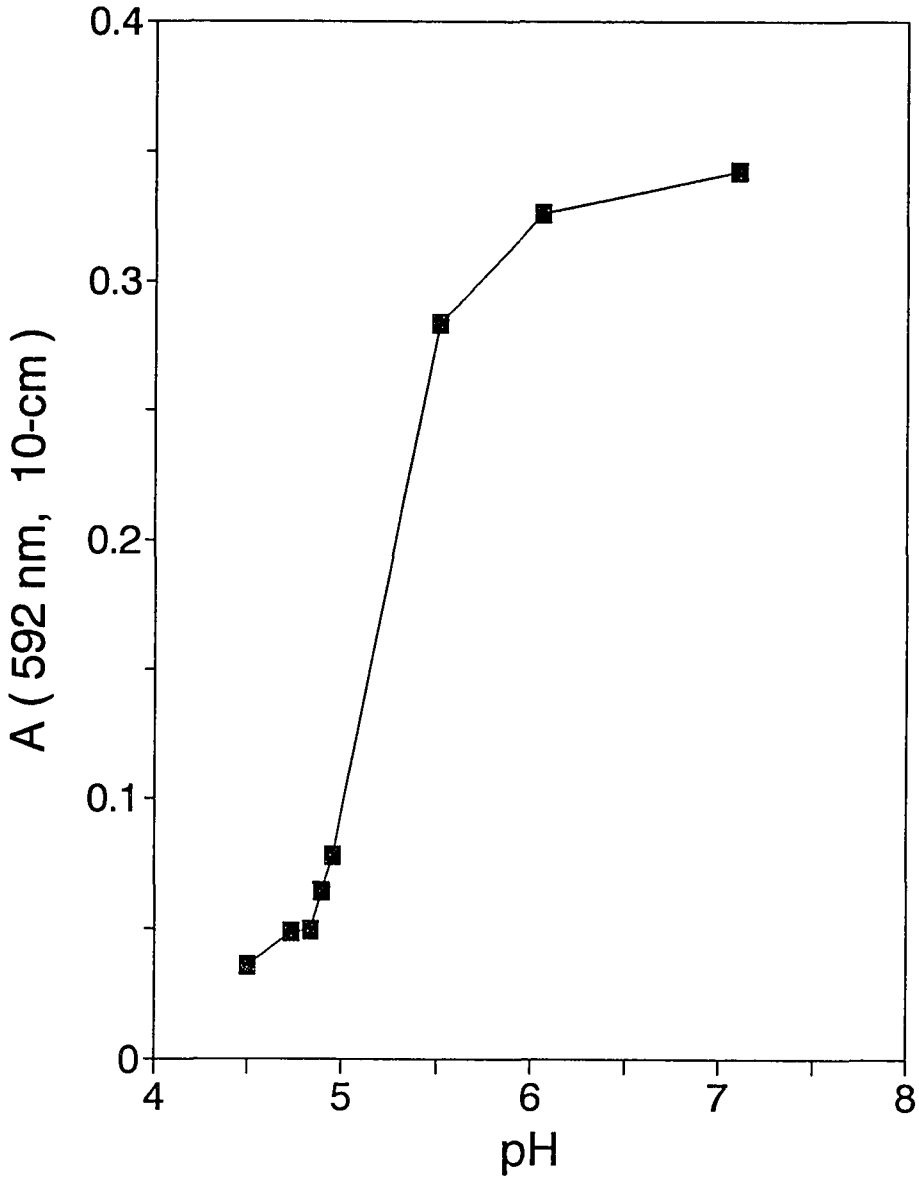


Fig. II-3-3

The precipitation of LCV, expressed as the absorbance at 592 nm, at different pH.

the first 24 hours, the absorbance decreased slightly at a rate of about 0.3% per hour (Fig. II-3-4). After the first 24 hours, the absorbance remained stable for the next four days. Thus, although the color of CV^+ does fade with time, the rate of decrease in absorbance is quite well defined and predictable. After CV^+ is formed in a sample, it would of course be best to read the absorbance immediately. However, it is also possible to store the sample after color development and measure the absorbance even a few days later if a small correction for fading is made.

Amount of horseradish peroxidase

The rate of an enzymatically catalyzed reaction, such as the catalytic oxidation of LCV to CV^+ by hydrogen peroxide in the presence of the enzyme HRP, is dependent on the concentration ratio of the enzyme and the reactant. In order to minimize the reaction time, and thus the time for the analytical procedure, it would be desirable for the reaction to be instantaneous. The instantaneous formation of CV^+ was followed between 0 and 59 purpurogallin of HRP/μg of H_2O_2 by measuring its absorbance at a fixed concentration of hydrogen peroxide of 0.4 μM and a range of concentrations of HRP in seawater and distilled de-ionized water. In both cases, the absorbance increased rapidly with an increasing ratio of HRP to hydrogen peroxide between 0 and 10 purpurogallin/μg (Fig. II-3-5). Above a ratio of 15, the increase in absorbance with an increasing ratio was small. Mottola *et al.* (1970)

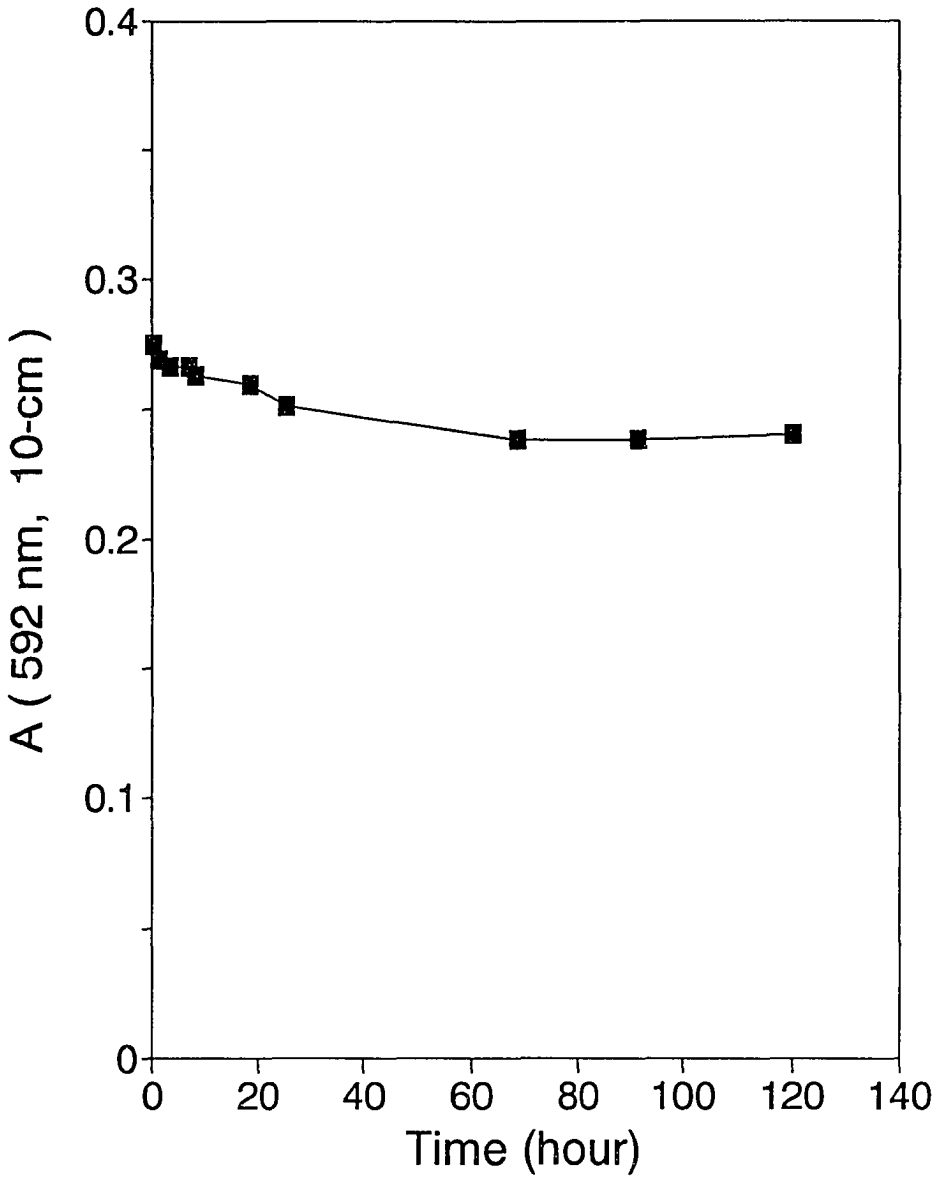


Fig. II-3-4

The variation in the absorbance of CV^+ with time.

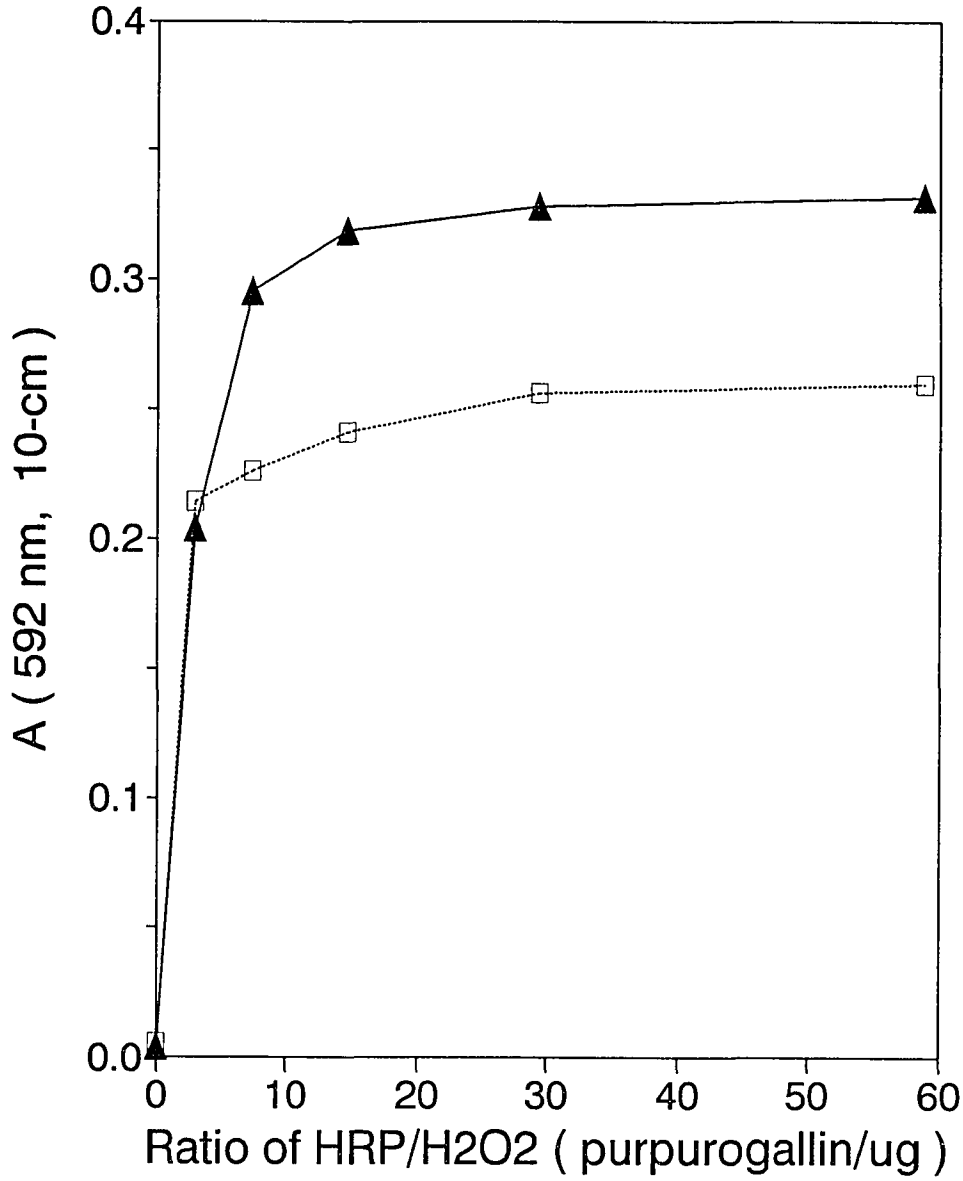


Fig. II-3-5

The catalytic effect of horseradish peroxidase, indicated by the absorbance, on the reaction between H_2O_2 and leuco crystal violet. The initial concentration of H_2O_2 was 0.4 μM. Seawater (□). Distilled de-ionized water (▲).

suggested the use of a ratio of 20. In the scheme reported here, the ratio will be above 20 for concentrations of H_2O_2 below 0.6 μM, the concentrations usually found in natural waters.

Salt effect

The molar absorptivity of CV^+ relative to the concentration of hydrogen peroxide was determined in seawater and diluted seawater with salinity between 0 and 33 psu. The molar absorptivity was about 89,000 at 0 psu. This value is somewhat higher than the value of 75,0000 reported by Mottola *et al.* (1970). The molar absorptivity decreased with increasing salinity (Fig. II-3-6). The decrease was more pronounced between 0 and 15 psu where the molar absorptivity decreased from 89,000 to 74,000 or a decrease of about 17%. Between 15 and 26 psu, the molar absorptivity further dropped to 70,000, or an additional decrease of 6%. Between 26 and 33 psu, there was no detectable change in molar absorptivity. Thus, when the concentrations of H_2O_2 in samples with a large range of salinity are measured, such as those collected from an estuary, calibration curves must be established at multiple salinity to cover the range of salinity encountered. In the open oceans, variations in salinity are small enough so that a correction for salt effect would not be necessary.

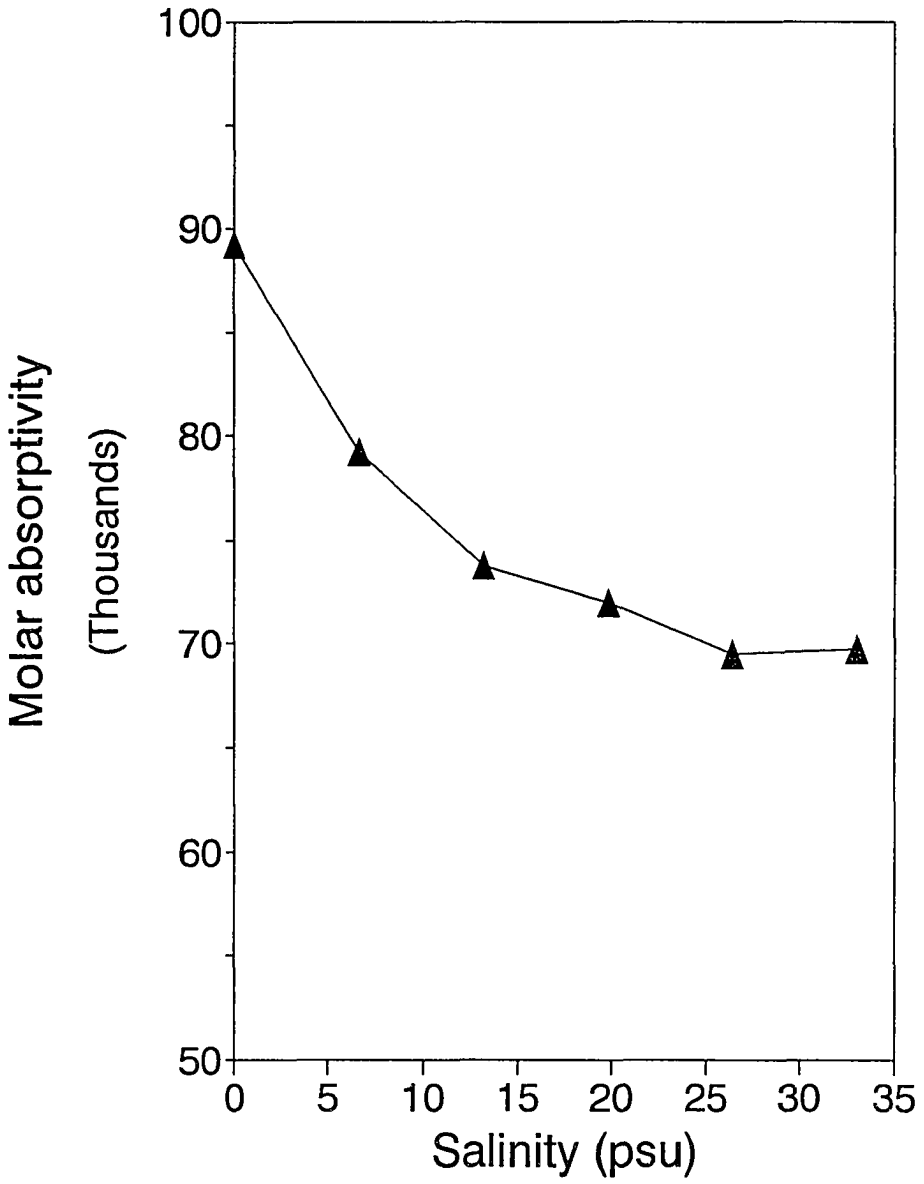


Fig. II-3-6

The variation in the molar absorptivity of crystal violet (CV^+) with salinity. The initial concentration of hydrogen peroxide was 0.4 μM.

Relationship between absorbance and the concentration of hydrogen peroxide

The absorbance of CV^+ was linearly related to the concentration of hydrogen peroxide in both seawater and distilled de-ionized water at concentrations between 0.1 to 0.6 μM (the highest concentration tested), according to the following equations:

in seawater,

$A = 0.66(\pm 0.01)\ [H_2O_2] - 0.024(\pm 0.004)$ r=1.00;

in distilled, de-ionized water,

$A = 0.77(\pm 0.03)\ [H_2O_2] - 0.028(\pm 0.005)$ r=1.00

where the concentration of H_2O_2 is in μM and the pathlength was 10 cm. The relationship between the absorbance of CV^+ and the concentration of hydrogen peroxide in seawater was shown in Fig. II-3-7. This linear range is adequate for the determination of H_2O_2 in most natural waters.

The calibration line did not pass through the origin in both seawater and distilled de-ionized water. Mottola *et al.* (1970) reported similar results and suggested that the negative intercept may be caused by the presence of another reducing species that reduces hydrogen peroxide or the occurrence of a competitive reaction which converts CV^+ to a product with a lower molar absorptivity at 592 nm and which is faster at low concentrations of CV^+. Both suggestions are

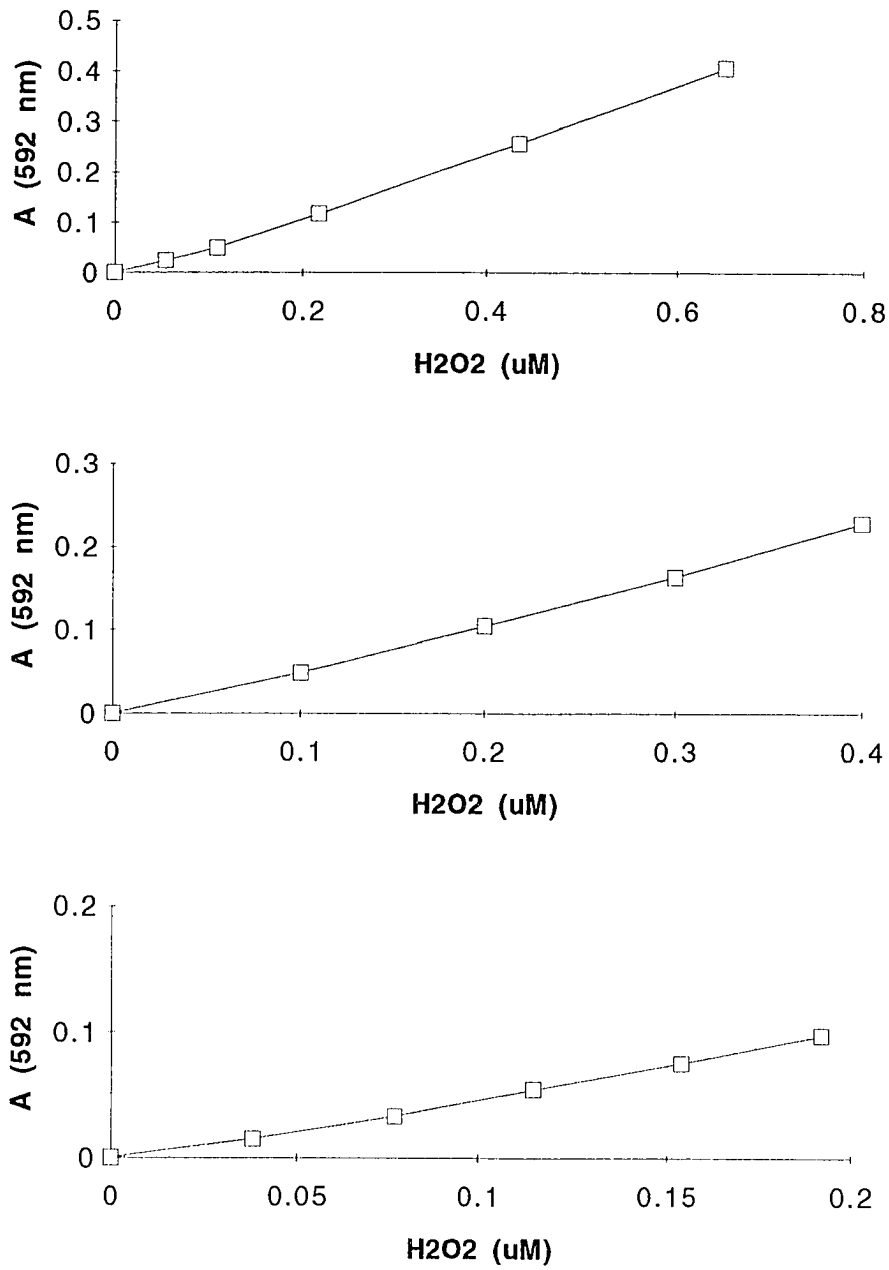


Fig. II-3-7

The calibration lines of LCV-H_2O_2 system.

speculative and not supported by experimental evidence. In this study, the relationship between absorbance of CV^+ and the concentration of H_2O_2 in seawater water at concentrations below 0.2 μM was determined repeatedly. The results indicate that the relationship cannot be represented well by an extension of the linear relationship at the higher concentrations to a non-zero intercept as suggested by Mottola *et al.* (1970). Instead, the relationships fall along well defined and reproducible curves which may be represented as linear lines which pass through the origin between the concentrations of 0 to 0.2 μM of H_2O_2, so that,

<u>in seawater,</u>

$A = 0.56(\pm 0.01)\ [H_2O_2] - 0.010(\pm 0.001)\quad r=1.00.$

Thus, concentrations of H_2O_2 below 0.1 μM may be determined with this method if a proper calibration curve covering this range of concentrations is constructed. The detection limit of the method, corresponding to a sample that may yield an absorbance of 0.01 in a 10 cm cell, is estimated to be about 0.02 μM. Furthermore, the reproducibility of the relationship between absorbance and concentration of H_2O_2 below 0.2 μM suggests that it is unlikely that the non-zero intercept of the linear line at higher concentrations can be explained by the presence of some unknown reducing substance in the sample.

The calibration curve at concentrations of H_2O_2 below 0.2 μM should be constructed with a sample from which the

naturally occurring H_2O_2 has been removed. Two methods have been found to be effective for preparing "H_2O_2-free" natural water. H_2O_2 in natural waters decomposes in the dark with a life-time of hours to several days (Zika *et al.*, 1985a; Cooper and Lean, 1989; Johnson *et al.*, 1989). Thus, "H_2O_2-free" natural water may be prepared by storing it in the dark for at least a week. Alternatively, H_2O_2 in natural waters may be removed by treating it with manganese dioxide. The auto-decomposition of H_2O_2 can be greatly accelerated in the presence of manganese dioxide (Hwang and Dasgupta, 1985). When 500 ml of seawater containing 0.3 μM of hydrogen peroxide was stirred with 0.5 g of manganese dioxide in the powder form, the half life of hydrogen peroxide was found to be about 10 minutes at room temperature. In order to insure the complete removal of H_2O_2, natural waters were stirred with manganese dioxide for two hours in the preparation of "H_2O_2-free" natural waters. The calibration curves prepared with these two kinds of "H_2O_2-free" seawater were identical.

Precision and comparison of the concentrations of H_2O_2 obtained by this method and by the method of fluorometry

A sample of seawater was collected from the lower Chesapeake Bay and stored in the lab under diffuse fluorescence light for nine days. The concentration of hydrogen peroxide in this water was then determined in triplicate by the spectrophotometric method described here and by the fluorometric method (Holm *et al.*,1987) which has been

widely used for the determination of H_2O_2 in natural waters. Then, to one sub-sample of this water, a known concentration of H_2O_2 was added. Another sub-sample was placed under direct sunlight for three hours so that H_2O_2 may be formed by the photo-oxidation of naturally occurring dissolved organic compounds. The concentrations of H_2O_2 in both of these sub-samples were again determined in triplicate by both method. The results are shown in Table II-3-1. The precision of the spectrophotometric method is about ±0.01 to ±0.02 μM which corresponds to about ±7% at a concentration of 0.3 μM. This precision is similar to that of the fluorometric method. In the sub-sample with added H_2O_2, the observed concentration corresponds to 91% of the expected H_2O_2. The difference is within the analytical uncertainties of concentration of the sample and of the standardized H_2O_2 solution. There is also an excellent agreement in the results obtained by the spectrophotometric and the fluorometric methods.

Application to the determination of H_2O_2 in seawater

A sample of seawater was collected in a coastal area of Oceanview, Norfolk, Virginia (0715 am, 6/6/91). After the water was filtered through glass fiber filter paper (1 μm nominal), it was placed under direct sunlight for three hours in the afternoon. The concentration of hydrogen peroxide in the sample was measured with time by the spectrophotometric method. Initially the water contained 0.06 μM of hydrogen peroxide. The concentration of hydrogen peroxide increased

Table II-3-1: The concentration of hydrogen peroxide in seawater determined by two methods (*)

	Seawater	Seawater treated with H_2O_2(**)	Seawater under sunlight
	Concentration of hydrogen peroxide (μM)		
Method I (*)	0.01	0.29	0.27
	0.02	0.29	0.26
	0.02	0.29	0.27
	(Average ± One deviation)		
	0.02±0.01	0.29±0.00	0.27±0.01
Method II(*)	0.03	0.32	0.34
	0.03	0.30	0.33
	0.03	0.31	0.33
		0.32	0.33
	(Average ± One deviation)		
	0.03±0.00	0.31±0.01	0.33±0.01

(*) Method I: the method given in this work.

Method II: the method by Holm *et al.*, 1987.

(**) The added hydrogen peroxide was 0.30 μM.

steadily with the time, reaching a concentration of 0.43 μM after three hours (Fig. II-3-8). This photochemical production of H_2O_2 in natural water is similar to those reported by other investigators (Cooper and Zika, 1983; Johnson *et al.*, 1989).

CONCLUSION

The spectrophotometric method by Mottola *et al.* (1970) was extended for the determination of hydrogen peroxide in seawater. Optimum pH range and optimum amount of horseradish peroxidase were established. Since either the reaction between hydrogen peroxide and leuco crystal violet or the absorbance of crystal violet was affected by seasalt, different calibration lines were needed for samples of different salinity, such as samples collected from an estuary. After hydrogen peroxide reacted with leuco crystal violet at the presence of horseradish peroxidase, the absorbance of the sample was relatively stable within several days. The absorbance could be measured some time later. The detection limit of the method can reach to 0.02 μM.

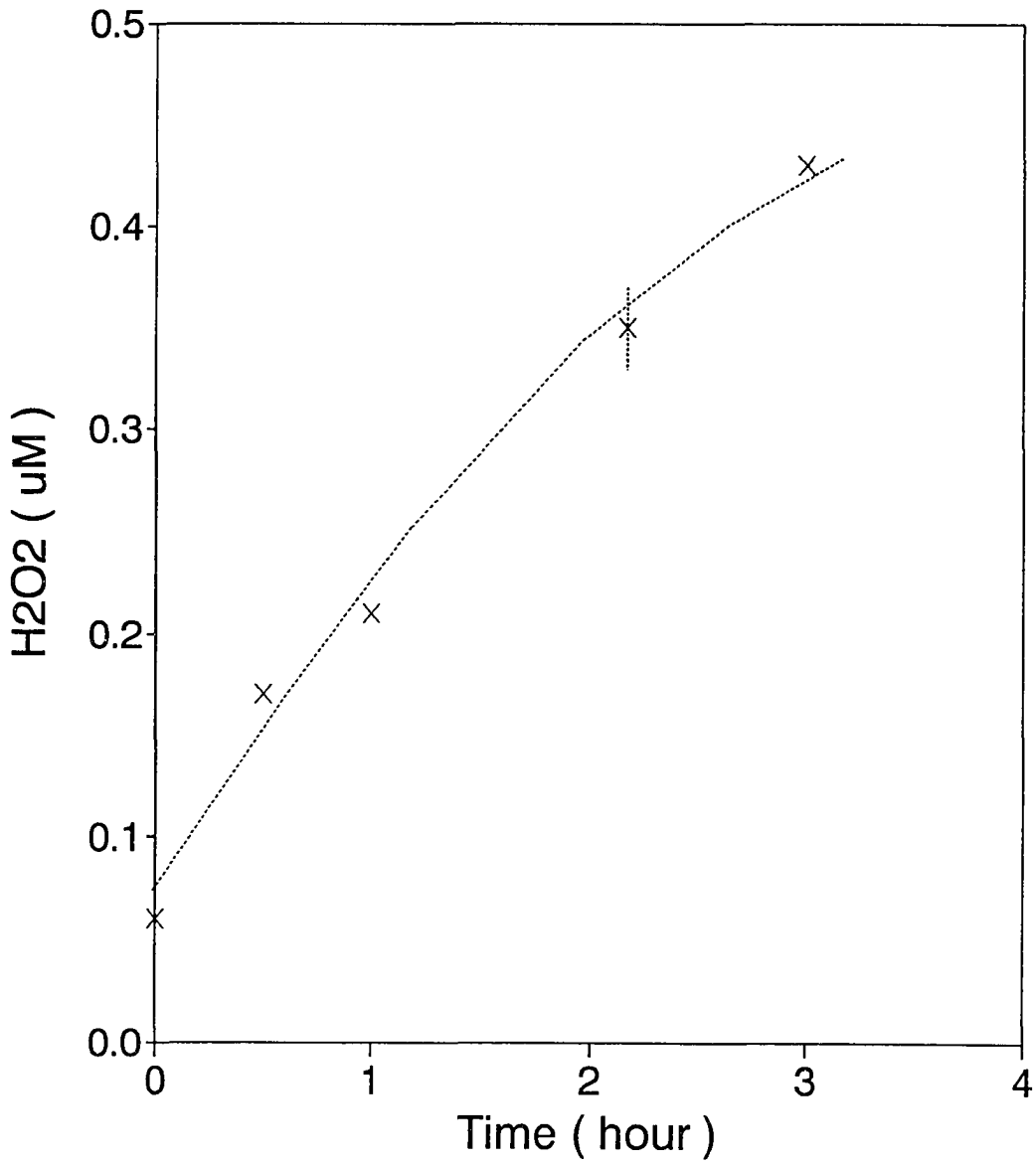


Fig. II-3-8

The concentration of hydrogen peroxide in seawater which was placed under sunlight.

II-4 OPTIMAL CONDITIONS AND SAMPLE STORAGE FOR THE FLUOROMETRIC DETERMINATION OF HYDROGEN PEROXIDE IN SEAWATER WITH HORSERADISH PEROXIDASE AND SCOPOLETIN

ABSTRACT

The optimal conditions for the scopoletin-horseradish peroxidase fluorOmetric method for the determination of hydrogen peroxide in marine waters have been re-examined. The method is based on the quenching of the fluorescence of the added scopoletin which reacts with hydrogen peroxide. While the wavelength of the emission maximum of the residual scopoletin is independent of the pH of the solution, the wavelength of the excitation maximum is pH dependent. It shifts from 390 nm at pH above 7.8 to 345 nm at pH below 5. Thus, the optimal combination of the wavelengths for excitation and emission is pH dependent. Furthermore, at the optimal combination, the fluorescence intensity is pH dependent. It increased by a factor of about 2.4 between pH 7 and 8. Above pH 9, the fluorescence intensity remains relatively constant. However, the precipitation of the hydroxides of the alkaline earth elements in seawater at these

higher pH and the resulting turbidity may become significant. This method may not have been utilized at its peak sensitivity in the presently widely used analytical scheme in which a pH of 7, an excitation wavelength of 365 nm and an emission wavelength of 490 were used. It is recommended that a pH of 8 (i.e., the natural pH of seawater), an excitation wavelength of 390 nm and an emission wavelength of 460 nm be used. In the latter combination, the ratio of quenched fluorescence to concentration of hydrogen peroxide was about 3.4 times higher than the ratio in the former combination. Furthermore, a calibration curve should be constructed by internal standard addition for each sample in order to minimize uncertainties resulted from minor changes in pH.

The presently used analytical scheme also requires that the analyses be completed immediately after sample collection. However, scopoletin is stable in seawater in the presence of horseradish peroxidase for at least four days. Horseradish peroxidase can still catalyze the reaction between hydrogen peroxide and scopoletin at least one day after it has been added to seawater. Thus, after scopoletin and horseradish peroxidase have been added to a sample to let hydrogen peroxide to react with scopoletin, the sample may be stored in the dark at room temperature for at least one day before it is analyzed subsequently by fluorimetry.

INTRODUCTION

The fluorometric scopoletin-horseradish peroxidase (HRP) method has been widely used for the determination of H_2O_2 in natural waters (e.g. Van Baalen and Marler, 1966; Zika *et al.*, 1985a; Kieber and Helz, 1986; Holm *et al.*, 1987; Cooper *et al.*, 1987; Szymczak and Waite, 1988). In this method, the reaction between H_2O_2 and scopoletin is catalyzed by the enzyme HRP. The concentration of H_2O_2 is estimated from the decrease in the fluorescence of scopoletin as it is consumed in the reaction. This method has a superior detection limit which has been reported to be about 2 to 10 nM (Zika *et al.*, 1982; Cooper and Lean, 1989). However, this method also suffers from some serious limitations, one of which is the necessity to analyze the sample immediately after sample collection. Serious errors may result if the sample is stored for more than an hour (Holm *et al.*, 1987; Cooper and Lean, 1989). This restrictive schedule creates severe logistic problems in coordinating the program for sample collection and sample analyses. Furthermore, different investigators who have used this method for measuring H_2O_2 in natural waters have reported slightly different experimental conditions. For example, Andreae (1955) and Perschke and Broda (1961) measured the fluorescence intensity of scopoletin at pH 10. On the other hand, Van Baalen and Marler (1966) used a pH of 8 while Zika *et al.* (1982) and Holm *et al.* (1987) used a pH of 7. Although the importance of pH-buffering was emphasized by Holm *et al.* (1987), the selection of a particular pH was not substantiated

by experimental data.

The necessity for immediate sample analyses upon sample collection is stemmed supposedly from the instability of H_2O_2 in natural waters. If this is the case and if scopoletin is stable, the sample may be stored once the reaction between H_2O_2 and scopoletin is allowed to go to completion. The fluorescence intensity of scopoletin may then be measured at a later time. Indeed, Andreae (1955) indicated that scopoletin in an aqueous solution is stable in diffused light and it is not oxidized by either peroxidase or hydrogen peroxide alone. In this study, this possibility for storing the samples will be explored. Furthermore, the possible associated effects of pH on the excitation and emission wavelengths will also be re-evaluated.

EXPERIMENTAL

Reagents

All chemicals were of ACS reagent-grade. Distilled deionized water was used throughout this work.

Standard solution of H_2O_2 (about 0.01 M): One ml of 30% (w/w) solution of H_2O_2 was diluted to 1000 ml. This solution was standardized iodometrically by using iodate as the primary standard.

Scopoletin (150 μM): Scopoletin (SIGMA, S-2500, 7-Hydroxy-6-methoxy-2H-1-benzopyran-2-one, $C_{10}H_8O_4$, MW=192.2) (15 mg) was dissolved in 500 ml of water. This reagent was stored

in the dark at room temperature and it was stable for at least one year.

Horseradish peroxidase (HRP): Horseradish peroxidase (SIGMA, P-8250, 200 purpurogallin unit/mg) (10 mg) was dissolved in 10 ml of distilled de-ionized water.

Artificial seawater

Artificial seawater was prepared according to the method of Lyman and Fleming (1940). However, the salts of calcium, magnesium, and strontium were substituted with an equimolar amount of the sodium salt in order to avoid the precipitation of the hydroxides of the alkaline earth elements at high pH.

Natural water

Seawater (salinity = 31.0) was collected in the Cobb Island Bay, the Eastern Shore of Virginia (7/1992). Estuarine water (salinity = 23.4) was collected from the lower Chesapeake Bay (2/1993. 37°01.8′ N, 76°08.6′ W). These samples were untreated and were stored in the lab at room temperature.

Apparatus

A Perkin-Elmer Model 650-10S fluorescence spectrophotometer was used for measuring the fluorescence intensity and recording the excitation and emission spectra.

An Orion Model 701A digital ion analyzer was used for measuring pH.

Procedure

Transfer a 50-ml aliquot of the sample to a 100-ml glass bottle. Add 0.25 ml, if the concentration of H_2O_2 in the sample is above 100 nM, or 0.1 ml, if the concentration of H_2O_2 in the sample is below 100 nM, of scopoletin and 0.1 ml of HRP to the sample. Prepare a blank by treating another sub-sample similarly without the addition of HRP. Store them in the dark at room temperature. Within one day, measure the fluorescence of the sample with a 1-cm cell at the following settings: excitation wavelength, 390 nm; excitation slit width, 6 nm when 0.25 ml of scopoletin was used and 10 nm when 0.1 ml of scopoletin was used; emission wavelength, 460 nm; emission slit width, 5 nm; sensitivity, 0.1. Measure the fluorescence of the blank as F1. Add 3 ml of the sample which was treated with scopoletin and HRP to the 1-cm cell, measure the fluorescence as F2. Then spike 0.05 ml of 10 μM hydrogen peroxide to the cell, mix for 20 seconds, measure the fluorescence as F3. Estimate the concentration of H_2O_2 by internal standard additions[1].

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[1]The relationship of fluorescence and concentration of hydrogen peroxide is:

$$\frac{C_{sam}}{F1-F2} = \frac{\frac{C_{std} \times V_{std}}{V_{sam} + V_{std}}}{F2-F3} \quad ;$$

where: Csam: Concentration of hydrogen peroxide in the sample which was treated with scopoletin and HRP. The dilution effect caused by the addition of scopoletin and HRP was omitted;
Vsam: Volume of the sample, 3 ml;
Cstd: Concentration of standard solution of hydrogen peroxide, 10 μM;

RESULTS AND DISCUSSION

The effect of pH on the excitation and emission maximum of scopoletin

The excitation and emission spectra of a 0.1 μM scopoletin in natural and artificial seawater, whose pH has been adjusted to a value between 4 and 10, were recorded between 250 and 750 nm. The excitation spectra were recorded at an emission wavelength of 460 nm while the emission spectra were recorded at excitation wavelengths of 365 nm and 390 nm, respectively. These are the wavelengths that are presently in use (e.g. Holm *et al.*, 1987; Cooper *et al.*, 1987) or found in this work. In all cases, there was a single excitation and a single emission maximum. The wavelength of the excitation maximum was pH-dependent. Shown in Fig. II-4-1 is the result of the wavelength of the excitation maximum of scopoletin in artificial seawater (Above pH 9, precipitates formed in natural seawater). Between pH 7.8 and 10.2, it was at 390 nm. Between pH 7.8 and 5, it decreased rapidly to 345 nm with

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Vstd: Volume of the spiked standard solution, 0.05 ml;
F1: Fluorescence of the blank;
F2: Fluorescence of the sample;
F3: Fluorescence of the sample after the spike of standard solution of hydrogen peroxide.

Then:

$$C_{sam} = \frac{F1-F2}{F2-F3} \times \frac{V_{std}}{V_{sam}+V_{std}} \times C_{std} \quad .$$

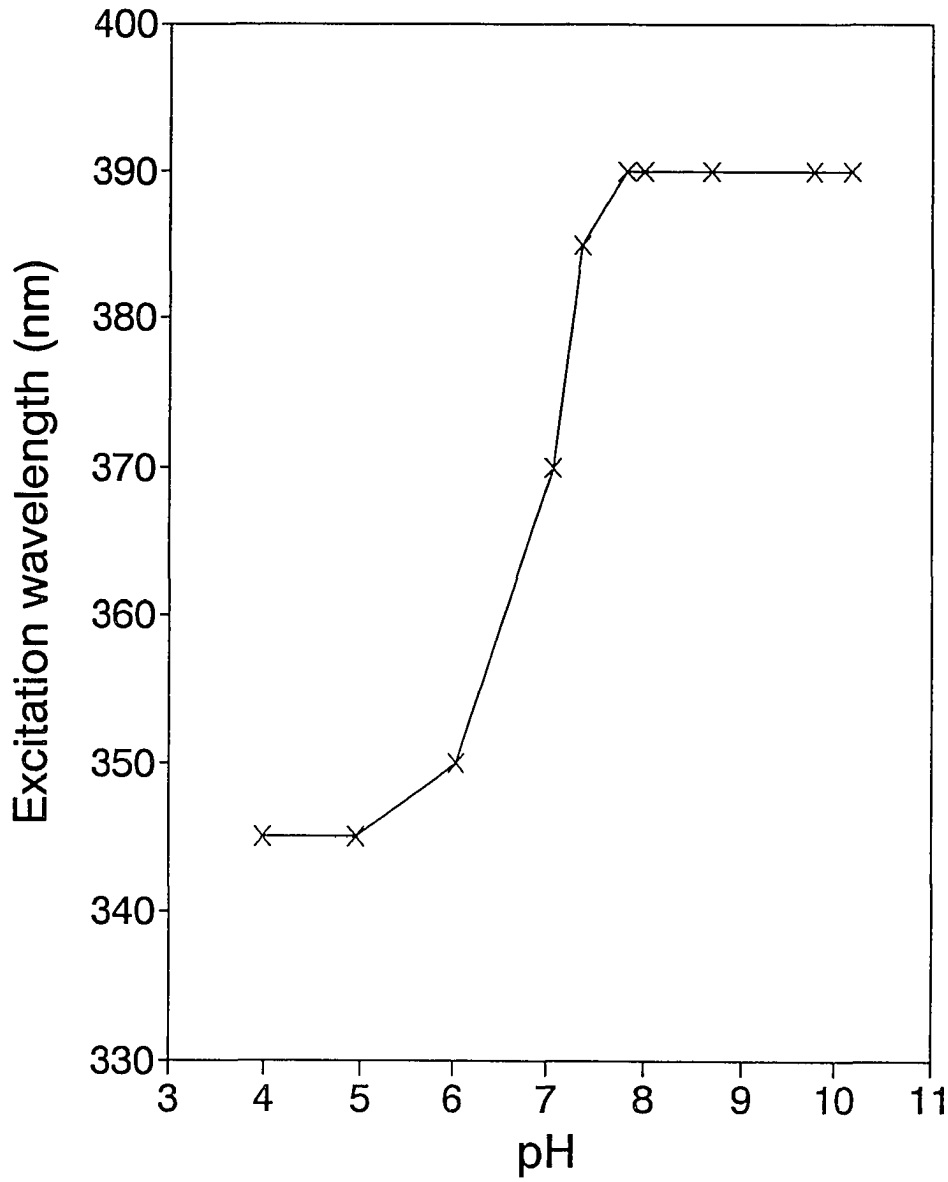

Fig. II-4-1

The wavelength of excitation maximum of scopoletin in artificial seawater at different pH when the wavelength of emission was set at 460 nm.

decreasing pH. Below pH 5, there was no further decrease in this wavelength. Thus, when the fluorescence intensity is measured at pH 7 (e.g. Holm *et al.*, 1987), the results may be sensitive to small changes in pH since the excitation spectrum is most sensitive to changes in pH around this pH value. In contrast to the excitation maximum, the wavelength of the emission maximum was pH-independent. It stayed at 460 nm between pH 4 and 10.2 at both excitation wavelength and in both artificial and natural seawater.

Shown in Fig. II-4-2 is the relationship between pH and the fluorescence intensity of a solution of 0.1 μM scopoletin in artificial seawater, obtained by using the wavelengths of the excitation and emission maximum simultaneously. Between pH 4 and 6, the fluorescence intensity was almost invariant with pH. It increased abruptly by 140% between pH 7 and 8.5. Above pH 9, the increase of fluorescence intensity with increasing pH was relatively small. Thus, a pH of 7, as preferred by Holm *et al.* (1987) and Cooper *et al.* (1987), is definitely not the optimal condition for this method. However, at a pH above 9, precipitation of the hydroxides of the alkaline earth elements in natural waters and especially seawater may occur and give rise to high turbidity. As a compromise, in the proposed procedure, the fluorescence intensity is measured at pH 8 at an excitation wavelength of 390 nm and an emission wavelength of 460 nm. A calibration curve is constructed for each sample by internal standard addition in order to correct for minor variations in pH and/or

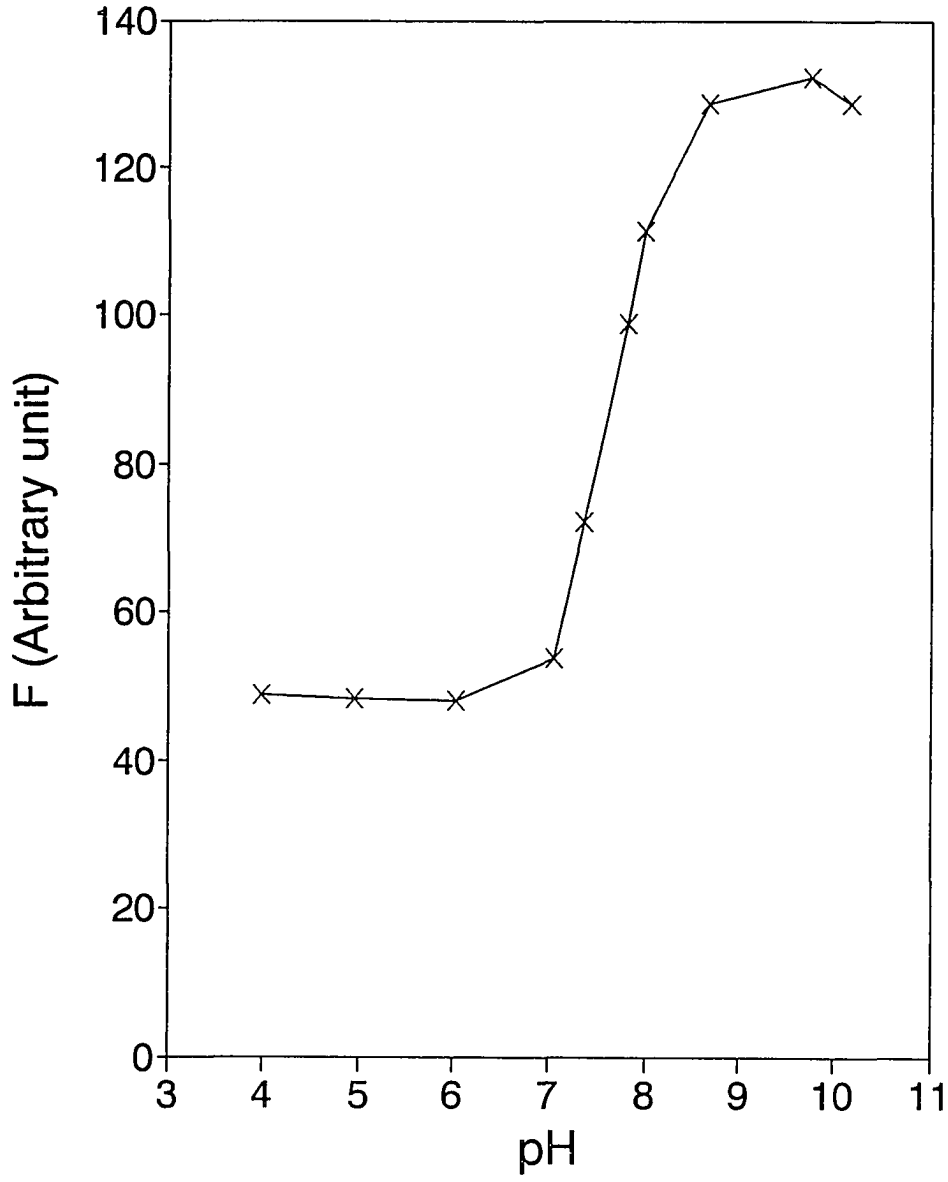

Fig. II-4-2

The fluorescence intensity of scopoletin in artificial seawater at different pH at each corresponding wavelength of excitation maximum (c.f. Fig. II-4-1). The emission wavelength = 460 nm.

variations of the bulk composition of the samples. For seawater, whose pH is about 8, the fluorescence intensity is determined at its natural pH without adding a buffer. The addition of reagents (scopoletin, HRP, and H_2O_2) did not alter the pH of the sample. The detection limit of this method, defined as three times the standard deviation of 5 blank samples, was about 15 nm.

A sample of estuarine water with a salinity of 23.4 psu was collected from the lower Chesapeake Bay in 2/1993. The concentration of hydrogen peroxide in this sample after it had been stored in the dark for three days, upon further addition of 0.30 μM of H_2O_2 and upon exposure to sunlight for three hours were measured by the scopoletin-HRP fluorometric method under the proposed experimental conditions (i.e. a pH of 8, an excitation wavelength of 390 nm, and an emission wavelength of 460 nm) and under those used by Holm *et al.* (1987) (i.e. a pH of 7, an excitation wavelength of 365 nm, and an emission wavelength of 490 nm). The ratio of quenched fluorescence unit to concentration of hydrogen peroxide, expressed as fu/μM, were about 85.0±9.8 fu/μM under the former conditions and about 25.3±2.0 fu/μM under the latter conditions. They differed by 3.4±0.7 times. The measured concentrations of hydrogen peroxide are shown in Table II-4-1. The concentrations obtained in both cases were highly precise with uncertainties of no more than ±0.02 μM. The amount of added H_2O_2 recovered was 107% in both cases. The concentrations obtained by using the former set of experimental conditions

Table II-4-1: Concentration of hydrogen peroxide in estuarine water determined by two methods (*1)

	Estuarine water	Estuarine water treated with H_2O_2(*2)	Estuarine water under sun-light
	Concentration of hydrogen peroxide (μM)		
Method I (*1)	0.02	0.34	0.30
	0.02	0.33	0.30
		0.34	0.31
	Average±one deviation		
	0.02±0.00	0.34±0.01	0.30±0.01
Method II(*2)	0.04	0.37	0.34
	0.04	0.37	0.33
	0.03	0.34	0.33
	Average±one deviation		
	0.04±0.01	0.36±0.02	0.33±0.01

(*1) Method I: the method given in this work.

Method II: the method by Holm *et al.*, 1987.

(*2) The added hydrogen peroxide was 0.30 μM.

were systematically slightly lower, by 0.02 μM, than those obtained by using the latter set of experimental conditions. The difference is small and should be considered negligible when the combined analytical uncertainties of both methods are taken into account.

Stability of scopoletin in natural waters

The fluorescence intensity of the residual scopoletin in samples of seawater containing 0, 0.21, 0.43 or 0.64 μM of added H_2O_2 and 0.75 μM of added scopoletin was followed with time for four days while the samples were stored in the dark at room temperature. There was no detectable trend of decreasing or increasing fluorescence intensity with time at all concentrations of added H_2O_2 (Fig. II-4-3). The variations around the mean were less than 2%. The calibration curve constructed from the fluorescence intensity of the samples at the end of 20 hours of storage indicates that fluorescence intensity is linearly related to the concentration of added H_2O_2 with a correlation coefficient of 0.998 (Fig. II-4-4). Thus, as suggested by Andreae (1955), the data reported here also indicate that scopoletin is stable at room temperature in the presence of HRP for at least 4 days in the dark.

The concentration of H_2O_2 of a sample of seawater (salinity = 23.4 psu, hydrogen peroxide had been added to 0.19 μM) was determined, as proposed in the procedure, after it has been stored for 23 hours. HRP, even 23 hours after it had been added to the sample, could still catalyze the reaction

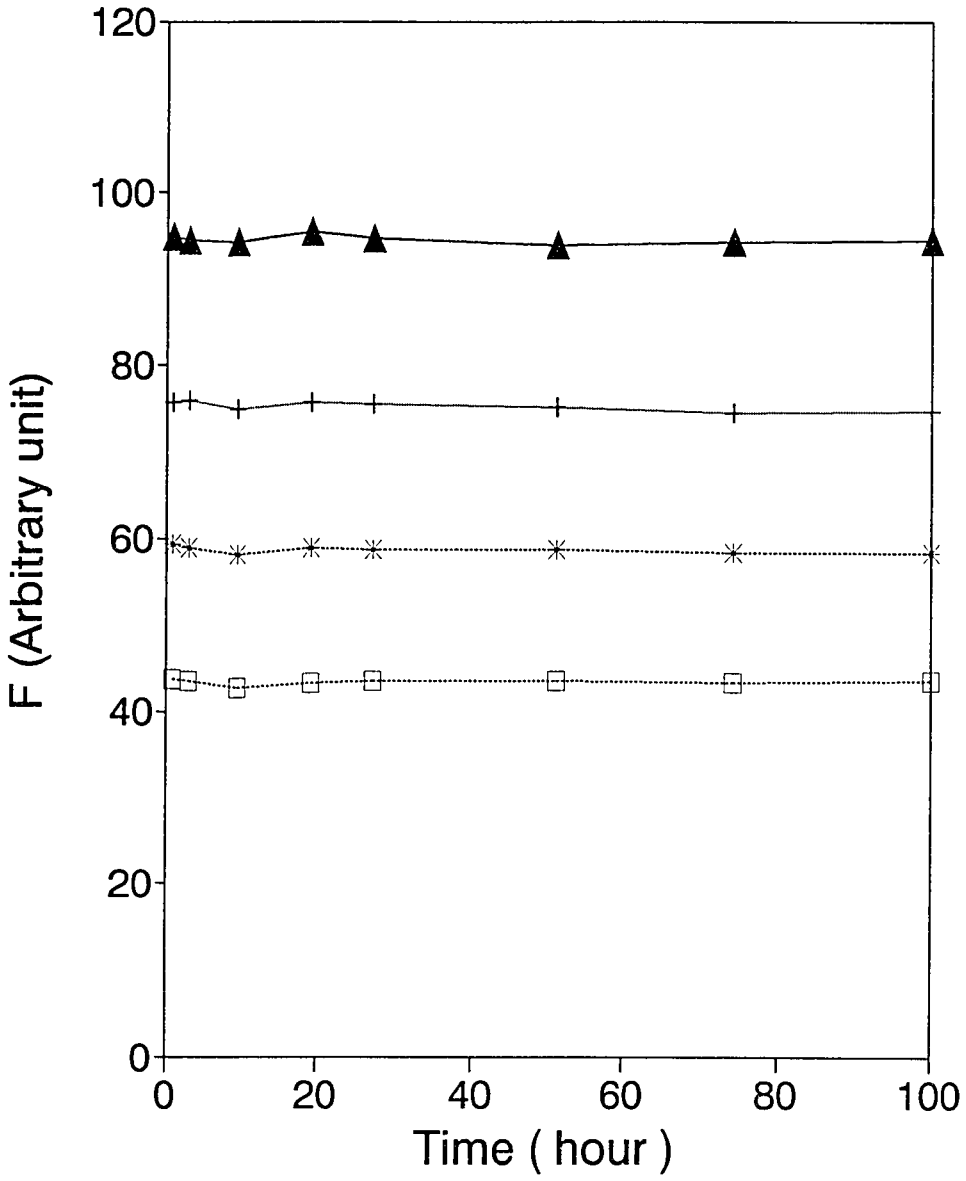

Fig. II-4-3

The fluorescence of residual scopoletin in seawater with time.

Added scopoletin: 0.75 μM.

Spiked H_2O_2 (μM): 0.64 (□); 0.43 (*); 0.21 (+); and 0 μM (▲).

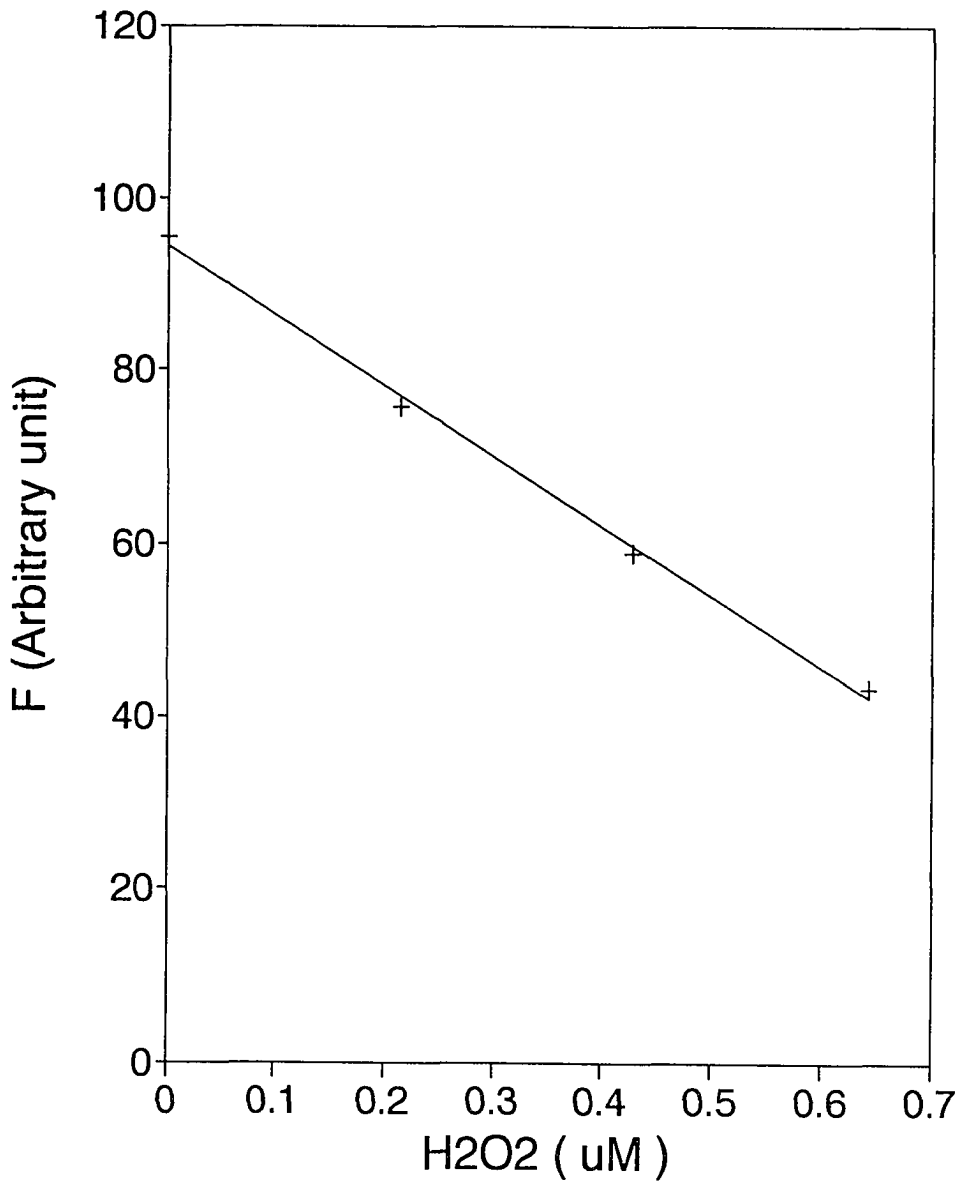

Fig. II-4-4

The calibration line of H_2O_2-Scopoletin-HRP system in seawater.

Added scopoletin: 0.75 μM.

between hydrogen peroxide and scopoletin when a solution of hydrogen peroxide was spiked into the sample. The concentrations of hydrogen peroxide, determined at different times, were indistinguishable from each other and the recovery of added hydrogen peroxide were better than 95% (Table II-4-2). The ratios of quenched fluorescence unit to concentration of hydrogen peroxide were indistinguishable among these samples measured at different times. Thus, samples may be stored in the dark, at least for one day, before they are analyzed by this scopoletin-HRP fluorometric method if the reagents are added immediately after sample collection prior to sample storage.

Table II-4-2: Concentration of hydrogen peroxide in a sample of seawater(*) measured at different times

Measured: immediately	at 12 hours	at 23 hours
Concentration of hydrogen peroxide (μM)		
0.20	0.18	0.19
0.19	0.17	0.17
0.16	0.19	0.17
Average±one deviation		
0.18±0.02	0.18±0.01	0.18±0.01
Ratio of fluorescence intensity to concentration of H_2O_2 (fu/μM)		
84	83	83
83	89	82
85	87	83
Average+/-one deviation		
84±1	86±3	83±0

(*) The seawater had been stored in the dark for 3 months. Hydrogen peroxide was added to 0.19 μM.

CONCLUSION

The scopoletin-HRP method for the determination of hydrogen peroxide in seawater has been re-examined. While the wavelength of emission maximum of scopoletin is independent of pH of seawater, the wavelength of excitation maximum is pH-dependent. Further, the fluorescence intensity of scopoletin is also pH-dependent, not only because the wavelength of excitation maximum is pH-dependent, but also because scopoletin might have different fluorescence intensity at different pH. For a sample of seawater whose pH is about 8, the optimum wavelengths of excitation and emission are 390 and 460 nm, respectively.

In the dark at room temperature, scopoletin is stable in seawater at the presence of HRP at least for four days. HRP can still catalyze the reaction between hydrogen peroxide and scopoletin in seawater even 23 hours after it was added to seawater. Thus, samples may be stored in the dark, at least for one day, before they are analyzed by this scopoletin-HRP fluorometric method if the reagents are added immediately after sample collection prior to sample storage.

CHAPTER THREE

SEASONAL VARIATIONS IN THE SPECIATION OF IODINE IN THE CHESAPEAKE BAY

ABSTRACT

Water samples were collected in the middle and lower Chesapeake Bay in the Spring of 1990, Fall of 1991 and four seasons of 1992 for the determination of iodine species: iodide, iodate, and total dissolved iodine. Significant seasonal and inter-annual variations in the speciation of iodine were observed. In the surface water (the water above 5 meter depth), inorganic iodine (the sum of iodide and iodate) was depleted mainly in the Spring, probably being converted to organic iodine. Between the Winter and the Fall, the concentration of iodate decreased but that of iodide increased, suggesting the reduction of iodate to iodide. In the deep water of the middle bay (the water below 17 meter depth), the concentration of inorganic iodine in the Summer was higher than its concentration in the other three seasons, indicating that there was a source of iodine to the deep water. The source of iodine was in the form of iodide. Between the Winter and the Fall, iodate was reduced. The

seasonal variations in the speciation of iodine were different in the surface water and in the deep water.

The Chesapeake Bay is a place where iodate was reduced to iodide and iodide was transported out to the ocean. This transported iodide might be substantial to the distribution of iodide in coastal waters.

III-1 INTRODUCTION

Iodine is a bio-intermediate redox-sensitive minor element in the oceans (Wong and Brewer, 1974; Elderfield and Truesdale, 1980; Jickells *et al.*, 1988; Wong, 1991). The concentration of total dissolved iodine in seawater is about 0.45 μM (Barkley and Thompson, 1960; Tsunogai, 1971) and the concentration in the surface waters is frequently slightly lower than that in the deep waters. Dissolved iodine is found primarily in the inorganic form as iodide and iodate. In the surface oceans, the concentrations of iodide and iodate range from 0.1 to 0.2 μM and 0.3 to 0.4 μM respectively (Barkley and Thompson, 1960; Tsunogai and Henmi, 1971). In the oxic deep oceans, in most cases, iodate is the only detectable form of inorganic iodine (Tsunogai, 1971). However, the speciation of iodine does change in response to changes in the prevailing redox condition. Thus, in anoxic basins, iodide becomes the only detectable form of inorganic iodine in the anoxic deep water (Wong and Brewer, 1977; Emerson *et al.*, 1979; Wong *et al.*, 1985; Chapman, 1983; Luther *et al.*, 1991). Organic iodine has also been found in seawater. In the open oceans, its concentration is usually less than 5% of that of dissolved inorganic iodine (Truesdale, 1975; Wong *et al.*, 1976; Jickells *et al.*, 1990). In coastal and estuarine waters, higher concentrations have been found. Luther *et al.* (1991) reported that organic iodine may constitute up to 70% of total dissolved iodine in some samples collected from the Chesapeake Bay.

The reduction of iodate to iodide in oxic seawater is an endothermic reaction. If an equilibrium is reached, the concentration ratio of iodate to iodide has been estimated to be $10^{13.5}$ (Sillen, 1961; Wong, 1980). Thus, the occurrence of iodide in surface seawater has been widely explained by the biologically mediated reduction of iodate (Tsunogai and Sase, 1969; Tsunogai and Henmi, 1971; Elderfield and Truesdale, 1980). Truesdale (1978) suggested the possibility of the reduction of iodate by terrestrial reducing substances in the coastal seas. A number of investigators have found high concentrations of iodide in river water (Smith and Butler, 1979, 1990; Butler and Smith, 1985; Luther and Cole, 1988; Ullman *et al.*, 1988; Rebello *et al.*, 1990). Wong and Zhang (1992c) also found high concentrations of iodide in the inner shelf of the South Atlantic Bight. Wong and Zhang (1991) suggested that the transport of coastal waters into the ocean interior may also be a source of iodide in the surface open oceans.

If the occurrence of iodide is controlled by the biologically mediated reduction of iodate, the speciation of iodine may vary as the level of biological activities varies from season to season (Mairh *et al.*, 1989). There are few systematic studies on the seasonal variations in the speciation of iodine. The limited data that have been reported seem to result in contrasting conclusions. Truesdale (1978), on the one hand, reported that there is no seasonal variation in the speciation of iodine in the Eastern Atlantic

Ocean, the North Channel of the Irish Sea, and the Menai Strait, although seasonal variations in the concentration of nutrients were observed. Jickells *et al.* (1988), on the other hand, found seasonal variations in the speciation of dissolved iodine in the Sargasso Sea and waters around Bermuda.

Chesapeake Bay is a productive estuary whose deep water may undergo seasonal hypoxia. The speciation of iodine in this bay in the summer has been reported previously (Luther and Cole, 1988; Ullman *et al.*, 1988; Luther *et al.*, 1991). Thus, it would be a logical location for further exploring how the iodine system may respond to seasonal changes in biological activity in the oxic surface waters and to the seasonal depletion of oxygen in the deep water.

III-2 STUDY AREA, SAMPLING AND ANALYTICAL METHODS

Study area

Chesapeake Bay (Fig. III-2-1) is a drowned river valley. It is the largest estuary in north America stretching from 39°40'N to 36°55'N and draining a basin of 166,200 km^2 (Pelczar, 1972). A number of rivers empty into the bay which, in turn, drains into the Atlantic Ocean. The major rivers are the Susquenhanna, the Potomac and the James which contribute 49, 18 and 16% of the annual freshwater inflow respectively. The remaining rivers contribute less than 5% of the freshwater inflow individually. The volume of the bay at low tide is 50 km^3 for the bay proper and 74 km^3 if the rivers are also

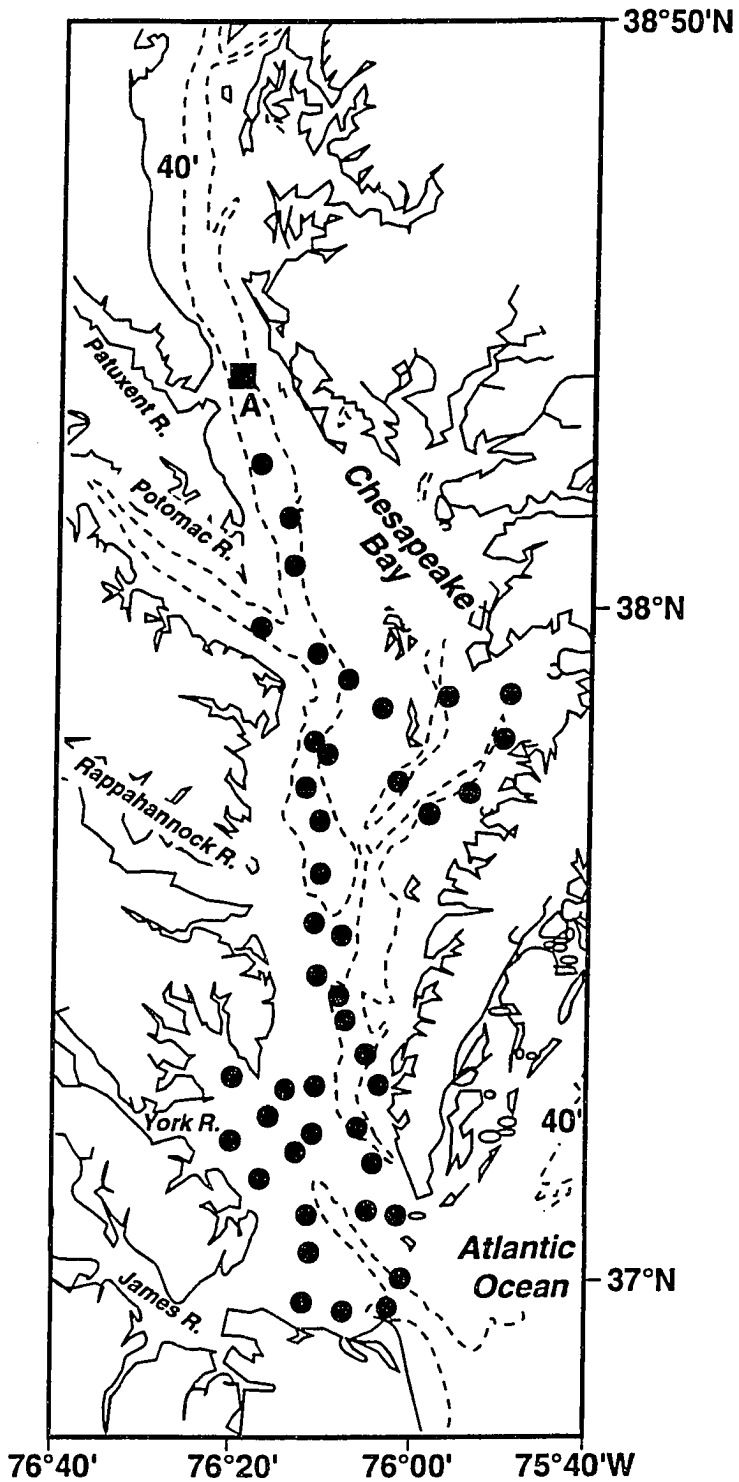

Fig. III-2-1
Map of the Chesapeake Bay with sample stations. Depth samples were collected at St. A. The dotted line is a 40-foot (about 10-meter) contour.

included (Pritchard, 1952; Cronin, 1971). Thus, with an average inflow of freshwater of 0.21 km^3 per day (National Estuarine Inventory, 1985), the residence time of the water in the bay, including the rivers, is about one year.

The bathymmetry of the bay (Hires *et al.*, 1963; Goldsmith and Sutton, 1977) indicates that the entire length of the bay may communicate freely with the Atlantic Ocean above 10 m (Fig. III-2-1). The water is well oxygenated year round and there is significant seasonal variations in its productivity (Taft *et al.*, 1980). Below about 13 m, the deep basin, which stretches from 37°30'N to 39°05'N, is enclosed, being separated from the Atlantic Ocean by a sill. The greatest depth within this basin is about 50 m. As a result of the restricted flushing, it has been well documented that the deep Chesapeake Bay may become depleted in oxygen annually in the Summer (Newcombe and Horne, 1938; Newcombe *et al.*, 1939; Taft *et al.*, 1976; Officer *et al.*, 1984).

The study area (Fig. III-2-1) covers roughly the southern half of the Bay south of the mouth of the Patuxent River at about 38°25'N. The major rivers that drain into this area are the Patuxent, the Potomac, the Rappahannock, the York and the James. About two thirds of the deep basin of Chesapeake Bay, where the oxygen depleted deep water may be found in the Summer, are situated in the northern half of the study area. In the rest of the study area, south of about 37°30'N, the ratio of the tidal volume to the volume at mean low tide is about 7 to 11% (Cronin, 1971). Thus, its composition will be

greatly affected by tidal exchanges with the incoming water from the Atlantic Ocean.

Sampling

Samples were collected from the southern Chesapeake Bay on board R/V Linwood Holton during the Spring (May) of 1990, the Fall (October) of 1991 and all four seasons (January, April/June, July/August and October) of 1992. Surface waters were collected throughout the entire study area with a polyethylene bucket. Discrete samples were collected with depth with NIO (National Institute of Oceanography) bottles or with a submersible pump at the deep seasonally hypoxic basin of Chesapeake Bay during the four seasons in 1992 and during the Spring of 1990. At other selected locations, samples were also collected with depth during some of the seasons. The locations of the stations are listed in Appendix A and shown in Fig. III-2-1. Sub-samples were drawn and stored unfiltered and frozen at -20°c in polyethylene bottles for the determination of iodide, iodate and total dissolved iodine (Wong, 1973). Other sub-samples were collected for the determination of salinity and oxygen. Temperature and salinity profiles were also recorded at selected stations with a Seabird CTD system.

Analytical methods

Iodide was determined directly by cathodic stripping square wave voltammetry (Luther *et al.*, 1988; Wong and Zhang

1992a; 1992b). The precision of the method was typically ±5% or better. Iodate was determined directly by differential pulse polarography (Herring and Liss, 1974; Wong and Zhang 1992a). The detection limit was about 30 nM and the precision was ±8% at 75 nM. Total dissolved iodine was determined in selected samples as iodate by differential pulse polarography after iodide and some fraction of organic iodine had been oxidized to iodate (Takayanagi and Wong, 1986; Luther *et al.*, 1991). The precision was about ±5%. All these measurements were made with an EG&G PARC Model 384b-4 voltammetric analyzer system. The details of these procedures are given in Appendix B.

Salinity was measured with a Minisal Model 2100 salinometer. Dissolved oxygen was measured in selected samples with the Winkler titrimetric method (Strickland and Parsons, 1972).

III-3 RESULTS AND DISCUSSION

The deep Chesapeake Bay

The Winter season

Shown in Fig. III-3-1 are the distribution of salinity, temperature, density (σ_t), iodate, iodide, iodate/iodide, inorganic iodine (the sum of iodate and iodide), specific iodate, specific iodide, and specific inorganic iodine in the seasonally hypoxic deep Chesapeake Bay in the Winter (February 3) of 1992 (The raw data, as well as the raw data of all other

seasons, are listed in Appendix A). Specific inorganic iodine is the ratio of the sum of the concentration of iodate and iodide to salinity. Specific iodate and specific iodide are the ratio of the concentration of iodate and iodide, respectively, to salinity. The deviation is about ±0.5 nM/psu in specific iodate and specific iodide and about ±0.7 nM/psu in specific inorganic iodine. The variations in the concentration of iodine species caused by the salinity change which can be very significant in estuarine waters has been corrected in specific iodine species. The cartoons describing the dynamics of the iodine system in the Winter season is shown in Fig. III-3-2.

In the Winter of 1992 (Fig. III-3-1, Fig. III-3-2), the water column was rather well mixed down to about 20 m with the density varying within 0.3 σ_t unit. The density gradient between 25 and 30 m was 0.2 σ_t/m, slightly higher than that above 20 m depth. Even then, the difference in density between the surface and bottom water, about 2 σ_t units, was the smallest among all the seasons. The density difference was maintained solely by a salinity gradient since the surface water was actually colder than the bottom water. The entire water column was well oxygenated. The concentration of oxygen in the bottom water was 344 μM. Specific inorganic iodine was also rather uniformly distributed, varying within a narrow range of about 10 to 12 nM/psu with an average of 11 nM/psu. The primary source of dissolved iodine to an estuary is most likely the intrusion of seawater since the concentration of

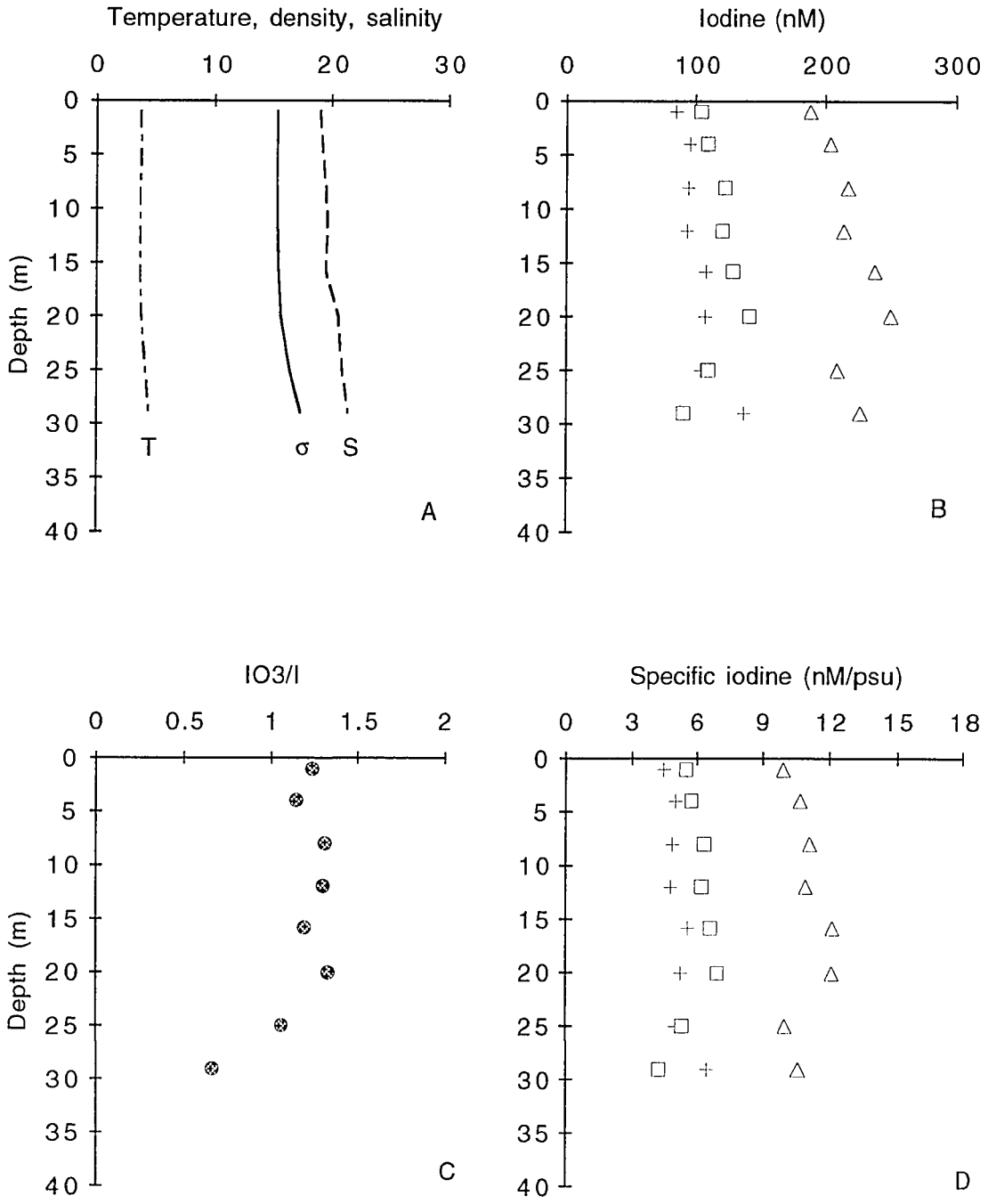

Fig. III-3-1 Result of February 1992.
A: T: temperature (°C); σ: density (σ_t) and S: salinity (psu)
B: Concentration of iodine (nM).
Iodide (+); Iodate (□) and inorganic iodine (△).
C: Ratio of iodate to iodide.
D: Specific iodine species.
Iodide (+); Iodate (□) and inorganic iodine (△).

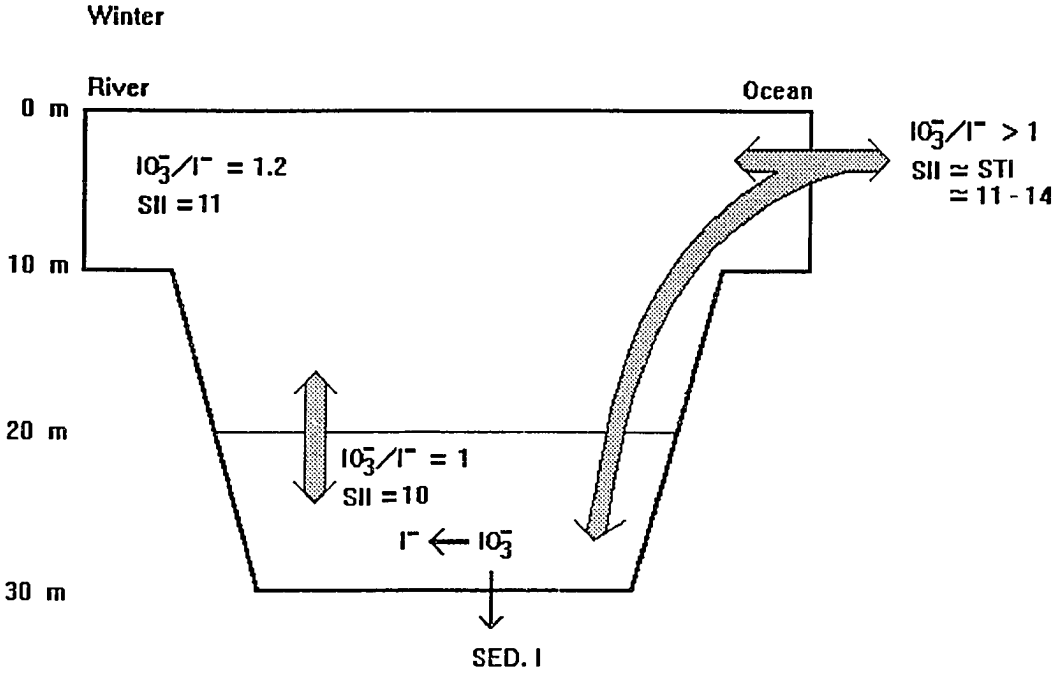

Fig. III-3-2
Behavior of iodine in the Winter. SII = specific inorganic iodine; STI = specific total dissolved iodine; dotted arrow: exchange of water.

iodine in river water is rather low (Luther *et al.*, 1991; Wong, 1991). Although the composition of the incoming Atlantic surface water was not determined, specific inorganic iodine in the surface Atlantic has been reported to be mostly in the range of 11 to 14 nM/psu (Elderfield and Truesdale, 1980; Jickells *et al.*, 1988). Luther and Cole (1988) and Luther *et al.* (1991) reported values of 12.5 to 14 nM/psu in surface waters around the mouth of Chesapeake Bay. Furthermore, since organic iodine in the surface open oceans constitutes no more than 5% of total dissolved iodine (Truesdale, 1975), specific inorganic iodine and specific total dissolved iodine (Similarly, specific total dissolved iodine is the ratio of the concentration of total dissolved iodine to salinity) in the incoming Atlantic water were probably similar to each other. Specific inorganic iodine in Chesapeake Bay in the Winter of 1992 was thus at most slightly lower than the specific inorganic and specific total dissolved iodine in the incoming oceanic water (Fig. III-3-2). This suggests, that, at the reduced level of biological activity in the Winter, if there was conversion of inorganic iodine into the organic and/or the particulate form, it was a minor process that could not materially decrease the specific inorganic iodine in the Bay. Furthermore, if organic iodine was present, its concentration would have been relatively low. Nonetheless, on a finer scale, the lowest specific inorganic iodine, 9.9 nM/psu, was found in the surface water and it did increase with depth to a maximum of 12.1 nM/psu at 16 to 20 m

suggesting that there might have been some, albeit quantitatively small, conversion of inorganic iodine to a particulate or organic form in the surface water. Below 20 m, specific inorganic iodine decreased from 12 to about 10 nM/psu suggesting a removal of inorganic iodine in these bottom waters.

Changes in the concentration of iodate and iodide with depth were more dramatic (Fig. III-3-1). Iodate was found throughout the water column. In fact, it was the dominant form of inorganic iodine for most of the water column. The ratio of iodate to iodide ranged between 1 and 1.3 down to 25 m. In contrast, Luther and Cole (1988) and Luther *et al.* (1991) reported that iodate was absent in the entire water column at the same vicinity in the Summer of 1986 and 1987. A better mixed, better oxygenated water column and a lower level of biological activity in the Winter might have prevented the complete biologically mediated and/or chemical reduction of iodate to iodide in the Winter. The concentration of iodate increased from 100 to 140 nM while that of iodide increased from 84 to 107 nM from the surface to about 20 m. In the bottom waters below 20 m, the concentration of iodate decreased abruptly to 90 nM at 30 m while that of iodide increased to 137 nM. Thus, between 20 and 30 m, while specific inorganic iodine and specific iodate decreased by 2 and 3 nM/psu respectively, specific iodide increased only by 1 nM/psu. The change in specific inorganic iodine was not large enough to explain the change in specific

iodate. This implies that there must be an *in situ* reduction of iodate to iodide. However, since the change in specific iodate was much larger than the change in specific iodide, there must also be a removal of iodate from the stratified bottom water. Biologically mediated reduction of iodate to iodide by phytoplankton and bacteria has been suggested for the production of iodide in the surface oceans (Tsunogai and Sase, 1969; Butler *et al.*, 1981). In the bottom water of the deep Chesapeake Bay, a reduction mediated by phytoplankton is unlikely since the sunlight cannot reach such depths. A bacterially mediated reduction is possible. However, since the water column was relatively well mixed and well oxygenated, this mechanism would imply the presence of a special population of bacteria that selectively operates in the bottom waters only. Furthermore, these bacteria must utilize iodate, a less energy efficient oxidant relative to oxygen, even in the presence of an abundance of oxygen. A more likely mechanism may be the chemical reduction of iodate by reducing species supplied from the underlying sediments by diffusion and/or other biological and physical processes as suggested by Luther *et al.* (1991). As to the removal of iodate, Francois (1987) suggested that, under oxidizing conditions, iodate may be reduced by humic materials at the sediment-water interface to an electrophilic I species which may then react with sedimentary organic matter and be incorporated into the particulate phase. This is a plausible mechanism for explaining the removal of iodate from the

oxygenated bottom water.

The Spring season

The distribution of various items, as in the case of the Winter season, are shown in Fig. III-3-3. In this season, total dissolved iodine was also determined. The dynamics of the iodine system is shown in Fig. III-3-4. In the late Spring/early Summer (June 8) of 1992, the water column was stratified into two layers. The surface water was well mixed down to only about 8 m. There was a sharp pycnocline between 8 and 13 m where the density increased by about 1 σ_t/m. The difference in density between surface and bottom water was over 7 σ_t units. Below 13 m, the temperature and salinity were again rather uniform with depth. Dissolved oxygen was present throughout the water column but at diminished concentrations relative to the preceding Winter. The concentration of oxygen in the bottom water was only around 100 μM. The distribution of specific inorganic iodine was also separated into two layers: about 7.5 nM/psu above 10 m and about 10 nM/psu at greater depths. With the analytical method used, total dissolved iodine includes not only iodide and iodate but also any organic iodine that may be oxidized to iodate by hypochlorite (Luther *et al.*, 1991). Specific total dissolved iodine decreased with depth from a maximum of 12.5 nM/psu at the surface to an approximately uniform value of 10 nM/psu below 10 m. Thus, specific total dissolved iodine was significantly higher than specific inorganic iodine in the

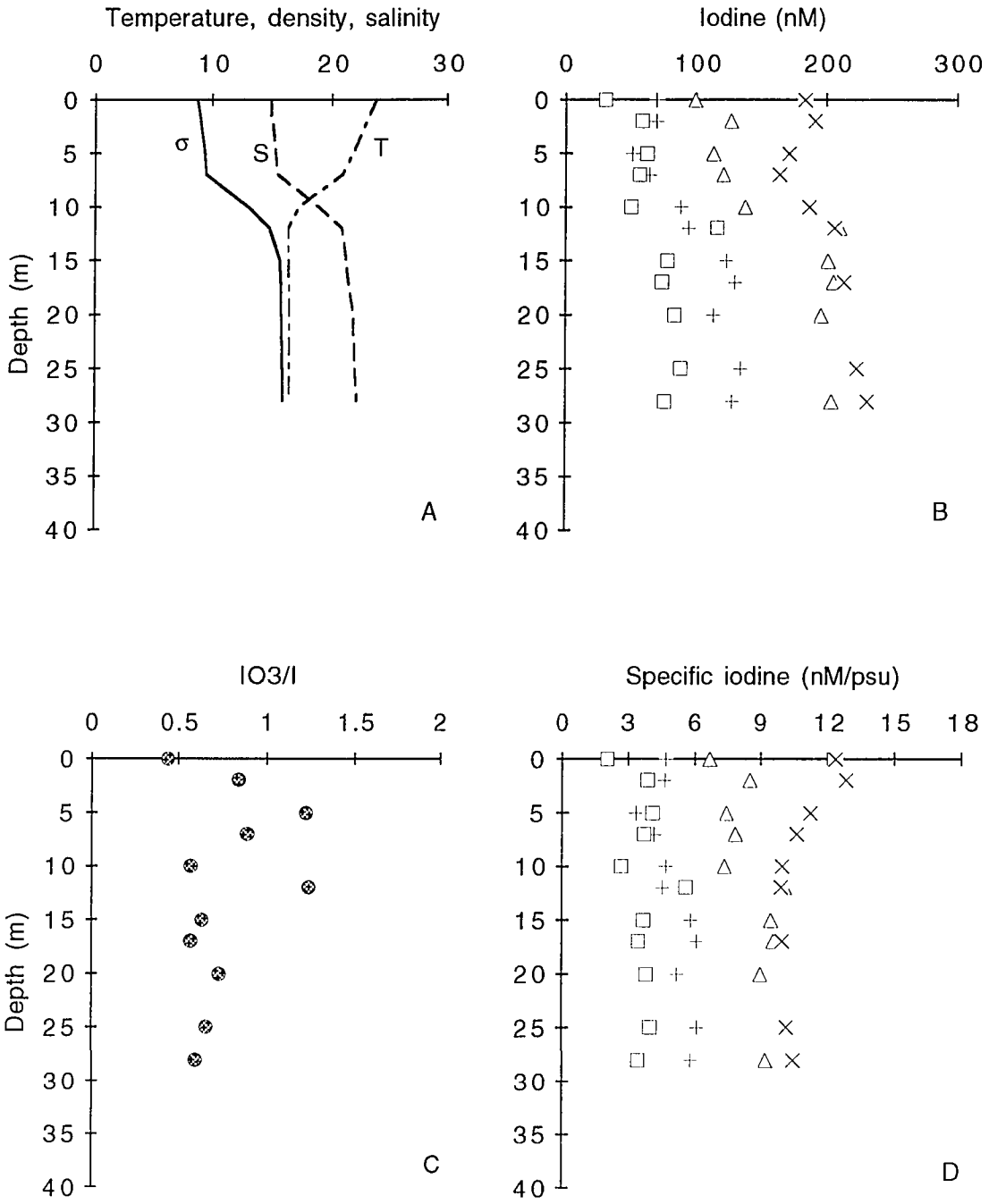

Fig. III-3-3 Result of June 1992.
A: T: temperature (°C); σ: density (σ_t) and S: salinity (psu)
B: Concentration of iodine (nM). Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).
C: Ratio of iodate to iodide.
D: Specific iodine species. Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).

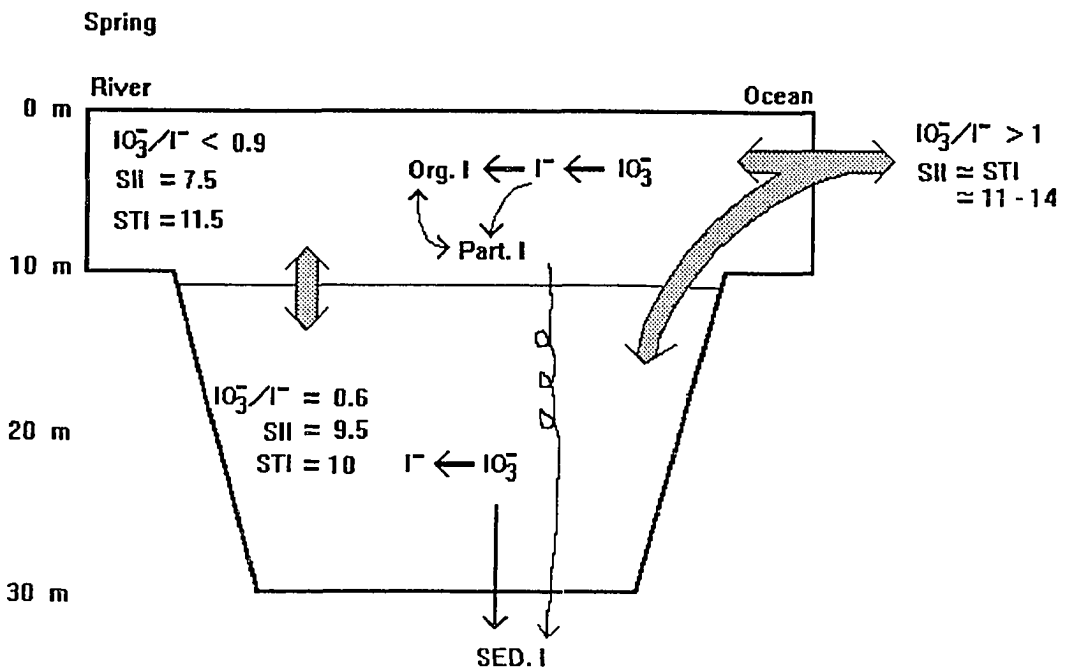

Fig. III-3-4
Behavior of iodine in the Spring. SII = specific inorganic iodine; STI = specific total dissolved iodine; dotted arrow: exchange of water.

surface mixed layer while they were indistinguishable from each other within their analytical uncertainties in the deep layer. If the difference between specific total dissolved iodine and specific inorganic iodine is taken as "organic" iodine (Luther *et al.*, 1991), about a third of the dissolved iodine in the surface layer would have existed as "organic" iodine. There was also a characteristic vertical structure in the distribution of "organic" iodine. The concentration of "organic" iodine was the highest in the surface waters with a maximum of 6 nM/psu at the surface. It decreased with depth and became negligible, <1 nM/psu, in the deep water. Luther *et al.* (1991) reported that up to 70% of total dissolved iodine in the surface waters of Chesapeake Bay in the Summer of 1987 existed as "organic" iodine. The data reported here are well within this range of reported values. The depletion of specific inorganic iodine in the surface layer may be explained by the conversion of inorganic iodine either to an "organic" and/or a particulate form. The excess in specific total dissolved iodine in the surface layer is not consistent with a conversion of dissolved iodine to the particulate form. Thus, the former mechanism seems to be the more likely explanation. Relative to the preceding Winter, specific inorganic iodine decreased from 11 to 7.5 nM/psu in the surface water while it stayed at about the same level in the deep water. Furthermore, specific inorganic iodine in the deep water in the Winter was similar to specific total dissolved iodine in the Spring. These observations are

consistent with the possibility that the water in the deep Chesapeake Bay did not change significantly in specific total dissolved iodine from the Winter to Spring and that there was relatively little "organic" iodine in the Winter so that specific total dissolved iodine in the Spring was similar to specific inorganic iodine in the Winter. However, in the surface waters in the Spring, a significant fraction of inorganic iodine was converted to "organic" iodine. As a result, specific inorganic iodine decreased from the Winter to the Spring. The excess in specific total dissolved iodine in the surface water in the Spring also suggests that there may be a source of "organic" iodine in the surface water and/or a sink, possibly a removal to the sediments, of dissolved iodine in the deep water. A possible source of the "organic" iodine may be the remineralization of organic particles, formed during the Spring bloom, that are washed into the Bay through the rivers during the high flow period in the Spring. The removal of iodine to the sediments under an oxidizing environment is also possible as discussed previously. Neither possibilities may be discarded at this point.

Iodate was again found in the entire water column in late Spring of 1992 (Fig. III-3-3). However, the concentrations, ranged from 30 to 120 nM, were lower than those found in the preceding winter. In the surface layer, iodate/iodide was more variable, varying between 0.4 and 1.2. In the deep layer, it was more uniform, ranging between 0.6 and 0.7. Thus, in contrast to the situation in the Winter, iodide was

the dominant form of inorganic iodine at most depths. The concentrations of both iodate and iodide were higher in the deep layer than in the surface layer. The changes in the concentration of iodate may be explained largely by changes in salinity since specific iodate hovered around 3.5 to 4 nM/psu at most depths. In contrast, specific iodide increased from about 4.5 nM/psu in the surface layer to 6 nM/psu in the deep layer. A logical sink for iodide in the surface waters would be its conversion to "organic" iodine. Thus, iodide, rather than iodate, was a partial source of "organic" iodine in the surface waters (Fig. III-3-4).

In some respects, the hydrographic conditions in the Spring (May 18) of 1990 (Fig. III-3-5) and the late Spring (June 8) of 1992 (Fig. III-3-3) were quite similar. While the water was cooler throughout the water column and the surface water was fresher in 1990, the difference in salinity and density between the surface and bottom water were about the same in both years. However, the distribution of oxygen was drastically different. While oxygen was present in the entire water column in 1992, in 1990, abundant oxygen was found only in the surface mixed layer within the top 7 m and it became undetectable below 15 m. Thus, in 1990, even though the samples were collected earlier on in the season and from a cooler water column, the deep Chesapeake Bay was actually more reducing than in 1992. The general distribution of specific inorganic iodine and specific total dissolved iodine were similar in both years. There was again a two-layered system

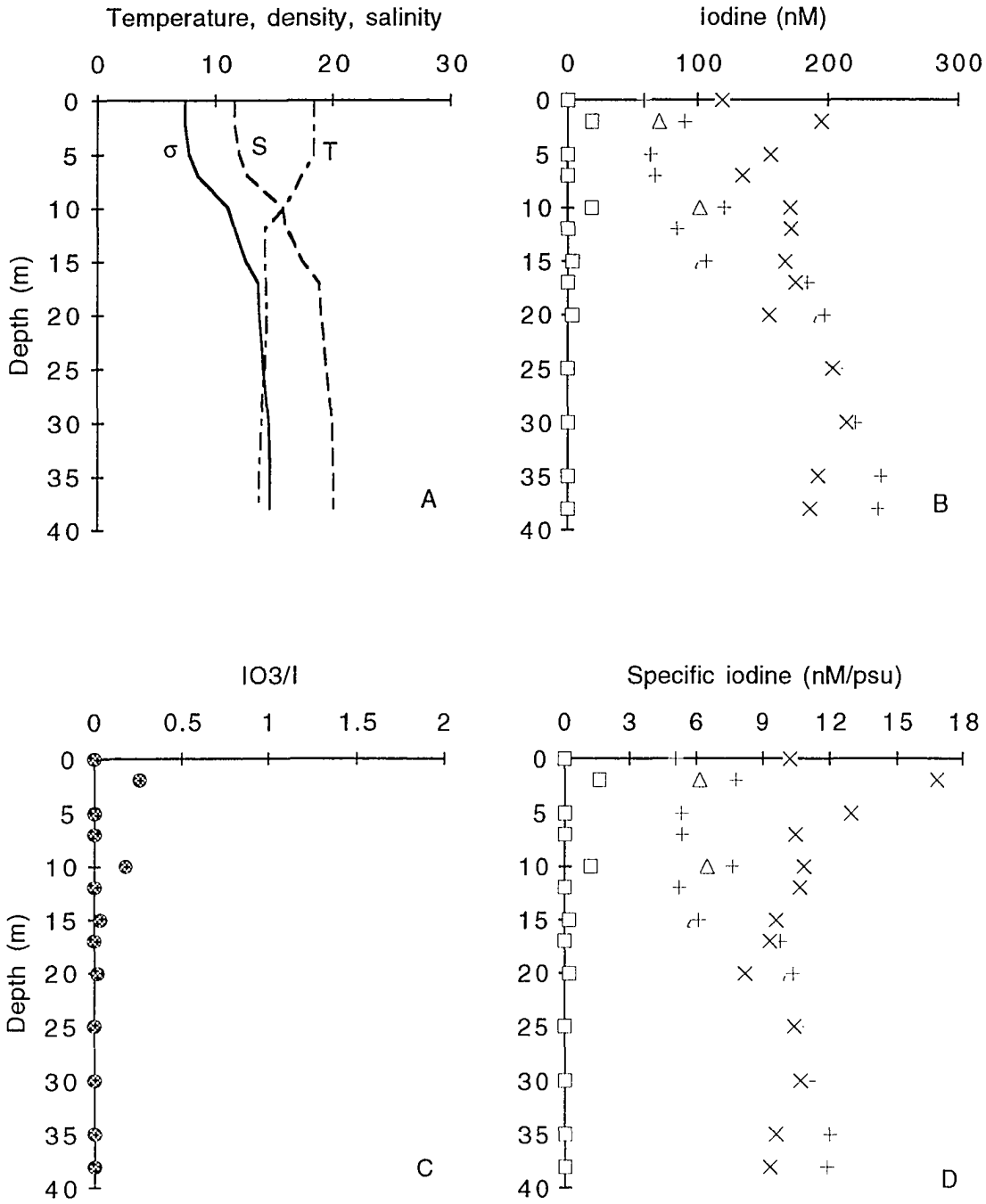

Fig. III-3-5 Result of May 1990.
A: T: temperature (°C); σ: density (σ_t) and S: salinity (psu)
B: Concentration of iodine (nM). Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).
C: Ratio of iodate to iodide.
D: Specific iodine species. Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).

separated by a pycnocline situated between 5 and 17 m. Specific inorganic iodine was lower in the top 15 m, at about 6 nM/psu, than in the deep layer, at about 11 nM/psu. Total dissolved iodine was also determined in 1990. Again, higher values, reaching a maximum of 17 nM/psu, were found in the top 5 m and it decreased to an approximately uniform value of 10 nM/psu at greater depths[1]. Thus, specific total dissolved iodine was again significantly higher than specific inorganic iodine in the surface layer and was indistinguishable from specific inorganic iodine in the deep layer. On an average, the difference, or "organic" iodine may account for about half of total dissolved iodine in the surface layer. The highest concentration found was 9 nM/psu.

In contrast to specific inorganic iodine and specific total dissolved iodine, the distribution of iodate and iodide in these two years were drastically different, probably as a reflection of the difference in the prevailing redox conditions. While iodate was ubiquitous in the water column in 1992, it was absent in almost the entire water column in 1990 (Fig. III-3-5). While specific iodide increased from 4 nM/psu in the surface layer to 6 nM/psu in the deep layer in

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[1] Total dissolved iodine (the sum of iodate, iodide, and some part of organic iodine) was measured as iodate after iodide and organic iodine was oxidized to iodate by hypochlorite. When the deep water became very reducing, the added hypochlorite might not be enough to oxidize all of iodide and organic iodine to iodate. This might explain that the concentration of total dissolved iodine was lower than the concentration of inorganic iodine (the sum of iodide and iodate) in some samples of the deep water.

1992 (Fig. III-3-3), it increased from 5 to 6 nM/psu to 10 to 12 nM/psu in 1990. Since the corresponding changes in specific inorganic iodine between 1990 and 1992 were small, these interannual variations in the speciation of iodine may result from the fact that the basin was more reducing in 1990 so that the reduction of iodate might have been more prevalent. The depletion of specific iodide in the surface layer could again be explained largely by the conversion of iodide to "organic" iodine. There was a small but well defined trend of an increase in specific iodide and specific inorganic iodine towards the bottom of the basin in the deep layer. Francois (1987) suggested that, whereas the sediment may remove iodate from the water column under oxidizing conditions, under reducing conditions, it may act as a source of iodide to the bottom water. A flux of iodide from the sediments would be a possible explanation for this gradient. The results of 1990 and 1992 illustrate that Chesapeake Bay is a physically and biogeochemically dynamic system which undergo significant interannual as well as intra-annual variations.

The Summer season

In 1992, by the Summer (August) (Figs. III-3-6, III-3-7), the entire water column had been heated up almost uniformly by surface heating. Temperature varied only by about 1°C from the surface to the bottom. Nonetheless, the water column continued to be stratified into two layers largely as a result of the salinity gradient. The top 4 m was well mixed. This

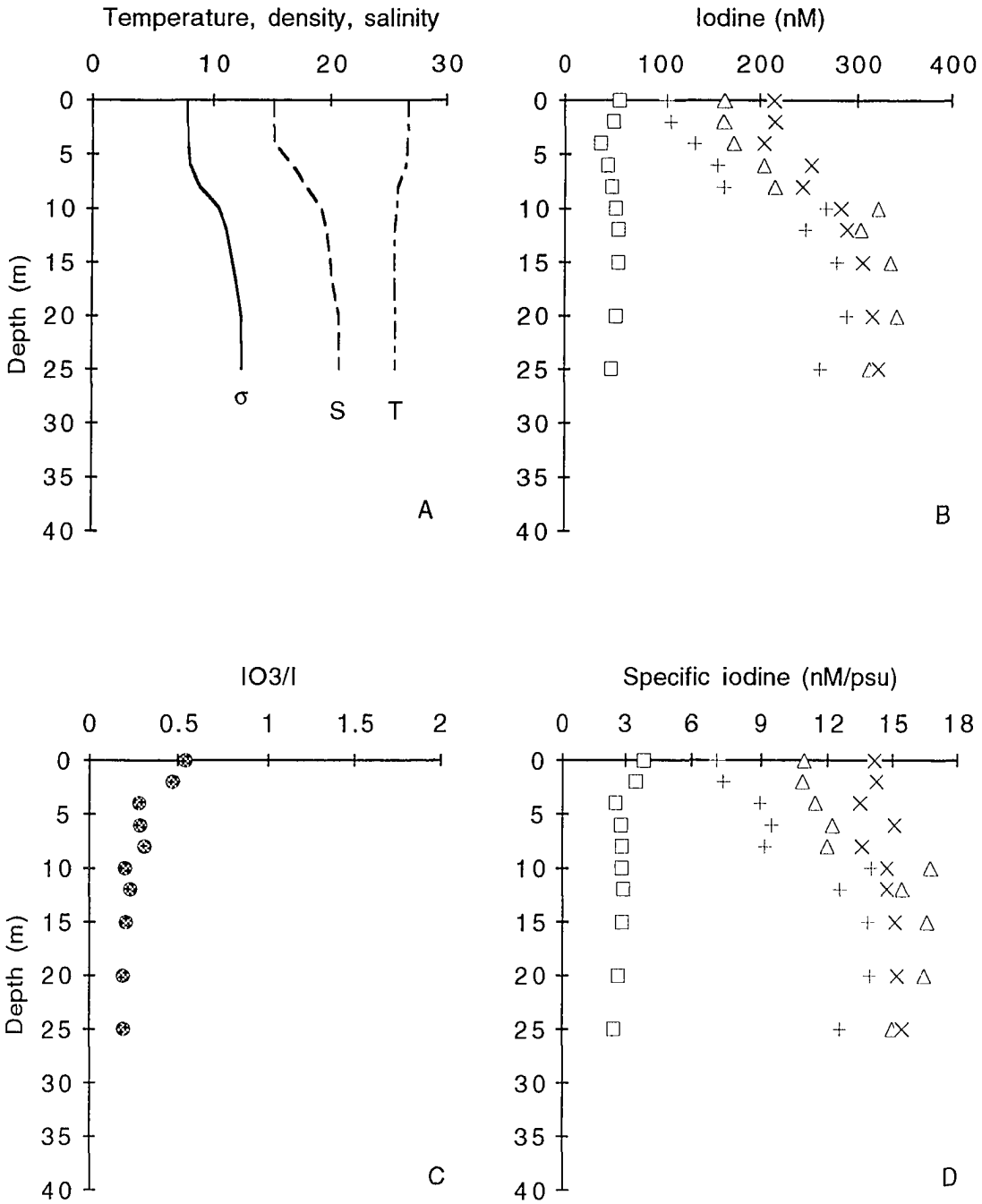

Fig. III-3-6 Result of August 1992.
A: T: temperature (°C); σ: density (σ_t) and S: salinity (psu)
B: Concentration of iodine (nM). Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).
C: Ratio of iodate to iodide.
D: Specific iodine species. Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).

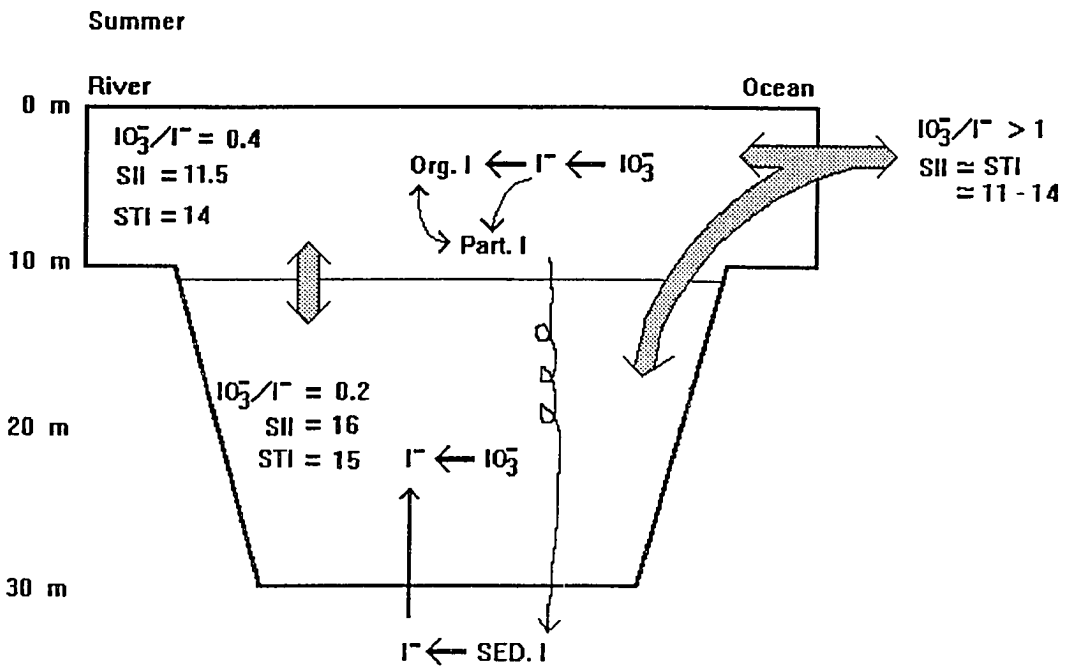

Fig. III-3-7
Behavior of iodine in the Summer. SII = specific inorganic iodine; STI = specific total dissolved iodine; dotted arrow: exchange of water.

was followed by a transition zone down to about 15 m. The deep water below 15 m was again quite well mixed. However, the density difference between the surface and bottom water has decreased to 4.5 σ_t units and the pycnocline was not as sharp as that in the preceding Spring. The density gradient in the pycnocline between 8 and 16 m was only 0.5 σ_t/m. Thus, the water column in this Summer was actually less well stratified than that in the preceding Spring. Specific inorganic iodine in the surface layer, at 11.5 nM/psu, was again significantly lower than that in the deep layer, at 16 nM/psu (Fig. III-3-6). On the other hand, specific total dissolved iodine in the surface layer, at 14 nM/psu, was only slightly lower than that in the deep layer. Thus, again, "organic" iodine was found in the surface layer (For the difference total dissolved iodine and inorganic iodine in deep water, see the footnote on p. 110). However, unlike the preceding Spring, the maximum in "organic" iodine was only about 3 nM/psu and it accounted for only about a fifth of total dissolved iodine. The specific total dissolved iodine of 15 to 16 nM/psu throughout the water column was higher than what would be expected in the incoming Atlantic surface water. This suggests that there may be a source of dissolved iodine to the deep Chesapeake Bay from the underlying sediment. Both specific inorganic and specific total dissolved iodine in the Summer were higher than those in the preceding Spring. The seasonal increase was especially noticeable in specific inorganic iodine. These seasonal changes are consistent with

the idea that the sediment acts as a sink of dissolved iodine by incorporating iodate in the bottom water into the sediments under oxidizing conditions in the Spring and it acts as a source of iodide to the bottom water under reducing conditions in the Summer (Francois, 1987).

While iodide was the dominant form of inorganic iodine in the entire water column in the Summer, low, at 40 to 60 nM, but barely detectable, amounts of iodate were also found (Fig. III-3-6). However, these concentrations were again lower than those found in the Spring. Iodate/iodide ranged from about 0.5 at the surface to 0.2 in the deep water. Thus, while the basin might have become progressively more reducing from the Winter to the Summer of 1992, even in the Summer of 1992, it was not as reducing as that in the Spring of 1990 when iodate was absent. While specific iodate decreased only slightly with depth by about 1 nM/psu, specific iodide increased from about 7 nM/psu at the surface to about 14 nM/psu in the deep water. Again, the depletion of iodide in the surface layer was due to its conversion into the "organic" rather than the particulate pool.

The Fall season

In the Fall (Figs. III-3-8, III-3-9), the water column began to de-stratified. The surface water, at 17.7°C, was colder than the bottom water, at 19.9°C. The density structure was sustained by the difference in salinity between the surface and deep water. The resulting difference in

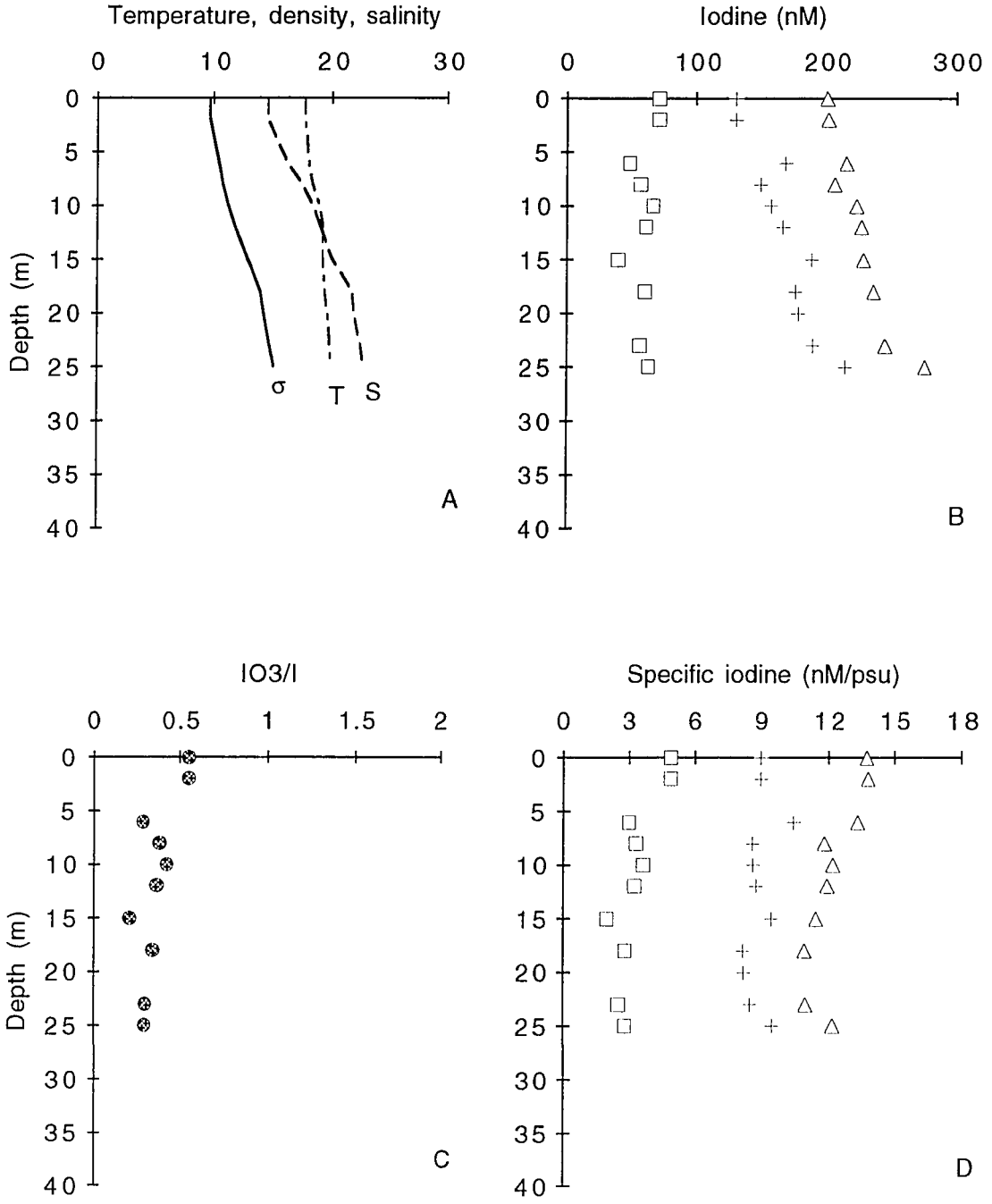

Fig. III-3-8 Result of October 1992.
A: T: temperature (°C); σ: density (σ_t) and S: salinity (psu)
B: Concentration of iodine (nM).
Iodide (+); Iodate (□) and inorganic iodine (△).
C: Ratio of iodate to iodide.
D: Specific iodine species.
Iodide (+); Iodate (□) and inorganic iodine (△).

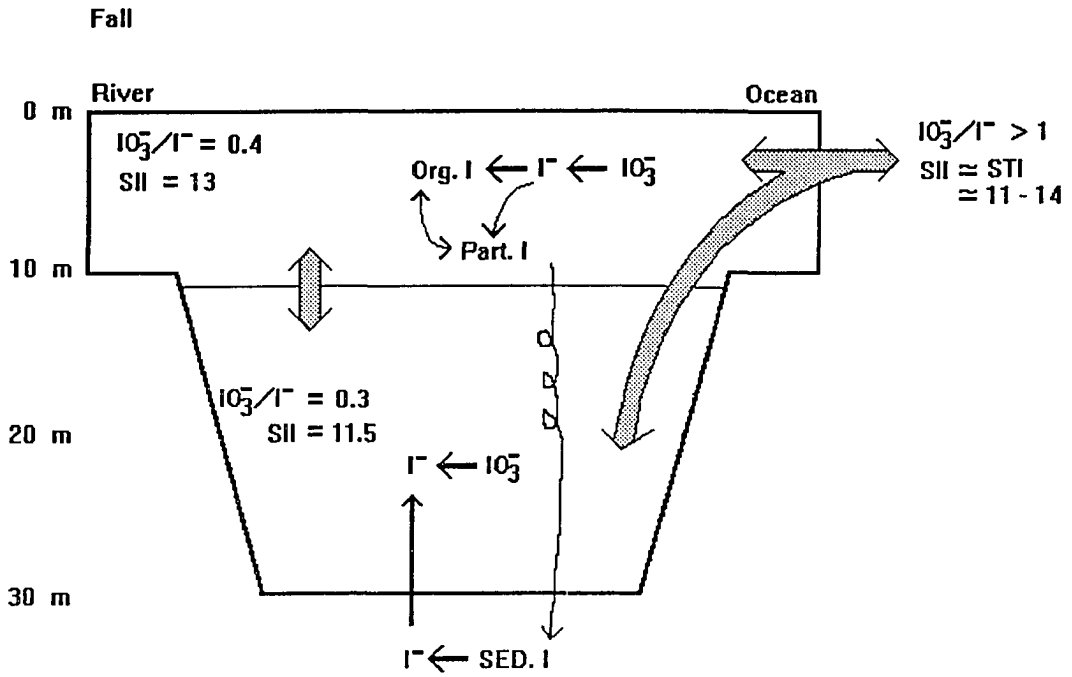

Fig. III-3-9
Behavior of iodine in the Fall. SII = specific inorganic iodine; STI = specific total dissolved iodine; dotted arrow: exchange of water.

density was 5.3 σ_t units. The pycnocline became even less distinct as the density increased gradually with depth down to about 20 m. Only iodate and iodide were measured during this season. Instead of an increase with depth as observed in the preceding Summer and Spring, specific inorganic iodine actually decreased slightly with depth with an average value of 14 nM/psu in the top 6 m and 12 nM/psu in the deep water. Thus, there was no evidence of the conversion of inorganic iodine to the "organic" or the particulate pool. Iodide continued to be the dominating species of inorganic iodine. Again, iodate was found in the entire water column. The concentrations were still low but they were somewhat higher than those found in the Summer. Iodate/iodide ranged between 0.2 to 0.5 in the water column. These distributions of iodate and iodide suggest that as the water column became de-stratified in the Fall, the basin became less reducing and thus less capable of reducing iodate to iodide. As a result, the water in the Bay may become increasingly iodate-rich as the iodide-rich water in the Bay is exchanged with the iodate-rich incoming water from the Atlantic. While specific iodide remained approximately uniform with depth at about 9 nM/psu, specific iodate seemed to decrease slightly but systematically from about 5 nM/psu at the surface to 2.5 nM/psu in the deep waters. This may suggests that as the water column becomes more oxidizing in the Fall, the removal of iodate by its and incorporation into the sediment may become operative again.

The role of Chesapeake Bay in the geochemistry of iodine in coastal waters

The seasonal cycle of the speciation of dissolved iodine in Chesapeake Bay suggests that the interconversion among iodate, iodide and "organic" iodine may occur at a rather rapid pace, in a time scale of months or shorter. Secondly, coastal systems, such as the Chesapeake Bay, may act as geochemical reactors that may affect the speciation of iodine in the oceans. Iodate-rich seawater from the open oceans enters the system and its composition may be significantly altered, being transformed to an iodide-rich, "organic" iodine-rich seawater before it is returned to the oceans. The approximate strength of the Chesapeake Bay as a source of iodide to the Atlantic may be estimated by assuming an average tidal height of 0.3 m. Given that there is a semi-diurnal tide in the Bay and the average depth of the Bay is 15 m, the residence time of the water in the Chesapeake Bay relative to tidal exchange will then be about 1 month. If iodate is reduced to iodide in six months of the year between the Spring and the Fall and if the incoming water has a total inorganic iodine of 300 nM and an iodate/iodide of 1.5 while the outgoing water has an iodate/iodide of 0.2 and the volume of the Bay is 50 Km^3, then, the additional flux of iodide to the oceans will be about 4×10^7 mole/yr if tidal exchange is 100% efficient. As a comparison, this flux is equivalent to about 10% of the annual riverine input of iodide to the oceans (Tsunogai, 1971). The volume of the inner shelf of the South

Atlantic Bight within the 20-m isobath is 326 Km^3 (Atkinson and Menzel, 1985) and its concentration of iodide is about 250 nM (Wong and Zhang, 1992c). The standing stock of iodide is 8×10^7 mole. Thus, the flux of iodide from the Chesapeake Bay will be able to replenish such a standing stock in about two years. Traditionally, the occurrence of iodide in the surface ocean has been explained by the *in situ* reduction of iodate (Tsunogai and Sase, 1969; Elderfield and Truesdale, 1980). Coastal systems, such as the Chesapeake Bay, may be another source of iodide to the surface oceans that may be geochemically significant but has yet to be quantified.

The surface southern Chesapeake Bay

The relationship between salinity and iodate, iodide, inorganic iodine and total dissolved iodine in the surface waters, within the top 5 m, in each season are shown in Fig. III-3-10 to Fig. III-3-15. The relationship between the concentration of a given species in an estuary to salinity has been used extensively for determining the reactivity of the species (Liss, 1976). However, such a mixing model, which assumes mixing between two end-members with time-invariant composition, may not be totally valid for the southern Chesapeake Bay. The range of salinity found in the samples in this study, 12 to 27 psu, was narrow. Within each season, the range was even narrower. As a result, the mixing curves could not be established reliably. Furthermore, it should be noted that multiple rivers drain into the southern Chesapeake Bay

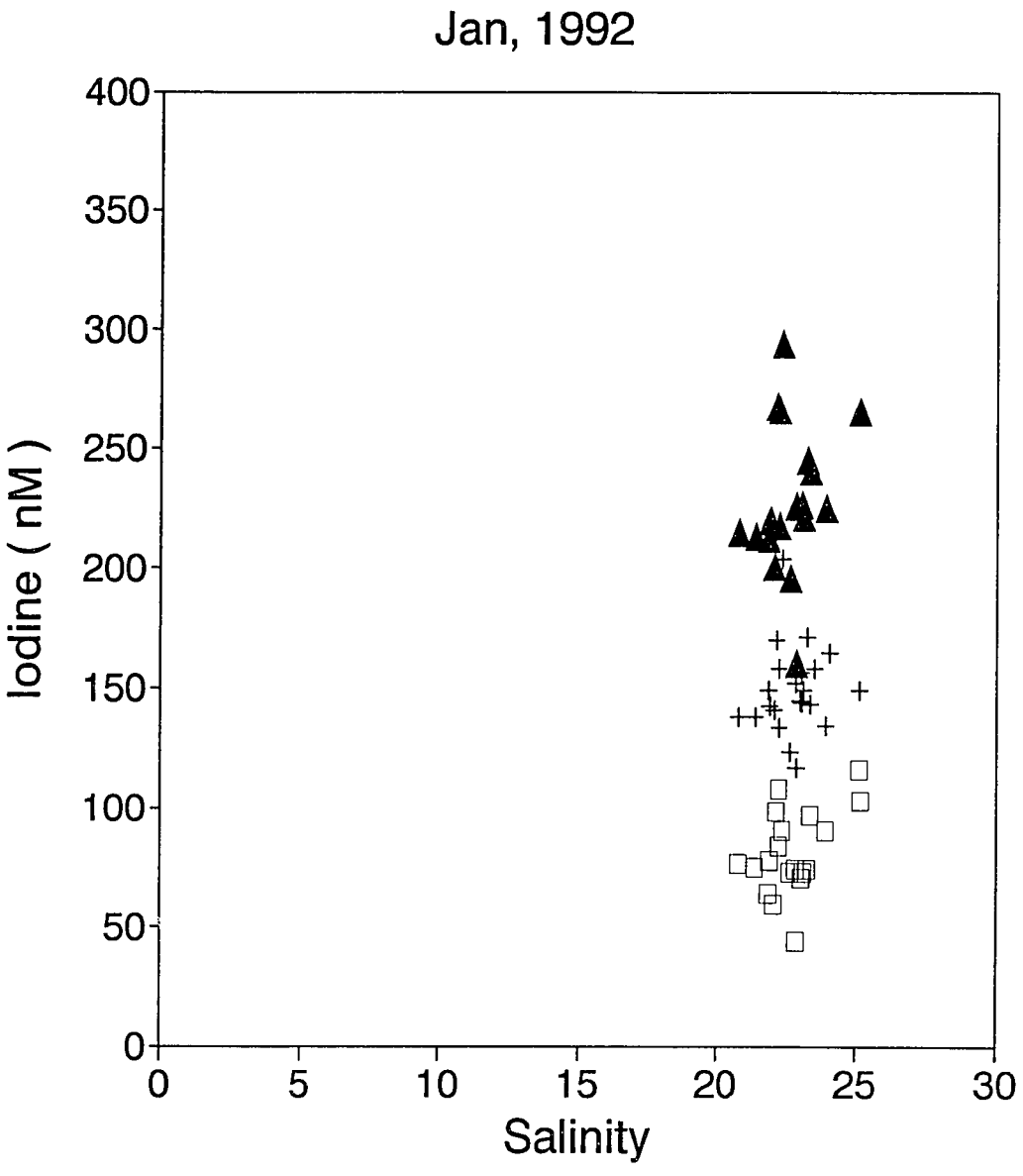

Fig. III-3-10

Concentrations of iodine species in the surface water of the southern Chesapeake Bay.

January 1992.

Iodide (+); Iodate (□) and inorganic iodine (△).

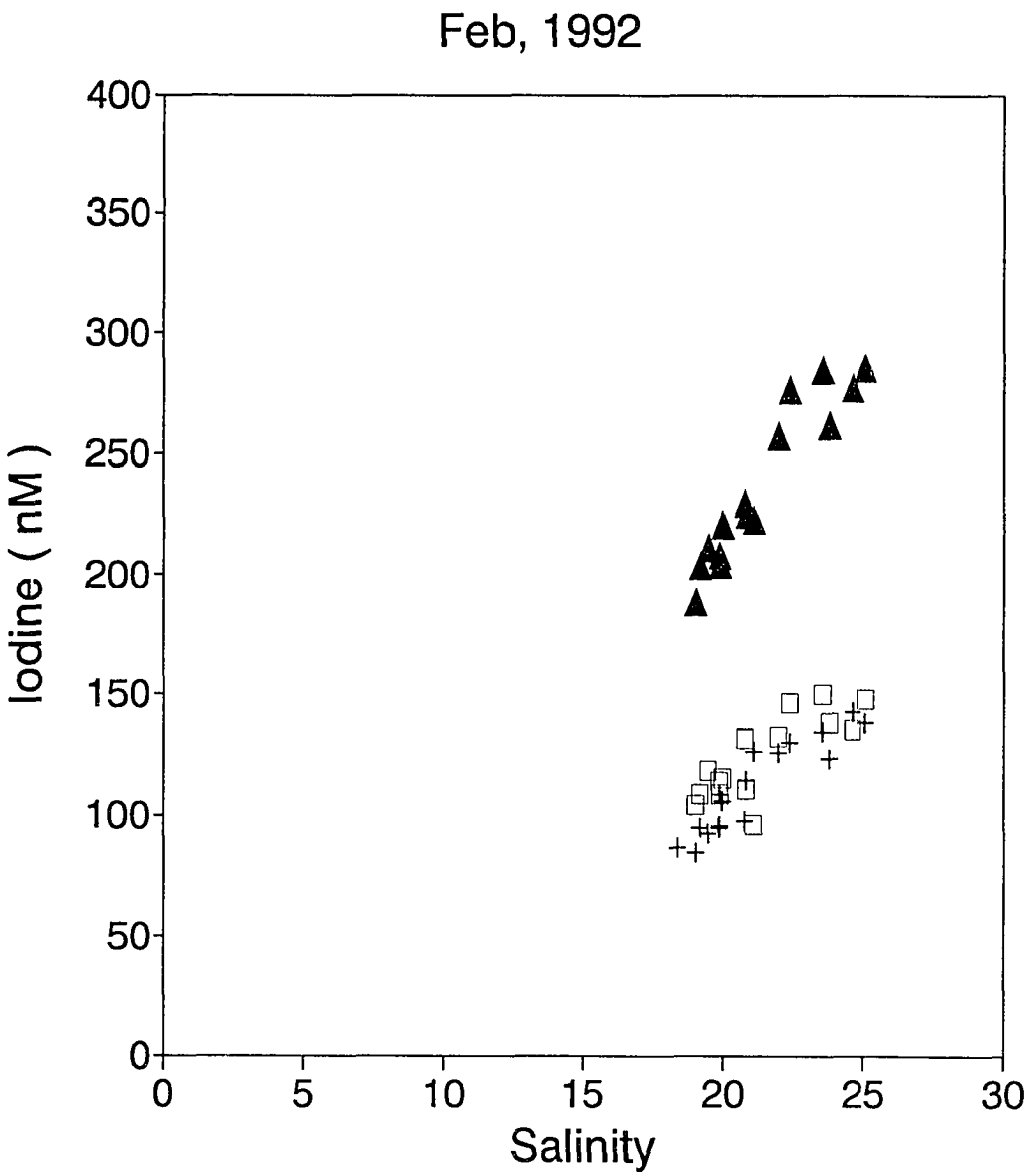

Fig. III-3-11

Concentrations of iodine species in the surface water of the southern Chesapeake Bay.

February 1992.

Iodide (+); Iodate (□) and inorganic iodine (△).

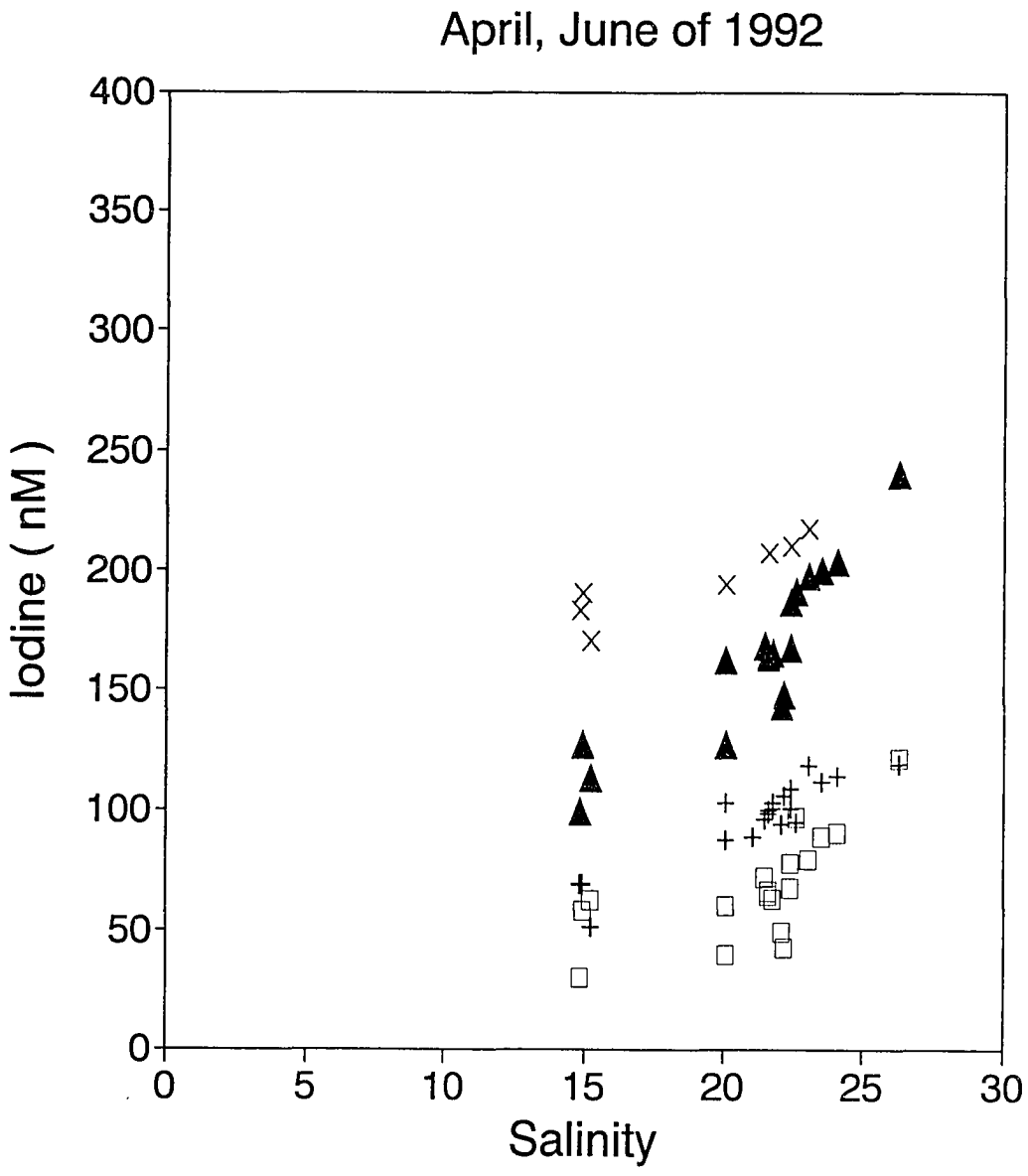

Fig. III-3-12

Concentrations of iodine species in the surface water of the southern Chesapeake Bay.

April and June, 1992.

Iodide (+); Iodate (□); inorganic iodine (△); and total dissolved iodine (×).

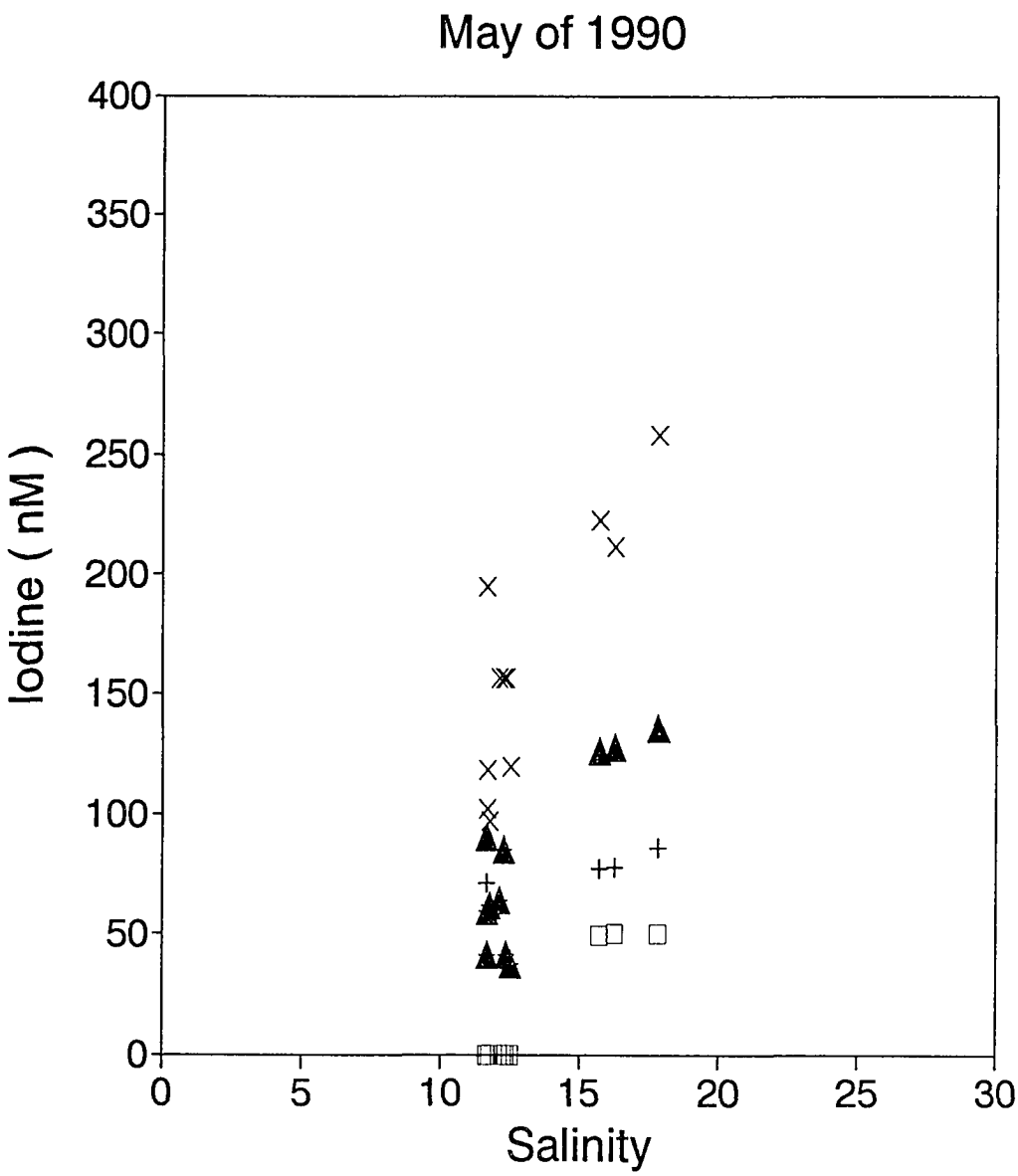

Fig. III-3-13

Concentrations of iodine species in the surface water of the southern Chesapeake Bay.

May 1990.

Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).

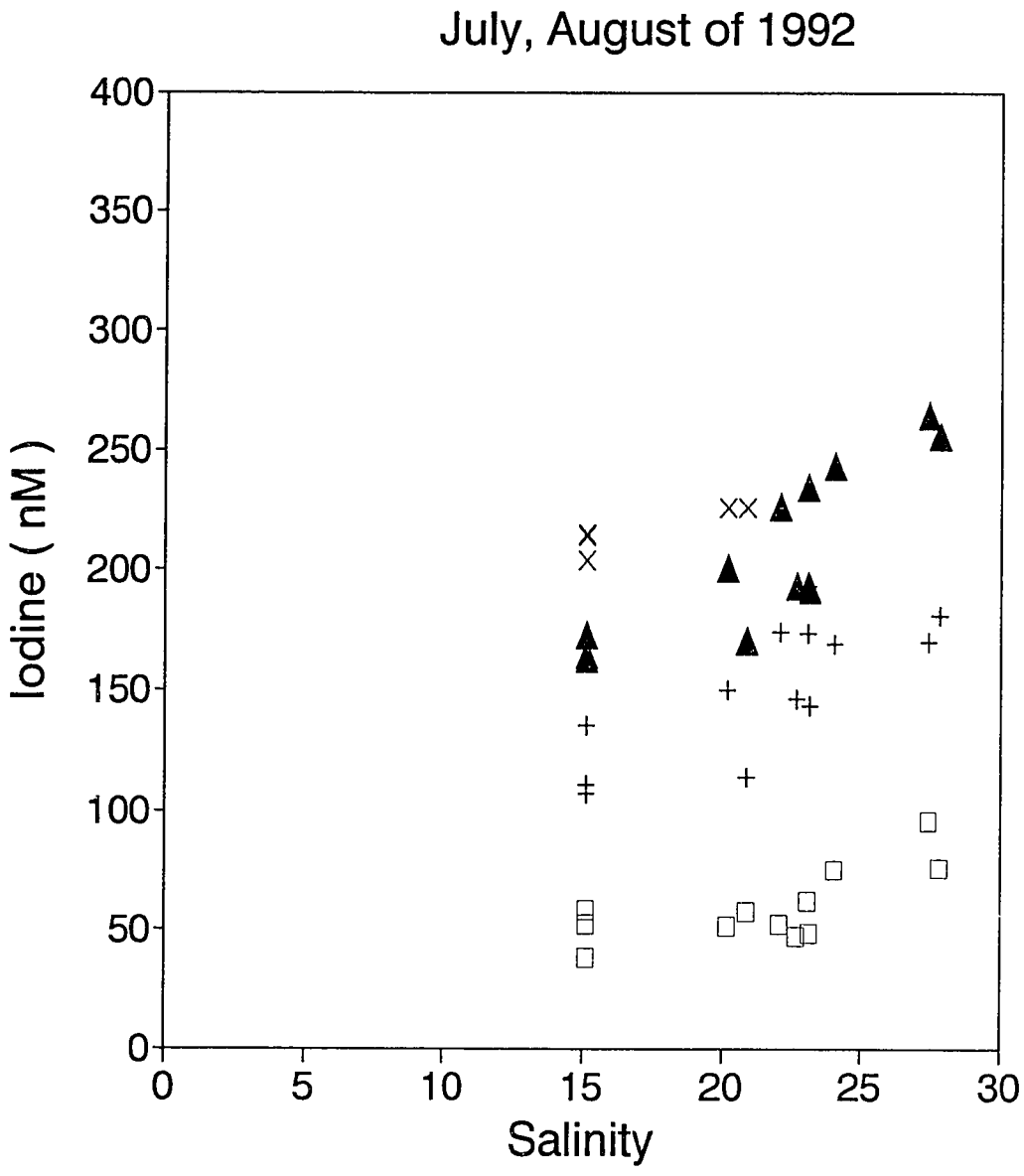

Fig. III-3-14

Concentrations of iodine species in the surface water of the southern Chesapeake Bay.

July and August, 1992.

Iodide (+); Iodate (□); inorganic iodine (△) and total dissolved iodine (×).

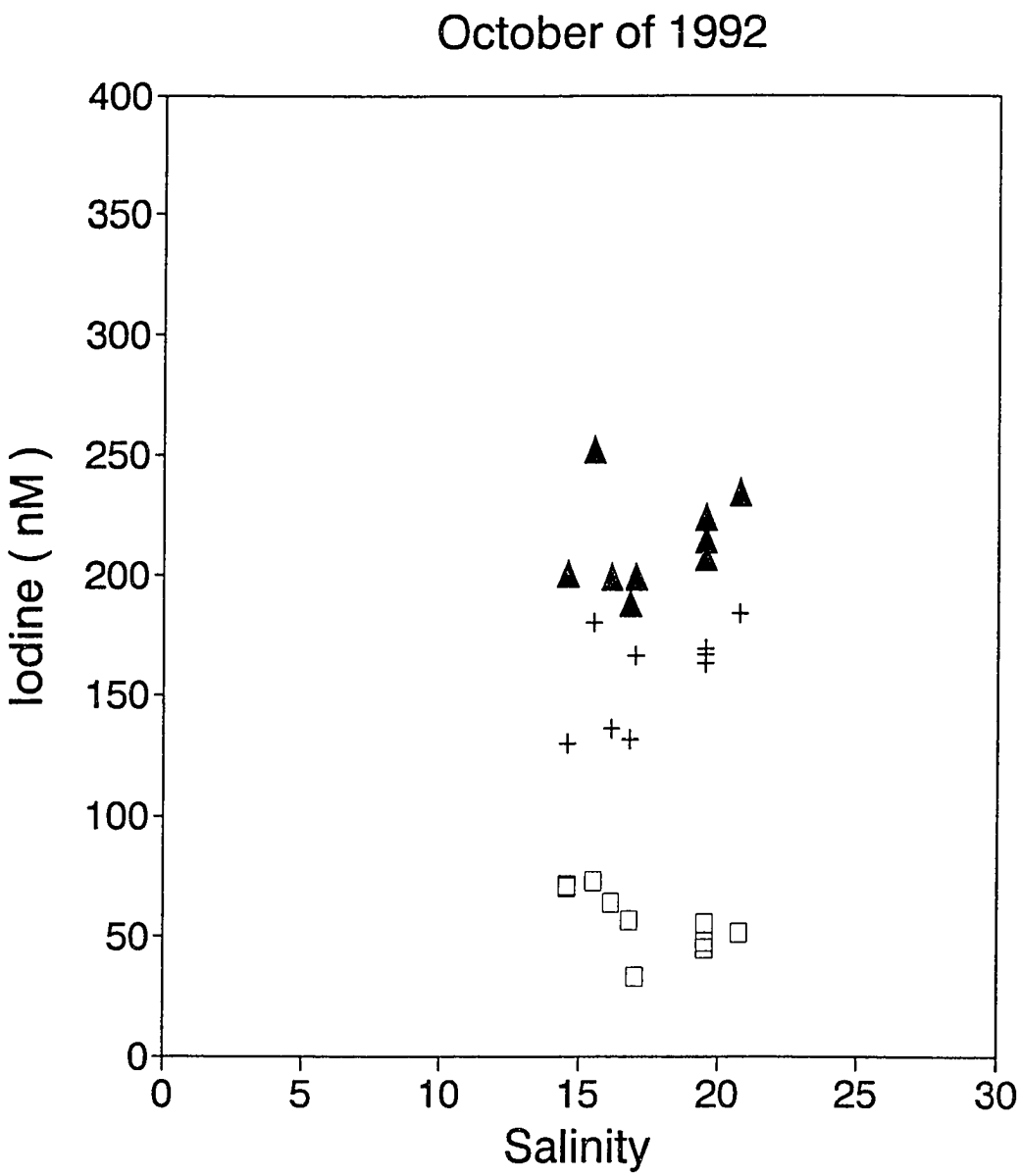

Fig. III-3-15

Concentrations of iodine species in the surface water of the southern Chesapeake Bay.

October 1992.

Iodide (+); Iodate (□) and inorganic iodine (△).

and there may be temporal variations in the composition of these end-members. Thus, the assumptions that may be required by this model may not be met. Nevertheless, Luther and Cole (1988), Ullman et al. (1988) and Luther *et al.* (1991) reported that total iodine was linearly related to salinity during the Summer of 1986 and 1987 and suggested that dissolved iodine is conservative in the Bay. In general, the data reported here for the Spring of 1990, the Winter (February), Spring and Summer of 1992 also fell along broad linear bands and the concentration decreased with decreasing salinity. A more careful examination of the data of Luther and coworkers also indicates that their data points actually fell on a band rather than a well defined line and the variations around the best fit line were larger than the analytical uncertainties. Thus, total iodine may, at best, only be quasi-conservative in the Chesapeake Bay as a first approximation. The data reported here indicate that there were seasonal and interannual differences. At a given salinity, total iodine in the Spring of 1992 is lower than the Summer of 1992. It was also lower than those reported by Luther and coworkers (Luther and Cole, 1988; Luther *et al.*, 1991) in the Summer of 1986 and 1987. In the Spring of 1990, total iodine was higher than those in 1992 and was similar to those reported by Luther and coworkers. Its relationship with salinity may also be affected by the removal of iodate to the sediment under oxidizing conditions and/or the addition of iodide to the water column from the sediments under reducing conditions and

the conversion of dissolved iodine to the particulate phase. These processes can be temporally and spatially variable. For example, the water column became more reducing from the Spring to the Summer of 1992. It was probably even more reducing in the Spring of 1990. As a result, total iodine may increase in the same order. Spring bloom might also be a contributing cause of the lower total iodine in the Spring of 1992.

Similarly, total inorganic iodine in the different seasons also fell on approximately parallel, but not coinciding, linear bands. Aside from the processes that can affect total iodine, the relationship between inorganic iodine and salinity may be affected by its conversion to the "organic" form. In fact, the lowest total inorganic iodine at a given salinity was found during the Spring when the concentration of "organic" iodine was the highest. There were also finer scale features. Samples that were collected three weeks apart in the Winter of 1992 fell into two slightly offsetting bands. This indicates that there might even be short-term intra-seasonal variations in the relationship between total inorganic iodine and salinity. Furthermore, the data from a shallow marginal bay, the Mobjack Bay, seemed to be more variable and somewhat different from the data from the deep main channel of the Bay. This suggests that the relative importance of the processes that may affect the concentration of inorganic iodine in the shallower waters may not be identical to that in the deep channel and may result in water types with different signatures in terms of dissolved iodine

and similar salinity in the Bay.

Luther *et al.* (1991) reported that, in the Summer of 1987, in the surface water of the Chesapeake Bay, iodate fell to undetectable concentrations below 21 psu. Above this salinity, it was linearly related to salinity. On the other hand, iodide is conservative up to 26 psu. The data reported here also exhibited the same general trends. Again, there was evidence of temporal and spatial variability. For example, the relationship between salinity and iodate in January (1992) and in February (1992) fell on two approximately parallel but distinct bands. Thus, the salinity at which iodate became undetectable might vary among seasons and even within a season. The data obtained from Mobjack Bay tended to deviate from the general trend in the Fall of 1991 and the Winter of 1992 in the case of iodate and in the Fall of 1991 in the case of 1992. Aside from the processes mentioned previously, the relationship between salinity and iodate and salinity and iodide can be further affected by the interconversion between these two species.

CONCLUSION

The speciation of iodine varied seasonally in the middle and the lower Chesapeake Bay. In the surface water, total dissolved iodine was depleted in the Spring with respect to total dissolved iodine in the Summer. Inorganic iodine was depleted in the Spring as compared to inorganic iodine in the other three seasons. Inorganic iodine might be converted to organic iodine mainly in the Spring. Organic iodine was about 20-30% of that of total iodine in the Spring and the Summer. In the Winter, the concentration of iodate was close to that of iodide, but in the Fall, the concentration of iodate was only one-third of that of iodide. Between the Winter and the Fall, iodate was reduced to iodide.

In the deep water of the middle bay, total dissolved iodine in the Summer was significantly higher than that in the Spring. Inorganic iodine in the Summer was also significantly higher than that in the other three seasons. There might be a source of iodine to the deep water in the Summer from the underlying sediment. This source might be in the form of iodide. Organic iodine was very minor in the deep water. In the Winter, the concentration of iodate was close to that of iodide, but in the Fall, it was one-third of the concentration of iodide. Between the Winter and the Fall, the concentration of iodate decreased, indicating that iodate was reduced. Besides the production of iodide from the reduction of iodate, there was a source of iodide in the Summer to the deep water from the sediment. The seasonal variations in the speciation

of iodine in the deep water were different from those in the surface water. In addition to the seasonal variations, inter-annual variations in the speciation of iodine were also observed in the deep water of the middle bay.

The Chesapeake Bay is a place where iodate was reduced to iodide and iodide was transported out to the ocean. The estimated flux of iodide from the bay to the ocean was about 4×10^{17} mole $year^{-1}$. This flux of iodide is enough to replace all of iodide in the South Atlantic Bight within coast to 20-meter isobath in about two years. Therefore, this transported iodide might be substantial to the distribution of iodide in the coastal water.

CHAPTER FOUR

THE KINETICS OF THE REACTION BETWEEN IODIDE AND HYDROGEN PEROXIDE

ABSTRACT

The kinetics of the reaction between hydrogen peroxide and iodide was studied in artificial seawater as a function of temperature (10-30°C), salinity (0-35), pH (7-9) and the concentration of molybdate (0-480 μM) at concentrations of H_2O_2 of 5 to 40 mM and concentrations of iodide of 0.1 to 1.2 mM. While hydrogen peroxide disappears at a much accelerated rate in the presence of iodide, the concentration of iodide remains unchanged even when the loss of hydrogen peroxide has greatly exceeded the concentration of iodide present. The net result is a quasi-catalytic decomposition of hydrogen peroxide. The disappearance of hydrogen peroxide is first order with respect to both concentrations of iodide and hydrogen peroxide. If the reaction between hydrogen peroxide and iodide involves the oxidation of iodide by hydrogen peroxide to, most likely, molecular iodine and/or hypoiodite and an ensuing reduction of the product back to iodide, the rate law may be expressed as

$$-d[H_2O_2]/dt = (2k_A)\ [I^-]\ [H_2O_2]$$

where k_A (in $mM^{-1}hour^{-1}$) is the rate constant for the oxidation of iodide by H_2O_2 alone, $[I^-]$ is the initial concentration of iodide and $[H_2O_2]$ is the concentration of hydrogen peroxide at any time t. The rate constant is independent of pH within the oceanographic range of pH of 7 to 9. It increases in the presence of molybdate. However, at the concentration of molybdate in seawater, the effect is negligible. The rate constant also increases with salinity and temperature. The general relationship between the rate constant and temperature and salinity is given by the equation:

$$\log(k_A) = (8.83\pm0.09) - (3047\pm25)/T + (0.0017\pm0.0001)\times S$$

where S is salinity in psu and T is the absolute temperature. The energy of activation of the reaction is 57.6±0.7 kJ/mole.

By extrapolating these results to the conditions found in surface seawater, it is found that the reaction between hydrogen peroxide and iodide contributes little to the reported rates of decomposition of hydrogen peroxide in seawater. If hypoiodite is formed as an intermediate in the reaction, this product may be an important reagent for the formation of iodinated organic compounds in the sea. Furthermore, hypoiodite potentially may act as an intermediate for the conversion of iodide to iodate.

IV-1 INTRODUCTION

Iodine is one of the most abundant biophilic, redox sensitive minor elements in seawater (Bruland, 1983; Wong, 1991, Wong and Brewer, 1974; Elderfield and Truesdale, 1980; Wong and Brewer, 1977; Luther and Cole, 1988). Although the biogeochemistry of iodine has been extensively investigated (e.g. Wong, 1991 and references cited therein), many unknowns still remain. One of the these unknowns is mechanism and rate of oxidation of iodide to iodate. In the surface seawater, the concentration of iodide ranges from 0.1 to 0.2 μM, and that of iodate from 0.3 to 0.4 μM. However, in the deep seawater, iodate is the only detectable form of dissolved inorganic iodine. Thus, somewhere during the grand scheme in the circulation of the oceans, iodide must be oxidized to iodate. Thermodynamically, iodate is the stable form of iodine in oxic seawater and the ratio of iodate to iodide at equilibrium is expected to be $10^{13.5}$ (Sillen, 1961). As a result, the oxidation of iodide to iodate in oxic seawater is favored. Nevertheless, the mechanism of this reaction is still unknown.

Hydrogen peroxide has been found in seawater in concentrations ranging between 0.01 and 0.3 μM (e.g. Zika *et al.*, 1985a; 1985b; Johnson *et al.*, 1989). Hydrogen peroxide is involved in photochemical and biological processes in the surface oceans (e.g. Moffett and Zafiriou, 1990; Palenik *et al.*, 1987; Palenik and Morel, 1988). It plays an important role in controlling the speciation of several redox-sensitive

elements in the oceans (e.g. Moffett and Zika, 1987; Pettine and Millero, 1990; Petasne and Zika, 1987). Therefore, the fate of hydrogen peroxide is important in the redox chemistry of seawater. The life time of hydrogen peroxide is days to weeks in open ocean waters and days in coastal waters (Zika *et al.*, 1985a; Johnson *et al.*, 1989). However, the mechanisms in which hydrogen peroxide is removed are still poorly understood.

In seawater, the reduction potential of the redox couple IO_3^-/I^- is smaller than that of H_2O_2/H_2O (Table IV-1-1). Thus, the oxidation of iodide by hydrogen peroxide in seawater is thermodynamically feasible. In fact, Cadle and Huff (1950) reported that, at pH 7, a pH not too dissimilar from that of seawater, iodide is oxidized to iodine by hydrogen peroxide in pure solutions. Furthermore, the concentration of iodide and hydrogen peroxide in surface seawater, at about 0.2 μM and 0.3 μM respectively, are similar and are quite high among trace species. In fact, they are the most abundant inorganic reducing and oxidizing substance in surface seawater respectively. Other strong oxidizing reagents, such as hydroxyl radical, have been found in much lower concentration in the surface waters (Mopper and Zhou, 1990). Thus, if iodide is oxidized by hydrogen peroxide in the surface oceans, this reaction may be a viable mechanism for accounting for the oxidation of iodide to iodate and the removal of hydrogen peroxide in seawater.

Table IV-1-1: Reduction potentials of several redox couples in seawater

Redox couple	E° (V)	--- In seawater (pH 8.0)--- Concentration (μM)	E (V)
$H_2O_2+2H^++2e = 2H_2O$	1.78	$[H_2O_2]=0.15$	1.09
$O_2+4H^++4e = 2H_2O$	1.23	$[O_2]=300$	0.69
$IO_3^-+6H^++6e = I^-+3H_2O$	1.09	$[IO_3^-]/[I^-]$ = 0.3/0.2	0.60
$O_2+2H^++2e = H_2O_2$	0.70	$[O_2]/[H_2O_2]$ = 300/0.15	0.31

In this work, the kinetics of the reaction between H_2O_2 and iodide in artificial seawater was investigated. The primary factors investigated were the concentration of iodide, temperature, salinity, and pH. The catalytic effect of molybdate on the kinetics of the reaction between hydrogen peroxide and iodide was also investigated.

IV-2 EXPERIMENTAL

Artificial seawater containing a known initial concentration of added iodide and H_2O_2 was placed in a 500-ml Erlenmeyer flask. This reaction flask was placed in a constant temperature bath whose temperature was controlled to within ±0.1°C of the desired temperature with a Lauda/Brinkman Model K2R-D circulator. The constant temperature bath was wrapped with aluminum foil to keep the reaction mixture in the dark. In the early experiments, the reaction mixture was continuously agitated by bubbling nitrogen through it. Later on, this practice was terminated since the rate constant of the reaction determined with or without the bubbling of nitrogen were indistinguishable from each other.

The reaction was monitored by following the concentrations of hydrogen peroxide and iodide during the course of the reaction. Sub-samples were taken with an Eppendorf pipette. The concentration of iodide was measured with an iodide electrode by using an Orion Model 94-53 iodide electrode, an Orion Model 90-02 double junction reference electrode together with an Orion Model 701A Digital Ionalyzer

(The detail is given in Appendix C). The concentration of hydrogen peroxide was determined in the sub-sample by reacting hydrogen peroxide with titanium and then measuring the absorbance of the H_2O_2-Ti complex at 420 nm with a Brinkmann PC800 dipping-probe colorimeter (Eisenberg, 1943; Pobiner, 1961; Sellers, 1980). The pH of the reaction mixture was also monitored by using an Orion Model 810200 combination electrode together with an Orion Model 701A Digital Ionalyzer.

All the chemicals used were of the ACS reagent-grade. Distilled deionized water was used throughout this work. Artificial seawater was made according to the formula of Lyman and Fleming (1940). Ca^{2+}, Mg^{2+} and Sr^{2+} were substituted with an equimolar amount of Na^{+} in order to avoid the precipitation of hydroxide at high pH. The salinity of the artificial seawater was 35.686. The artificial seawater was buffered with 5 mM of phosphate (disodium hydrogen phosphate). The pH of the solution was brought to the desire value, between 7 and 9 by using 1 M HCl or 1 M NaOH.

A standard solution of hydrogen peroxide (about 10 mM) was prepared by diluting 1 ml of 30% (w/w) solution of hydrogen peroxide to 1000 ml and then standardizing the solution by iodometric titration.

A 10 mM standard solution of iodide was made by dissolving 1.660 gram of potassium iodide with artificial seawater to form a one liter solution. This solution was added to the reaction mixture to give the desired initial concentration of iodide in the experiments.

IV-3 RESULTS AND DISCUSSION

Dependence on the concentration of hydrogen peroxide and iodide

In the absence of iodide, hydrogen peroxide undergoes auto-decomposition slowly. The rate constant of the auto-decomposition of hydrogen peroxide was quite small and did not vary greatly under different experimental conditions in comparison to the rate constant found in the presence of iodide. Nonetheless, this minor contribution to the total rate of disappearance of hydrogen peroxide in the presence of iodide was determined repeatedly and was subtracted from the total rate when the rate constant for the reaction between hydrogen peroxide and iodide was calculated.

The rate of the disappearance of hydrogen peroxide in the presence of iodide was measured at initial concentrations of hydrogen peroxide of 5, 10, 20 and 40 mM with a fixed initial concentration of iodide of 0.5 mM at a pH of 8.0 and a temperature of 20°C[1]. While there was no detectable change in the concentrations of iodide during the experiments (Fig. IV-3-1), the concentration of hydrogen peroxide decreased

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[1] The concentrations of iodide and hydrogen peroxide used in these experiments are 10^3 to 10^4 of their natural concentrations in surface seawater. Elevated concentrations have to be used because the rate of the reaction becomes too slow to be readily measurable at the natural concentrations. Furthermore, at the slower rates, the contributions from other side reactions, such as the self-decay of hydrogen peroxide and the possible catalytic effect of trace metals, may become significant and it may be difficult to define these contributions with a high degree of accuracy.

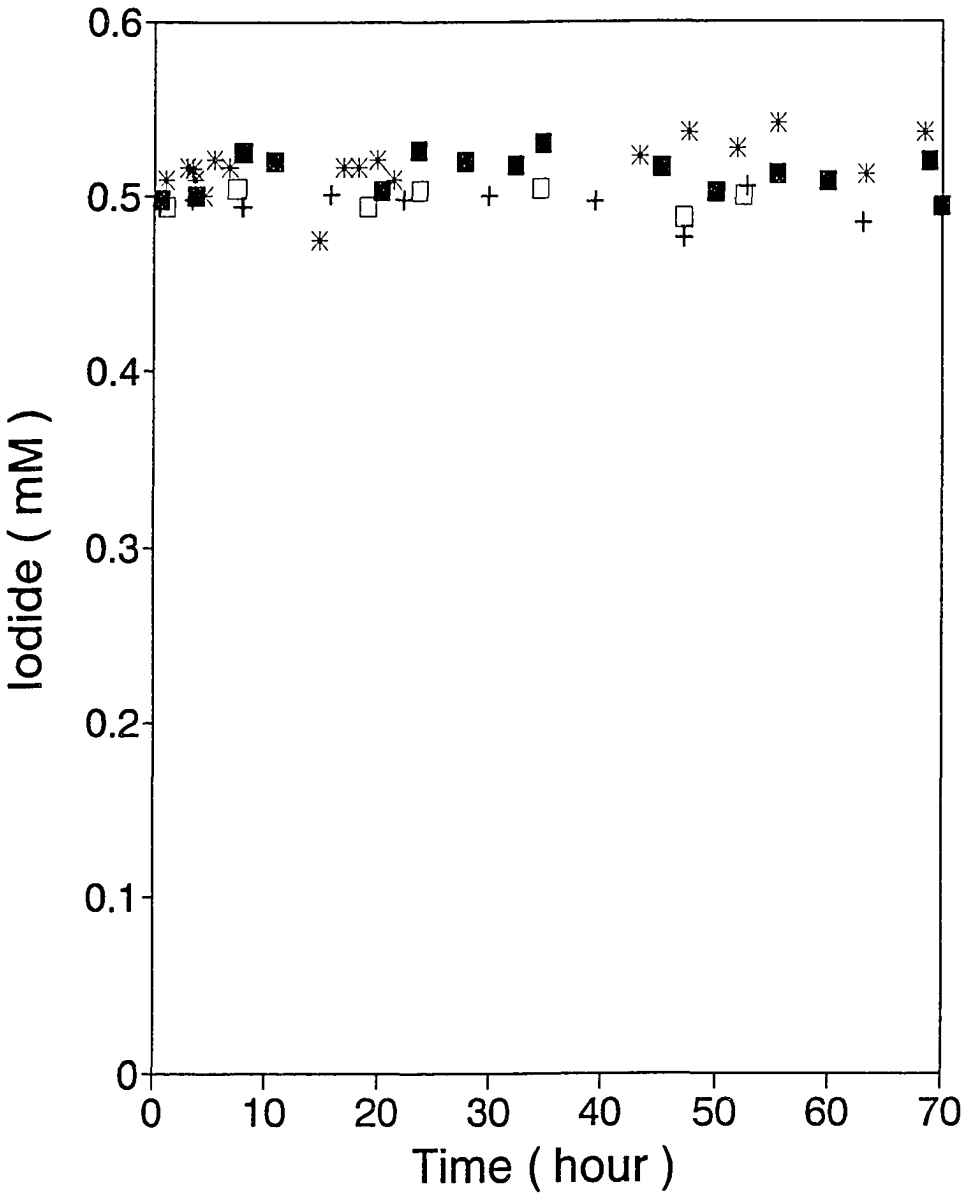

Fig. IV-3-1

The concentration of iodide during the reaction. The initial concentrations of iodide were 0.5 mM. The initial concentrations of hydrogen peroxide were 5 mM (□), 10 mM (+), 20 mM (▪), and 40 mM (×).

exponentially with time, following first order kinetics (Fig. IV-3-2). The rate law of the reaction may be given as

$$-d[H_2O_2]/dt = k_1 [H_2O_2] \quad (1)$$

so that

$$\ln [H_2O_2] = -k_1 t + \ln [H_2O_2]^\circ$$

where k_1 is the first order rate constant in $hour^{-1}$, $[H_2O_2]^\circ$ the initial concentration of hydrogen peroxide, and $[H_2O_2]$ the concentration of hydrogen peroxide at time t. The rate of disappearance of hydrogen peroxide was much faster with the presence than in the absence of iodide. This suggests that hydrogen peroxide does react with iodide in seawater. The first order rate constant was independent of the initial concentration of hydrogen peroxide with a value of 0.0315± 0.0003 $hour^{-1}$ at 20°C, a pH of 8.0 and in the presence of 0.5 mM of iodide, after the rate of auto-decomposition of hydrogen peroxide has been corrected for. Previous investigators have also reported that the reaction between hydrogen peroxide and iodide follows first order kinetics with respect to the concentration of hydrogen peroxide (Azaz *et al.*, 1973; Bray and Liebhafsky, 1931; Liebhafsky and Mohammad, 1933; Liebhafsky and Mohammad, 1934; Cadle and Huff, 1950; Matsuzaki *et al.*, 1972).

The effect of the concentration of iodide on the rate of the reaction was examined at initial concentrations of iodide ranging from 0.1 to 1.2 mM and at a fixed initial

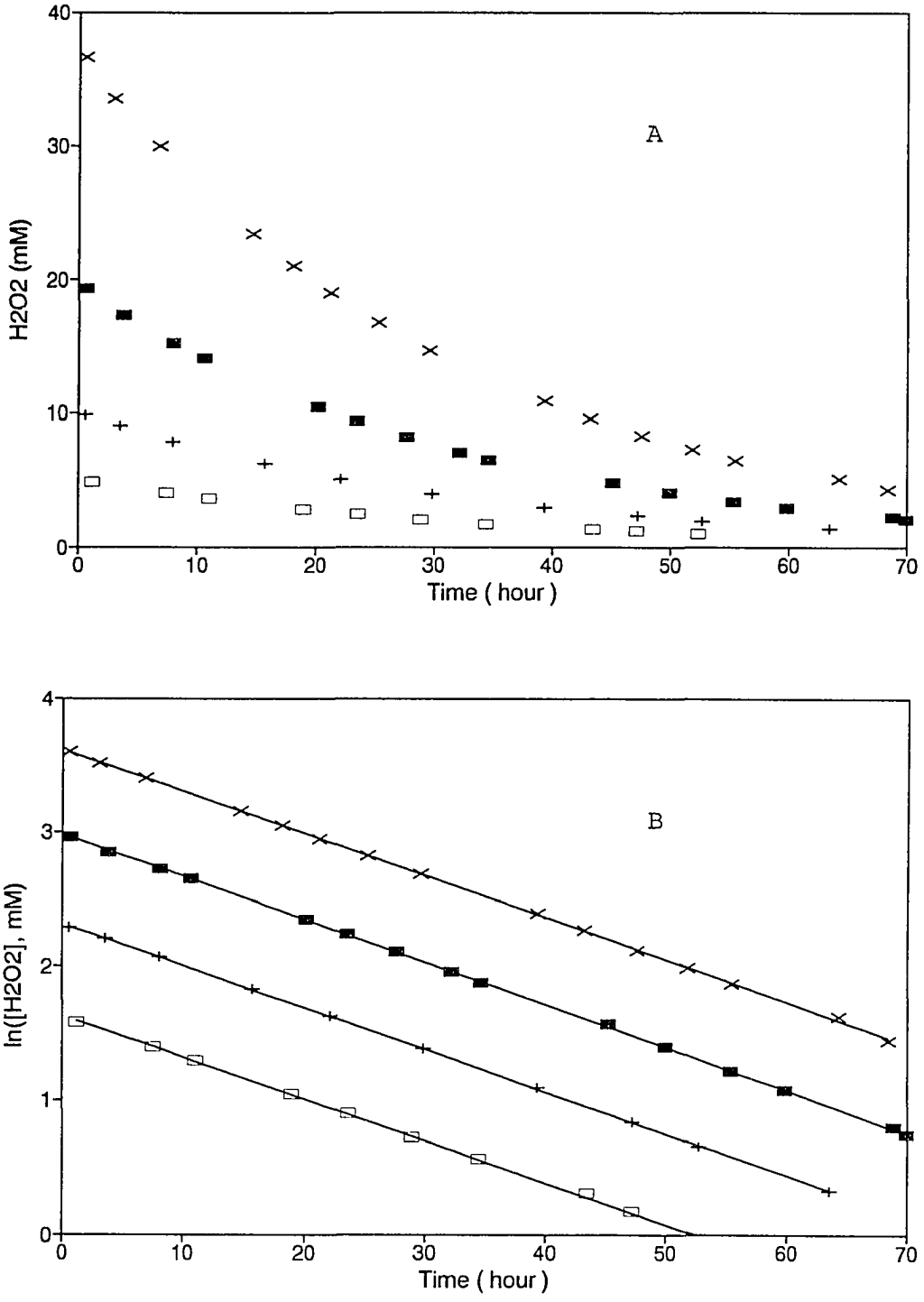

Fig. IV-3-2
The concentration of hydrogen peroxide during the reaction. A: [H_2O_2, mM] vs time. B: ln([H_2O_2], mM) vs time. The initial concentrations of iodide were 0.5 mM. The initial concentrations of hydrogen peroxide were 5 mM (□), 10 mM (+), 20 mM (▪), and 40 mM (×).

concentration of hydrogen peroxide of 5 mM. Again, while the concentration of hydrogen peroxide decreased exponentially with time, there was no detectable change in the concentration of iodide at all initial concentrations of iodide. No loss of iodide was observed even when the loss of hydrogen peroxide has far exceeded the initial concentration of iodide. Thus, the reaction between hydrogen peroxide and iodide is a pseudo-catalytic reaction with respect to iodide. The rate constant k_1 increases with an increasing initial concentration of iodide, I° in mM, such that

$$k_1 = (10^A)\ ([I^-]^\circ)^B$$

or

$$\log k_1 = A + B \log [I^-]^\circ \qquad (2)$$

where A and B are constants. At 20°C and a pH of 8, A and B are equal to -(1.23±0.01) and (0.93±0.01) respectively and the correlation coefficient was 0.9995 (Fig. IV-3-3). Since B is close to unity, k_1 will be approximately directly proportional I° as reported by Cadle and Huff (1950) for the reactions between organic peroxides and iodide.

When the dependence of the disappearance of hydrogen peroxide on the concentration of hydrogen peroxide and iodide is taken together, the rate law may be re-written as:

$$-d[H_2O_2]/dt = k_1\ [H_2O_2] = (k\ [I^-])\ [H_2O_2] \qquad (3)$$

where $[I^-]$ is the concentration of iodide which is invariant,

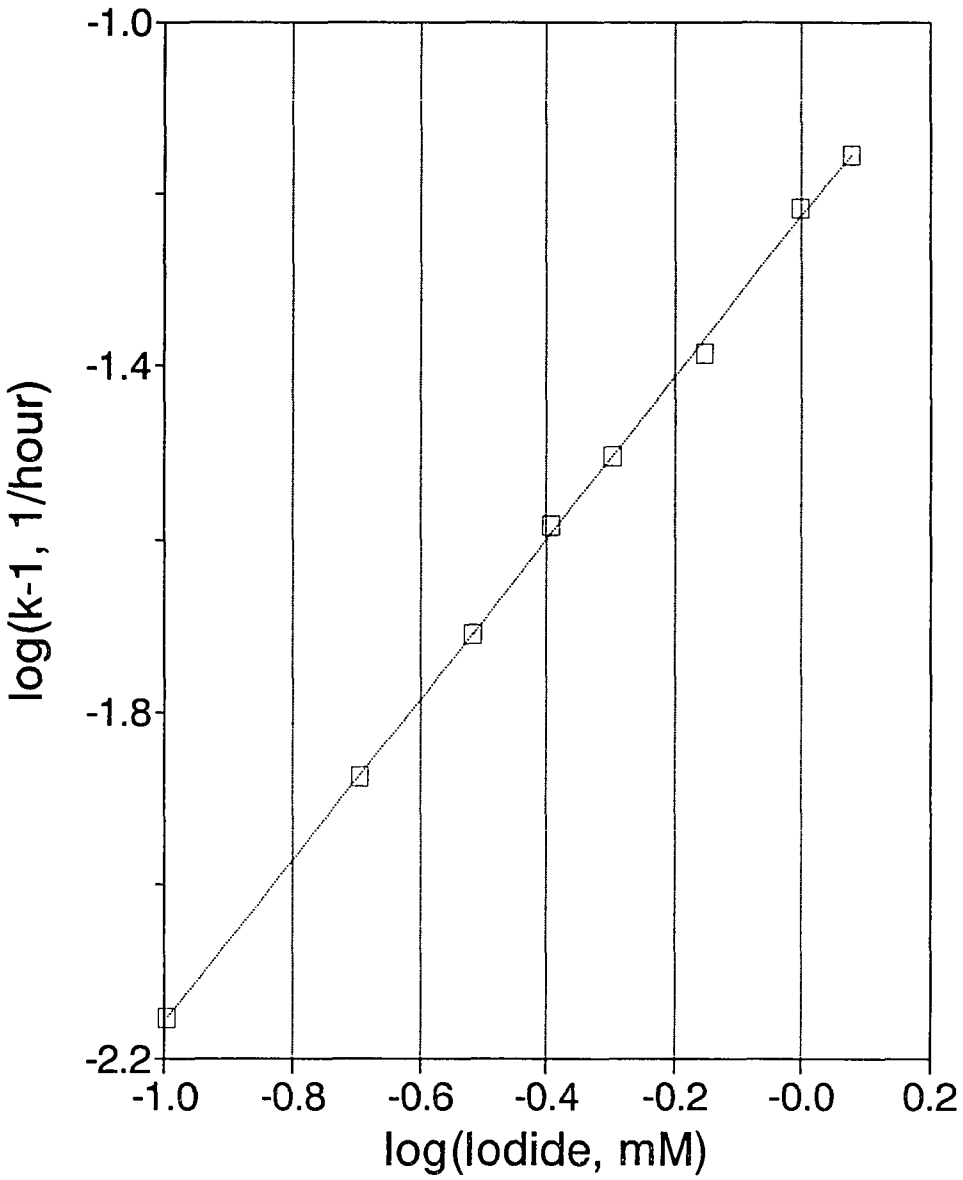

Fig. IV-3-3

The relationship of rate constant, $\log(k_1)$, to the concentrations of iodide, $\log(I^\circ)$, where I° is the initial concentration of iodide.

and k, the pseudo second order rate constant, is 0.059±0.001 $(mM\ hour)^{-1}$ at a pH of 8.0 and a temperature of 20°C in artificial seawater.

Mechanistic considerations and the meaning of k

Based on previous studies on the reaction between hydrogen peroxide and iodide in pure solutions (Bray and Liebhafsky, 1931; Eigen and Kustin, 1962), the reaction may follow a scheme as shown in Fig. IV-3-4. In this scheme, iodide is oxidized by hydrogen peroxide to form I_2:

$$H_2O_2 + 2\ I^- + 2\ H^+ \rightarrow I_2 + 2\ H_2O \qquad (4)$$

with a rate constant k_A. Molecular iodine may then be reduced back to iodide either by direct reduction by hydrogen peroxide:

$$I_2 + H_2O_2 \rightarrow 2\ I^- + 2\ H^+ + O_2 \qquad (5)$$

with a rate constant k_B, or, by its rapid hydrolysis to form HIO:

$$I_2 + H_2O \rightarrow HIO + I^- + H^+ \qquad (6)$$

and the ensuing reduction of HIO to iodide by hydrogen peroxide:

$$HIO + H_2O_2 \rightarrow I^- + H_2O + O_2 + H^+ \qquad (7)$$

with a rate constant k_C. In either case, one mole of hydrogen peroxide is consumed in the oxidation of 2 moles of iodide to form one mole of I_2 and an additional mole of hydrogen peroxide is consumed to reduce it back to form 2 moles of iodide. The resulting overall reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

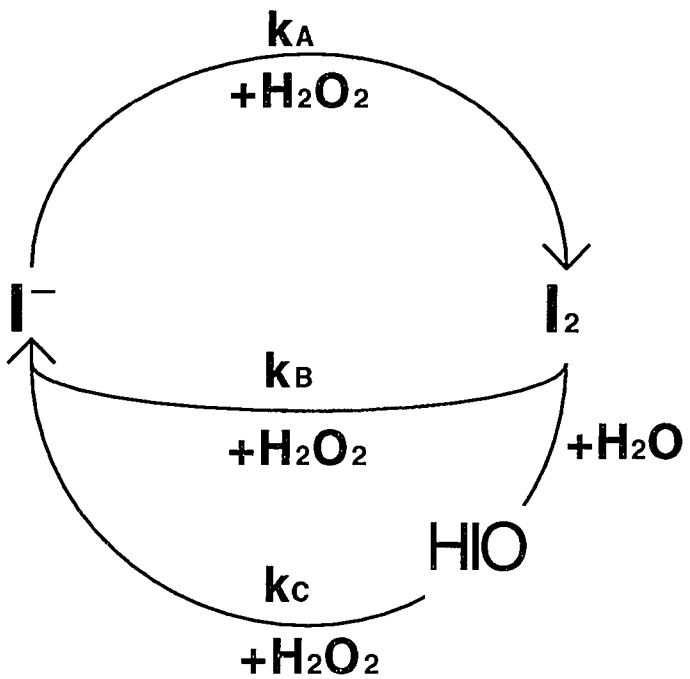

Fig. IV-3-4

Reactions of hydrogen peroxide and iodine species in neutral solution. See the text.

is a pseudo-catalytic decomposition of hydrogen peroxide. Assuming that the orders of the reactions are x with respect to I^-, y with respect to I_2, and z with respect to HIO, the rate law of Eq. 1 may be rewritten as:

$$-d[H_2O_2]/dt = k_1[H_2O_2] = (k_A[I^-]^x + k_B[I_2]^y + k_C[HIO]^z)\ [H_2O_2]$$

or

$$-d[H_2O_2]/dt = (k_A[I^-]^x)[H_2O_2] + (k_B[I_2]^y + k_C[HIO]^z)[H_2O_2]. \quad (8)$$

The first term on the right side of the above equation (Eq. 8) represents the consumption of iodide and the second term represents the production of iodide. Since the concentration of iodide did not change with time (Fig. IV-3-1), I_2 and HIO must be reduced instantaneously to iodide by hydrogen peroxide once they are produced. Furthermore, the rate of consumption and production of iodide must be identical. Thus,

$$(k_A[I^-]^x) = (k_B[I_2]^y + k_C[HIO]^z)\ ;$$

$$-d[H_2O_2]/dt = (k_A[I^-]^x)[H_2O_2] + (k_B[I_2]^y + k_C[HIO]^z)[H_2O_2]$$

$$= 2\ k_A\ [I^-]^x[H_2O_2]. \quad (9)$$

By comparing Eq. 9 with Eq. 3, one may conclude that

$$x = 1,$$

and,
$$k_A = k/2 = k_1/(2\ [I^-]) \quad (10).$$

While k in Eq. 3 represents the overall consumption of

hydrogen peroxide resulted from the oxidation of iodide and the reduction of iodine and HIO, k_A in Eq. 9 represents the oxidation of iodide by hydrogen peroxide alone. Therefore, k_A may be estimated to be 0.030±0.001 $(mM\ hour)^{-1}$ at pH 8.0 and 20°C.

The dependence of rate constant k_A on temperature

The rate constant, k_1, was determined in artificial seawater at 9.8°C, 20.0°C to 30.1°C, at a pH of 8 and at initial concentrations of iodide and hydrogen peroxide of 0.5 and 5 mM respectively. The results and the corresponding k_1, k, k_A and $\log(k_A)$ are listed in Table IV-3-1. Log k_A was linearly related to the reciprocal of the absolute temperature (1/T) (Fig. IV-3-5) within this range of temperature so that:

$$\log k_A = (8.80\pm0.01) - (3018\pm34)\ (1/T). \qquad (11)$$

The activation energy for the reaction between hydrogen peroxide and iodide may then be estimated to be:

$$\Delta E = 57.6\pm0.7\ \ kJ/mole.$$

This activation energy is very similar to the value of 53.1 kJ/mole which was reported for the reaction between ethyl peroxide and iodide (Cadle and Huff, 1950).

The variation of rate constant k_A with salinity

The rate constant, k_1, was determined as a function of salinity from 0 to 35.7 psu at 20°C and pH 8.0 in various

Table IV-3-1: The effect of temperature on the rate constant of the reaction between iodide and hydrogen peroxide

T (K)	k_1 (hour^{-1})	k (=$k_1/[I^-]^\circ$)	k_A (=k/2)	log(k_A)
282.95	0.0138	0.0274	0.0138	-1.86
282.95	0.0138	0.0274	0.0138	-1.86
293.15	0.0312	0.0619	0.0312	-1.51
303.25	0.0715	0.1419	0.0715	-1.15
303.25	0.0712	0.1413	0.0715	-1.15

$[H_2O_2]^\circ$ = 5 mM, $[I^-]^\circ$ = 0.504 mM, pH = 8.0.

Artificial seawater.

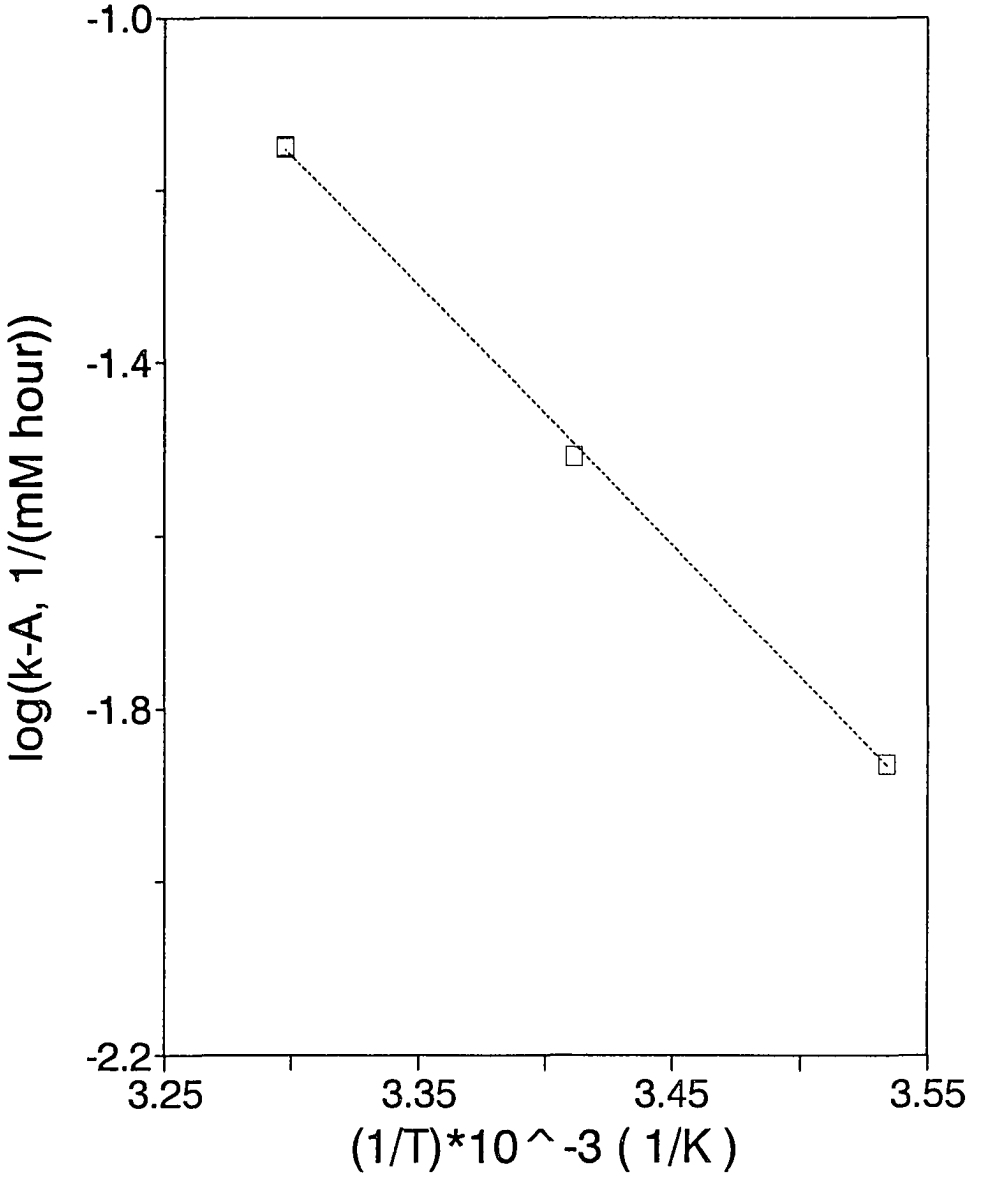

Fig. IV-3-5

The rate constant, $\log(k_A)$, versus the reciprocal of temperature, 1/T.

dilutions of artificial seawater initially containing 0.5 mM of iodide and 5 mM of hydrogen peroxide. The results and the corresponding k_A and log k_A are listed in Table IV-3-2. Log k_A is linearly related to salinity, S, according to the following relationship (Fig. IV-3-6):

$$\log k_A = -(1.56\pm0.00) + (0.0018\pm0.0001)\ S \qquad (12)$$

with a correlation coefficient of 0.984. The effect of salinity on the k_A is small. Between 0 psu and full strength artificial seawater at 35.7 psu, it increases only by 17%.

The dependence of rate constant k_A on pH

The rate constant, k_1, was determined between pH 7 and 9, the oceanographic range of pH, at 20°C in artificial seawater initially containing 0.5 mM of iodide and 5 to 40 mM of hydrogen peroxide. The results are shown in Table IV-3-3. The rate constant, expressed as log k_A, was approximately independent of the initial concentration of hydrogen peroxide and pH between pH 7 and 9. Cadle and Huff (1950) reported that the rate of the reaction between hydrogen peroxide and iodide was independent of pH between pH 4 and 7. This work further extends the independence of the rate constant on pH to pH 9.

Table IV-3-2: The effect of salinity on the rate constant of the reaction between iodide and hydrogen peroxide

Salinity (psu)	k_1 (hour^{-1})	k (=$k_1/[I^-]^\circ$)	k_A (=k/2)	log(k_A)
35.686	0.0334	0.0649	0.0325	-1.49
28.549	0.0318	0.0617	0.0309	-1.51
21.412	0.0309	0.0600	0.0300	-1.52
14.274	0.0303	0.0588	0.0294	-1.53
7.137	0.0294	0.0571	0.0286	-1.54
0.000	0.0285	0.0553	0.0277	-1.56

$[H_2O_2]^\circ$ = 5 mM, $[I^-]^\circ$ = 0.515 mM, pH = 8.0, t = 293.15 K.

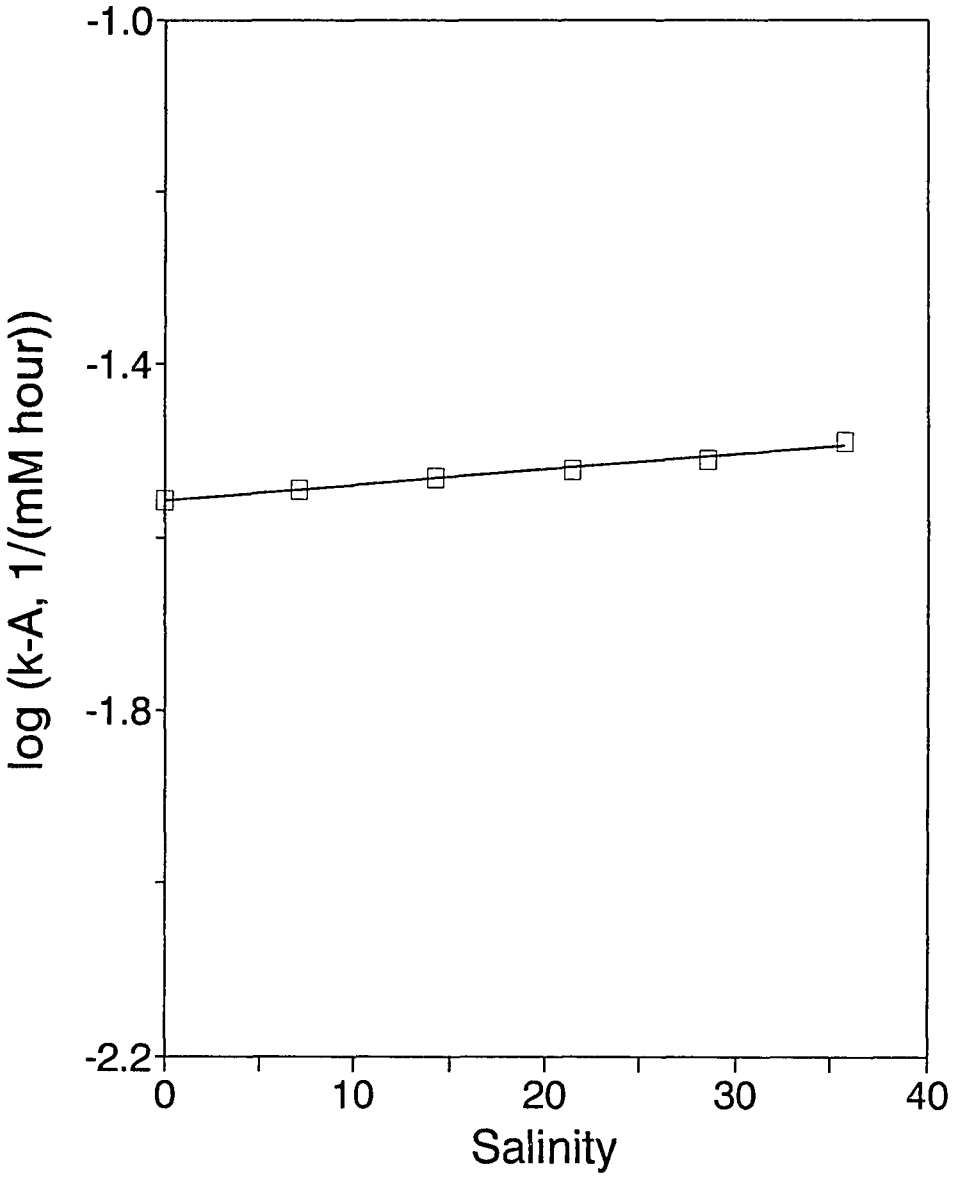

Fig. IV-3-6

Dependence of rate constant, log(k_A), on salinity.

Table IV-3-3: The effect of pH on the rate constant of the reaction between iodide and hydrogen peroxide

pH	$[H_2O_2]^\circ$ (mM)	k_1 ($hour^{-1}$)	k_A	$\log(k_A)$
6.65	20	0.0304	0.0302	-1.82
6.92	5	0.0305	0.0303	-1.82
6.92	20	0.0306	0.0304	-1.82
7.82	40	0.0314	0.0312	-1.81
7.89	10	0.0314	0.0312	-1.81
7.95	5	0.0312	0.0310	-1.81
7.95	10	0.0317	0.0315	-1.80
7.96	18	0.0308	0.0306	-1.81
7.99	10	0.0313	0.0311	-1.81
8.01	10	0.0316	0.0314	-1.80
8.09	20	0.0318	0.0316	-1.80
8.75	5	0.0317	0.0315	-1.80
8.94	16	0.0314	0.0312	-1.81
9.09	20	0.0334	0.0331	-1.78

$[I^-]^\circ$ = 0.504 mM, t = 293.15 K.

Artificial seawater.

The catalytic effect of molybdate on the reaction between hydrogen peroxide and iodide

Molybdenum in the form of molybdate is a trace element that has been known to catalyze the reaction between hydrogen peroxide and iodide (Smith and Kilford, 1976). The catalytic effect of molybdenum on this reaction has been used for trapping hydrogen peroxide in a solution of iodide for the determination of hydrogen peroxide by iodometry. Molybdenum is a quasi-conservative trace element in seawater which can be found in the form of molybdate in a concentration of about 0.1 μM, a concentration that is similar to that of iodide and hydrogen peroxide in the surface oceans. In order to investigate the possible catalytic effect of molybdate on the reaction between hydrogen peroxide and iodide, k_I was determined in artificial seawater in the presence of 0 to 480 μM of ammonium molybdate at 20°C, a pH of 8 and initial concentration of iodide and hydrogen peroxide of 0.5 mM and 5 mM, respectively. As a control, the rate of auto-decomposition of hydrogen peroxide was also determined as a function of the concentration of molybdate. The results are shown in Table IV-3-4. With the presence of molybdate, the rate of auto-decomposition of hydrogen peroxide can also be accelerated significantly. Between 0 and 481 μM of molybdate, the rate of auto-decomposition increased by about 320 times. However, there was a threshold concentration of about 1 μM below which the catalytic effect was not evident and the rate constant stayed the same. The rate constant, k_A, of the

Table IV-3-4: The effect of molybdate on the rate constant of the reaction between iodide and hydrogen peroxide

Molybdate (μM)	K_1(s) (hour^{-1})	K_1(c) (hour^{-1})	k_1	log(k_A)
481	0.8460	0.1626	0.6834	-0.17
384	0.7073	0.1273	0.5800	-0.24
288	0.5630	0.0899	0.4731	-0.33
192	0.3964	0.0490	0.3474	-0.46
97	0.2146	0.0157	0.1989	-0.70
9.7	0.0521	0.0029	0.0492	-1.31
0.97	0.0341	0.0005	0.0336	-1.48
0.097	0.0317	0.0005	0.0312	-1.51
0.049	0.0316	0.0004	0.0312	-1.51
0	0.0312	0.0005	0.0307	-1.52

$[H_2O_2]^\circ$ = 5 mM, $[I^-]^\circ$ = 0.502 mM, pH = 8.0, t = 293.15 K. Artificial seawater.

k_1(s) was the first-order rate constant for samples which contained iodide. k_1(c) was the first-order rate constant for controls which did not contain iodide.

$k_1 = k_1(s) - k_1(c)$.

reaction between hydrogen peroxide and iodide in the presence of molybdate was estimated after the rate constant of auto-decomposition at the same concentration of molybdate has been subtracted from the total rate (Table IV-3-4). Again, while the reaction rate increased with increasing concentration of molybdate, there was a threshold concentration below which the catalytic effect of molybdate was negligible. Log k_A increased linearly with log [Mo], where [Mo] is the concentration of added molybdate in μM, above a log [Mo] of 1 which is equivalent to a concentration of molybdate of 10 μM. Below 10 μM of molybdate, the catalytic effect cannot be detected. Thus, at the oceanic concentration of molybdate of 0.1 μM, molybdate has little effect on the reaction between hydrogen peroxide and iodide.

The total rate constant

The combining effect of salinity and temperature on the rate constant, k_A, in marine waters between pH 7 and 9 is given by the following equation:

$$\log k_A=(8.83\pm0.09)-(3047\pm25)(1/T)+(0.0017\pm0.0001)S. \quad (13)$$

where k_A is in $(\text{mM hour})^{-1}$ and the standard deviation in the estimation of log k_A is 0.12. It is not necessary to include any term in the equation to take into account the effect of pH and molybdate since the constant is independent of pH within this range of pH and is not affected by the presence of

molybdate at the concentrations found in seawater.

In a solution containing 140 mM of iodide and 0.15 mM of hydrogen peroxide, Cadle and Huff (1950) reported a rate constant for the disappearance of hydrogen peroxide of 0.0909 min^{-1} at 30°C. Normalized for the effect of the concentration of iodide, this rate constant can be converted to 0.000649 $(mM\ min)^{-1}$ or 0.039 $(mM\ hour)^{-1}$. The salinity of their test solution was not given. At any rate, the k_A at 30°C may be estimated from equation (13) to be 0.060 to 0.069 $(mM\ hour)^{-1}$. These values are comparable to but slightly higher than that reported by Cadle and Huff (1950). The discrepancy is small and may just be the result of the experimental uncertainties. However, it may also be a result of the difference in the experimental setup. In the study of Cadle and Huff (1950), the disappearance of hydrogen peroxide was inferred from the amount of tri-iodide formed by the complexation of the molecular iodine produced in the reaction with excess iodide. The further reduction of molecular iodine to iodide by hydrogen peroxide was not taken into consideration. Any loss of molecular iodine would have resulted in an underestimation of hydrogen peroxide consumed and a reduced rate constant.

Ramifications of the marine geochemistry of hydrogen peroxide and iodide

In the surface seawater, the concentration of hydrogen peroxide is about 0.3 μM. The concentration of iodide is about 0.2 μM. If the results from this study are extrapolated to

these conditions, the rate of disappearance of hydrogen peroxide in seawater at a salinity of 35 psu, a pH of 8 and a temperature of 20°C is given by:

$$-d[H_2O_2]/dt = k_A[I^-][H_2O_2]$$
$$= 0.030 \times 0.0002[H_2O_2] = 6 \times 10^{-6}[H_2O_2]$$

where the concentrations are in mM and the time in hour. Based on this rate law, the half life of hydrogen peroxide can be calculated as about 13 years in seawater. Since the half life of hydrogen peroxide in seawater is on the order of days or weeks (Zika *et al.*, 1985a; Johnson *et al.* 1989), it is not likely that the geochemistry of hydrogen peroxide in seawater is affected by its reaction with iodide.

This study indicates that iodide does react with hydrogen peroxide in seawater. The net result is a pseudo-catalytic decomposition of hydrogen peroxide. There is no evidence to suggest that iodide may be oxidized to iodate in the process. However, hypoiodite and/or molecular iodine may be formed as intermediates[2]. In the experiments reported here where elevated concentrations of hydrogen peroxide, mM level, were used, the excess hydrogen peroxide dominates the subsequent fate of the molecular iodine and/or hypoiodite by reducing

[2] Wong (1980, 1982) suggested that the hydrolysis of molecular iodine to form hypoiodite at the pH of seawater is almost instantaneous. Thus, even if molecular iodine is formed, the subsequent chemistry may be dominated by reactions involving hypoiodite.

them back into iodide. However, in seawater, where the concentration of hydrogen peroxide is much lower, μM to sub-μM level, other competing reactions may occur. First, molecular iodine and hypoiodite may be reduced back to iodide, either by hydrogen peroxide or other reducing substance. This process will have little effect on the cycling of iodine species in seawater. Secondly, hypoiodite may react with dissolved organic material to form iodinated organic compounds. Harvey (1980) has found such compounds in sediments and suggested that the formation of these compounds must involve iodine in the +1 oxidation state such as hypoiodite. More recently, Francois (1987) also suggested the incorporation of iodine into organic molecules by reactions involving hypoiodite. However, hypoiodite has never been detected in seawater. Thus, this reaction route would provide the necessary reactant for iodinated organic compounds to be formed. Little is known about the chemistry of organic iodine in the oceans. It is a small pool of total dissolved iodine (Truesdale, 1975). The subsequent fate of organic iodine is unknown. However, iodinated organic compounds are considered the least stable among halogenated organic compounds. They are more likely to decompose to form iodide than to undergo auto-oxidation to form iodate. Thus, while this reaction route may potentially have a significant impact on the chemistry of organic iodine in the oceans, it may have little influence on the conversion of iodide to iodate. Thirdly, hypoiodite may further disproportionate to form iodate. This reaction is probably

slow relative to the other reactions that may consume hypoiodite (Truesdale, 1974). However, the end product, iodate, is stable in seawater once it is formed and this third reaction route may be important in the conversion of iodide to iodate in seawater.

If the proposed reaction scheme for the reaction between hydrogen peroxide and iodide is correct, the consumption of one mole of hydrogen peroxide will involve two moles of iodide. Then, the rate of the chemical cycling of iodide will be:

$$-d[I^-]/dt = -2(d[H_2O_2]/dt)$$
$$= 2(k_A[I^-][H_2O_2]).$$

At 20°C, a pH of 8 and a concentration of hydrogen peroxide of 0.3 μM,

$$-d[I^-]/dt = 2(0.030 \times 0.0003)\ [I^-]$$
$$= (1.8 \times 10^{-5})\ [I^-]$$

where the concentrations are in mM and time in hour. The turnover half life of iodide in seawater will then be about 4 years. At a concentration of iodide in seawater of 0.2 μM, the removal rate of iodide in seawater is 0.03 μM year^{-1}. As a comparison, the rate of production of iodate in deep seawater by remineralization has been estimated to be about 2.4×10^{-5} μM year^{-1} (Wong and Brewer, 1974). Thus, even if only a fraction of a percent of the iodide that has been cycled through the reaction scheme is ultimately converted into iodate, the resulting rate of conversion of iodide to iodate may still be geochemically significant.

CONCLUSION

Hydrogen peroxide oxidizes iodide to, mostly likely, molecular iodine and/or hypoiodite in the medium of artificial seawater at a neutral condition. At a low concentration of iodide (< 1.2 mM), hydrogen peroxide reduces the product back to iodide immediately after iodide is oxidized. Hydrogen peroxide disappears, but the concentration of iodide remains unchanged. The net result is a pseudo-catalytic decomposition of H_2O_2 by iodide. The rate law may be expressed as:

$$-d[H_2O_2]/dt = (2k_A)\ [I^-]\ [H_2O_2]$$

where k_A (in $mM^{-1}hour^{-1}$) is the rate constant for the oxidation of iodide by H_2O_2 alone, $[I^-]$ is the initial concentration of iodide and $[H_2O_2]$ is the concentration of hydrogen peroxide at any time t. Within the oceanographic range of pH 7 to pH 9, the general relationship between the rate constant and temperature and salinity is given by the equation:

$$\log(k_A) = (8.83\pm0.09) - (3047\pm25)/T + (0.0017\pm0.0001)\times S$$

where S is salinity in psu and T is the absolute temperature.

The results are applied to the seawater system. The reaction between hydrogen peroxide and iodide is negligible to the geochemistry of hydrogen peroxide. On the other hand, iodide may be oxidized to hypoiodite in seawater by hydrogen peroxide. This hypoiodite may be the precursor of organic iodine in seawater, and/or may be the intermediate for the conversion of iodide to iodate in seawater.

CHAPTER FIVE

CONCLUSIONS AND DIRECTIONS FOR FUTURE RESEARCH

CONCLUSIONS

The analytical chemistry of hydrogen peroxide in natural waters

Hydrogen peroxide from μM to sub-mM level can be determined by square wave voltammetry. For most natural waters, this method is not affected by the problems of pH and ionic strength. Hydrogen peroxide at sub-μM level can be determined by spectrophotometry and fluorometry. In both modes, the pH of the samples need to be well controlled. In the former mode, the pH is controlled by adding the pH-buffer solution. In the latter mode, the method of standard internal addition is adopted to overcome the pH problem. The fluorometric method has the advantage that the sample, after hydrogen peroxide in it has reacted with added reagents, can be stored for a period of time. The spectrophotometric method has the advantage that the instrument (i.e. spectrophotometer) is more wildly available.

The geochemistry of iodine in the coastal environment

(1) There can be significant seasonal variations in the speciation of iodine in the coastal marine environment. In the surface water of the Chesapeake Bay, the ratio of the concentration of iodate to iodide varies seasonally. While iodate may be present in significant concentrations and may even be the dominant form of inorganic iodine in the Winter, iodide is the dominant species in most of the rest of the year. Iodide can be converted to organic iodine and this is particularly conspicuous in the Spring when the concentration of "organic" iodine reaches a maximum and it may constitute up to 35% of total iodine.

In the deep water, the concentration of inorganic iodine is significantly higher in the Summer than that the other three seasons. The sediment may act as a source of iodide to the deep water under the reducing conditions in the Summer. However, under the oxidizing conditions in the Winter, the sediment may actually act as a sink and removed iodate from the water column.

(2) The coastal waters may act as a geochemical reactor that alters the speciation of iodine and may play a role in the global geochemical cycling of different species of iodine. During tidal mixing, iodate-rich Atlantic water is brought into the Chesapeake Bay where it is reduced to iodide. The iodide-rich water in the Bay is then returned to the Atlantic. Thus, the ocean margin may act as a substantial source of iodide to the ocean interior. *In situ* reduction of iodate to

iodide may not be the only mechanism for explaining the occurrence of iodide in the open oceans.

The reaction between iodide and hydrogen peroxide

(1) The net result of the reaction between iodide and hydrogen peroxide is a pseudo-catalytic accelerated decomposition of hydrogen peroxide. The rate law of the reaction is:

$$-d[H_2O_2]/dt = 2k_A [I^-] [H_2O_2]$$

where k_A is rate constant for the oxidation of iodide, $[I^-]$ is the initial concentration of iodide which remains invariant and $[H_2O_2]$ is the concentration of hydrogen peroxide at time t.

(2) Under the conditions found in surface seawater, the reaction between hydrogen peroxide and iodide is not a major mechanism for controlling the decomposition of hydrogen peroxide in seawater. On the other hand, hypoiodite may be formed as an intermediate in the reaction and, potentially, it may play a significant role in the geochemistry of iodinated organic compounds in the oceans and may contribute to the conversion of iodide to iodate in seawater.

FUTURE RESEARCH

Although the seasonal variations in the speciation of iodine were observed in the Chesapeake Bay, the factors controlling the seasonal variations still remain poorly known. Some of the questions that have yet to be resolved are:

(A) How is iodate reduced to iodide in the coastal areas such as the Chesapeake Bay?

Iodate may be reduced to iodide by a biologically mediated reduction, by reacting with terrestrial reducing substance, or by reacting with reducing substance that are diffused into the deep water from the sediments. Evidence needs to be found to evaluate the relative importance of these three possible mechanisms.

(B) What is the flux of iodide from the coastal area such as the Chesapeake Bay to the oceans?

Traditionally, the occurrence of iodide in the open oceans is explained by the *in situ* reduction of iodate to iodide. The flux of iodide from the coastal areas is another source whose quantitative importance is still unknown.

(C) Where, how, and at what rate is iodide oxidized to iodate in the seawater?

Since the deep ocean is almost free of iodide while iodide is almost ubiquitous in the surface oceans, somewhere during the global circulation, iodide must be oxidized to iodate. Much remains unknown about this reaction.

Appendix A: Station locations, depth and data from Chesapeake Bay.

St	D	T	Sigma-t	S	DO	I	IO3	I+IO3	Total	Latitude		Longitude		Date
	m			psu	uM	nM	nM	nM	nM	N		W		
	Spring of 1990													
A	0	18.4	7.5	11.682	272	59	ND	59	119	38	20.2	76	18.0	5/18/90
A	2	18.4	7.4	11.624	272	71	ND	90	195	38	20.2	76	18.0	5/18/90
A	5	18.4	7.8	12.104	277	64	ND	64	156	38	20.2	76	18.0	5/18/90
A	7	17.4	8.5	12.786	250	68	ND	68	134	38	20.2	76	18.0	5/18/90
A	10	16.0	11.1	15.804	111	102	ND	120	171	38	20.2	76	18.0	5/18/90
A	12	14.3	11.7	16.158	40	84	ND	84	172	38	20.2	76	18.0	5/18/90
A	15	14.3	12.7	17.455	10	103	ND	106	167	38	20.2	76	18.0	5/18/90
A	17	14.4	13.7	18.836	0	184	ND	184	175	38	20.2	76	18.0	5/18/90
A	20	14.5	13.8	19.039	0	194	ND	197	155	38	20.2	76	18.0	5/18/90
A	25	14.3	14.2	19.507	0	205	ND	205	203	38	20.2	76	18.0	5/18/90
A	30	14.0	14.6	19.975	0	220	ND	220	213	38	20.2	76	18.0	5/18/90
A	35	13.8	14.8	20.104	0	240	ND	240	192	38	20.2	76	18.0	5/18/90
A	38	13.8	14.7	20.084	0	238	ND	238	186	38	20.2	76	18.0	5/18/90
S1	0			11.681		41	ND	41	102	38	13.5	76	16.5	5/18/90
S2	0			12.492		37	ND	37	119	38	8.0	76	14.5	5/18/90
804	4	18.0	8.4	12.818	316	101	ND	118		38	3.9	76	13.5	5/18/90
804	10	17.0	9.7	14.231	200	75	ND	92		38	3.9	76	13.5	5/18/90
804	13	16.4	12.0	17.057	69	105	33	138		38	3.9	76	13.5	5/18/90
804	19	15.6	13.1	18.340	11	451	ND	457		38	3.9	76	13.5	5/18/90
S3	0			11.730		62	ND	62	97	37	56.5	76	10.8	5/18/90
S4	0			12.343		41	ND	41	157	37	49.1	76	10.7	5/18/90
744	4	18.7	9.1	13.922	284	152	33	186		37	44.1	76	11.9	5/18/90
744	7	18.6	10.7	16.021	206	55	56	111		37	44.1	76	11.9	5/18/90
744	10	18.2	10.9	16.141	197	72	60	132		37	44.1	76	11.9	5/18/90
744	13	18.0	12.3	17.904	120	110	66	176		37	44.1	76	11.9	5/18/90
744	16	17.8	12.5	18.187	137	92	72	164		37	44.1	76	11.9	5/18/90
744	19	17.1	12.7	18.193	116	90	68	158		37	44.1	76	11.9	5/18/90
744	22	17.0	12.8	18.308	10	227	56	283		37	44.1	76	11.9	5/18/90
744	25	16.0	13.3	18.787	7	213	36	249		37	44.1	76	11.9	5/18/90
S5	0			12.283		85	ND	85	156	37	37.0	76	9.4	5/18/90
S6	0			16.299		78	50	128	212	37	30.6	76	7.2	5/18/90
S7	0			15.721		77	49	127	223	37	24.6	76	5.1	5/18/90
S8	0			17.852		86	50	136	258	37	13.1	76	6.8	5/18/90
	Fall of 1991													
1	0			23.795		216	148	363		37	12.9	76	19.4	10/8/91

St	D	T	Sigma-t	S	DO	I	IO3	I+IO3	Total	Latitude		Longitude		Date
	m			psu	uM	nM	nM	nM	uM	N		W		
	Fall of 1991													
2	0			24.322		199	85	284		37	14.0	76	16.1	10/8/91
3	0			24.755		194	83	278		37	15.9	76	17.5	10/8/91
4	0			24.399		199	115	314		37	17.9	76	19.3	10/8/91
5	0			23.292		205	131	336		37	19.6	76	20.8	10/8/91
6	0			24.389		189	101	290		37	17.5	76	18.6	10/8/91
7	0			24.784		202	102	304		37	16.6	76	15.8	10/8/91
D8	0			24.951		208	67	275		37	19.6	76	12.5	10/8/91
D8	1	20.3	16.8	24.856		193	70	263		37	19.6	76	12.5	10/8/91
D8	2	20.3	16.8	24.843	228	226	68	295		37	19.6	76	12.5	10/8/91
D8	3	20.3	16.8	24.865	227	217	71	288		37	19.6	76	12.5	10/8/91
D8	7	20.2	16.8	24.915	232	225	80	305		37	19.6	76	12.5	10/8/91
D8	9	20.2	16.8	24.951	223	208	73	281		37	19.6	76	12.5	10/8/91
14	0			24.618		180	78	258		37	20.4	76	8.4	10/8/91
15	0			24.653		194	73	267		37	20.9	76	5.1	10/8/91
D16	0			24.923		178				37	21.0	76	4.4	10/8/91
D16	3	20.3	17.2	25.189	249	215				37	21.0	76	4.4	10/8/91
D16	6	20.3	17.2	25.507		183	80	262		37	21.0	76	4.4	10/8/91
D16	8	20.4	17.4	25.497		170	82	253		37	21.0	76	4.4	10/8/91
D16	10	20.4	17.4	25.516		244	94	339		37	21.0	76	4.4	10/8/91
D16	12	20.4	17.4	25.577		297	82	379		37	21.0	76	4.4	10/8/91
22	0			25.357		197				37	15.8	76	4.9	10/8/91
23	0			25.553		210	96	305		37	14.0	76	5.1	10/8/91
24	0			25.183		133	91	224		37	12.8	76	9.7	10/8/91
25	0			25.167		210	85	295		37	12.1	76	12.4	10/8/91
26	0			24.731		194	65	259		37	8.5	76	11.0	10/8/91
27	0			25.196		236	73	309		37	5.8	76	10.1	10/8/91
28	0			24.847		175	80	254		36	58.2	76	11.0	10/9/91
29	0			25.658		212	80	292		37	0.9	76	11.2	10/9/91
30	0			24.994		212	59	271		37	3.0	76	11.5	10/9/91
31	0			26.465		200	76	276		37	3.1	76	7.2	10/9/91
32	0			28.411		232	122	354		37	2.5	76	3.8	10/9/91
33	0			31.453		181				37	3.3	75	58.6	10/9/91
				28.818		208				37	0.1	76	0.5	10/9/91
				27.392		204				36	58.5	76	1.6	10/9/91
36	0			26.078		206	98	303		36	58.4	76	6.9	10/9/91

St	D	T	Sigma-t	S	DO	I	IO3	I+IO3	Total	Latitude		Longitude		Date
	m			psu	uM	nM	nM	nM	uM	N		W		
Winter of 1992														
1	0			22.998		145				36	58.2	76	11.5	1/8/92
2	0			24.026		165				37	1.3	76	12.3	1/8/92
3	0			23.528		158				37	4.2	76	12.8	1/8/92
4	0			23.248		171	74	245		37	10.0	76	16.1	1/8/92
5	0			23.123		149	72	221		37	12.8	76	19.5	1/8/92
6	0			23.051		156	70	226		37	19.5	76	20.8	1/8/92
7	0			23.053		144				37	17.7	76	18.6	1/8/92
8	0			22.839		152	74	226		37	16.2	76	17.1	1/8/92
9	0			22.072		141	60	201		37	15.9	76	15.7	1/8/92
10	0			21.874		149	64	213		37	18.0	76	13.9	1/8/92
D11	0			22.231		134	84	218		37	19.3	76	12.9	1/8/92
D11	1	6.7	18.9	22.360	338	204	90	294		37	19.3	76	12.9	1/8/92
D11	3	6.7	17.5	22.173	337	170	98	269		37	19.3	76	12.9	1/8/92
D11	5	6.7	17.5	22.248		158	108	266		37	19.3	76	12.9	1/8/92
D11	7	6.7	17.5	21.546	330	155	73	228		37	19.3	76	12.9	1/8/92
D11	8	6.7	17.5	21.416		148	95	243		37	19.3	76	12.9	1/8/92
17	0			20.804		138	76	215		37	28.5	76	10.0	1/8/92
18	0			21.411		138	75	213		37	26.0	76	8.1	1/8/92
19	0			21.920		142	78	220		37	23.6	76	6.4	1/8/92
D20	0			25.110		149	116	266		37	21.1	76	4.5	1/8/92
D20	3	7.0	19.7	25.144		725	103	828		37	21.1	76	4.5	1/8/92
D20	6	6.9	20.0	25.687	329	215				37	21.1	76	4.5	1/8/92
D20	9	7.2	21.0	27.211	317	192				37	21.1	76	4.5	1/8/92
D20	14	7.3	21.5	27.650		172	143	315		37	21.1	76	4.5	1/8/92
26	0			23.921		135	90	225		37	16.2	76	4.9	1/8/92
27	0			23.351		143	97	240		37	14.0	76	5.0	1/8/92
28	0			22.637		123	72	195		37	13.1	76	8.3	1/8/92
29	0			22.872		117	44	160		37	12.1	76	12.3	1/8/92
31	0			23.737		123	138	262		36	58.4	76	10.1	1/29/92
32	0			25.035		138	148	286		37	3.6	76	10.1	1/29/92
33	0			24.576		142	135	277		37	13.5	76	10.1	1/29/92
34	0			23.502		135	150	285		37	18.3	76	10.1	1/29/92
35	0			22.369		130	146	276		37	23.1	76	10.3	1/29/92
36	0			21.943		125	132	258		37	27.8	76	9.9	1/29/92
37	0			21.069		127	96	223		37	32.5	76	10.2	1/29/92
38	0			20.791		114	111	225		37	36.9	76	10.1	1/29/92
39	0			20.202		103	115	218		37	42.3	75	57.0	1/29/92

St	D	T	Sigma-t	S	DO	I	IO3	I+IO3	Total	Latitude		Longitude		Date
	m			psu	uM	nM	nM	nM	uM	N		W		
Winter of 1992														
40	0			19.838		101	115	216		37	44.3	75	53.3	1/29/92
41	0			20.023		98	117	215		37	49.0	75	49.0	1/29/92
42	0			17.866						37	53.1	75	48.1	1/29/92
43	0			19.327		97				37	53.2	75	56.4	1/29/92
44	0			19.058		88				37	59.0	75	55.0	1/29/92
45	0			19.855		95	114	208		37	44.8	76	1.3	1/30/92
46	0			19.896		109				37	52.0	76	3.3	1/30/92
47	0			19.972		106	115	221		37	47.8	76	9.9	1/30/92
48	0			20.770		97	132	229		37	41.8	76	10.1	1/30/92
A	1	3.7	15.3	18.996	381	84	104	188		38	21.3	76	19.4	2/3/92
A	4	3.8	15.3	19.173		95	109	204		38	21.3	76	19.4	2/3/92
A	8	3.7	15.3	19.543		94	123	217		38	21.3	76	19.4	2/3/92
A	12	3.7	15.4	19.654		93	121	214		38	21.3	76	19.4	2/3/92
A	16	3.7	15.4	19.533	371	108	129	237		38	21.3	76	19.4	2/3/92
A	20	3.8	15.6	20.573		107	142	249		38	21.3	76	19.4	2/3/92
A	25	4.1	16.4	20.910		104	106	209		38	21.3	76	19.4	2/3/92
A	29	4.4	17.4	21.425	344	137	90	226		38	21.3	76	19.4	2/3/92
57	0			19.868		96	109	204		38	9.1	76	13.3	2/3/92
58	0			18.369		87				37	59.1	76	17.5	2/3/92
59	0			19.454		92	118	211		37	54.2	76	7.1	2/3/92
Spring of 1992														
1	0			21.770		100				37	6.9	76	14.5	4/7/92
2	0			21.618		100	64	164		37	10.0	76	15.7	4/7/92
3	0			21.159		116	52	168		37	12.7	76	18.9	4/7/92
4	0			21.486		96	72	168		37	14.1	76	15.8	4/7/92
5	0			21.223		93	70	163		37	17.6	76	18.1	4/7/92
6	0			21.665		91	79	170		37	20.2	76	19.7	4/7/92
7	0			21.773		103	63	166		37	17.8	76	13.1	4/7/92
8	0			20.067		87	40	127	194	37	19.6	76	12.2	4/7/92
9	0			21.597		98	66	165	207	37	20.5	76	7.3	4/7/92
10	0			22.464		112	66	178	243	37	21.2	76	3.8	4/7/92
11	0			22.700		123	70	193	216	37	18.7	76	4.1	4/7/92
12	0			22.936		124	76	200	213	37	15.9	76	4.3	4/7/92
13	0			22.815		104	70	174	219	37	13.9	76	4.5	4/7/92
14	0			23.048		119	79	198	218	37	12.8	76	8.9	4/7/92
15	0			22.383		109	78	186	210	37	12.0	76	11.7	4/7/92
16	0			22.141		106	42	148		37	8.6	76	11.5	4/7/92

St	D m	T	Sigma-t	S psu	DO uM	I nM	IO3 nM	I+IO3 nM	Total nM	Latitude N		Longitude W		Date
Spring of 1992														
17	0			22.098		94	49	143		37	5.6	76	11.1	4/7/92
18	0			21.061		89				37	2.8	76	10.9	4/7/92
19	0			22.589		94	97	191		37	2.6	76	8.0	4/7/92
20	0			24.092		113	90	204		37	2.4	76	4.6	4/7/92
21	0			26.308		119	121	240		37	2.4	76	2.5	4/7/92
22	0			26.344		123	104	227		37	2.8	76	0.1	4/7/92
23	0			26.713		127	78	204		37	3.1	75	58.0	4/7/92
24	0			23.511		112	88	200		36	58.3	76	0.9	4/7/92
25	0			22.399		100	67	168		36	58.3	76	3.8	4/7/92
26	0			20.094		103	60	162		36	57.1	76	8.1	4/7/92
A	0	23.8	8.7	14.876		69	30	99	183	38	20.0	76	18.0	6/8/92
A	2	23.0	9.0	14.945		69	58	127	191	38	20.0	76	18.0	6/8/92
A	5	21.8	9.4	15.225	311	51	62	113	171	38	20.0	76	18.0	6/8/92
A	7	20.9	9.6	15.441	273	64	57	121	164	38	20.0	76	18.0	6/8/92
A	10	17.2	12.9	18.818	159	88	50	138	187	38	20.0	76	18.0	6/8/92
A	12	16.3	14.8	20.838	99	94	116	210	206	38	20.0	76	18.0	6/8/92
A	15	16.3	15.6	21.238	99	123	78	201		38	20.0	76	18.0	6/8/92
A	17	16.4	15.7	21.421	100	130	74	205	213	38	20.0	76	18.0	6/8/92
A	20	16.4	15.8	21.821	103	113	83	196		38	20.0	76	18.0	6/8/92
A	25	16.4	15.9	21.970	104	134	88	223	223	38	20.0	76	18.0	6/8/92
A	28	16.4	15.9	22.166	103	128	76	204	231	38	20.0	76	18.0	6/8/92
Summer of 1992														
1	0			23.051		193				37	2.8	76	10.9	7/7/92
2	0			20.993		164	56	220		37	12.7	76	18.9	7/7/92
3	0			20.916		164	57	221		37	19.4	76	20.2	7/7/92
4	0			20.179		150	52	201	226	37	19.4	76	11.9	7/7/92
5	0			20.825		114	57	171	226	37	12.1	76	11.7	7/7/92
6	0			23.046		173	61	235		37	6.1	76	10.7	7/7/92
7	0			24.048		169	75	243		36	58.4	76	1.4	7/8/92
8	0			27.814		181	75	256		37	0.3	75	59.7	7/8/92
9	0			27.431		170	95	265		37	3.3	75	58.1	7/8/92
10	0			27.073		203	92	296		37	6.4	75	59.8	7/8/92
11	0			24.325		141	65	206	267	37	10.5	76	2.9	7/8/92
12	0			24.369		151	62	213	284	37	13.8	76	4.5	7/8/92
13	0			21.641		150	54	204	267	37	17.9	76	2.5	7/8/92
14	0			21.113		162	35	198	263	37	20.9	76	3.8	7/8/92
15	0			23.116		143	48	192		37	7.1	76	7.6	7/8/92

St	D m	T	Sigma-t	S psu	DO uM	I nM	IO3 nM	I+IO3 nM	Total nM	Latitude N		Longitude W		Date
Summer of 1992														
16	0			22.035		174	52	226		37	1.9	76	8.6	7/8/92
17	0			22.655		147	47	194		36	58.1	76	10.2	7/8/92
A	0	26.7	7.9	15.147		107	58	165	214	38	20.0	76	18.0	8/11/92
A	2	26.7	8.0	15.135		111	52	164	215	38	20.0	76	18.0	8/11/92
A	4	26.6	8.0	15.135		135	38	173	204	38	20.0	76	18.0	8/11/92
A	6	26.5	8.2	16.690		158	46	204	252	38	20.0	76	18.0	8/11/92
A	8	25.8	9.0	17.942		164	51	215	243	38	20.0	76	18.0	8/11/92
A	10	25.7	10.4	19.129		267	54	321	282	38	20.0	76	18.0	8/11/92
A	12	25.5	11.1	19.609		246	57	303	289	38	20.0	76	18.0	8/11/92
A	15	25.5	12.0	20.164		278	57	335	305	38	20.0	76	18.0	8/11/92
A	20	25.6	12.4	20.736		288	55	342	315	38	20.0	76	18.0	8/11/92
A	25	25.6	12.5	20.821		261	51	312	322	38	20.0	76	18.0	8/11/92
Fall of 1992														
A	0	17.7	9.7	14.589		130	71	200		38	19.6	76	18.4	10/8/92
A	2	17.7	9.7	14.590		130	71	201		38	19.6	76	18.4	10/8/92
A	6	18.0	10.4	16.169		168	48	215		38	19.6	76	18.4	10/8/92
A	8	18.3	10.8	17.449		149	57	206		38	19.6	76	18.4	10/8/92
A	10	18.9	11.2	18.306		157	66	223		38	19.6	76	18.4	10/8/92
A	12	19.2	11.8	19.020		166	61	227		38	19.6	76	18.4	10/8/92
A	15	19.2	12.9	19.981		188	39	228		38	19.6	76	18.4	10/8/92
A	18	19.4	14.0	21.670		176	60	236		38	19.6	76	18.4	10/8/92
A	20	19.6	14.3	21.857		178				38	19.6	76	18.4	10/8/92
A	23	19.8	14.7	22.376		189	56	245		38	19.6	76	18.4	10/8/92
A	25	19.9	15.1	22.670		214	63	276		38	19.6	76	18.4	10/8/92
18	0			15.533		180	72	252		38	11.9	76	15.8	10/8/92
19	0			16.843		132	56	188		38	3.5	76	13.2	10/8/92
20	0			16.191		136	64	200		37	56.6	76	10.2	10/8/92
21	0			17.060		166	33	199		37	48.7	76	9.4	10/8/92
22	0			19.520		169	55	224		37	40.7	76	10.5	10/8/92
23	0			19.520		163	45	208		37	31.5	76	9.8	10/8/92
24	0			19.529		167	48	215		37	20.7	76	10.1	10/8/92
25	0			20.779		183	51	235		37	12.9	76	10.8	10/8/92

Appendix B: The determination of dissolved iodine species in natural waters

The determination of iodine species in natural waters are based on the procedures published in internationally recognized journals. Iodide is determined by cathodic stripping square wave voltammetry (Luther *et al.*, 1988b; Wong and Zhang, 1992a; 1992b). Iodate is determined by differential pulse polarography (Herring and Liss, 1974; Wong and Zhang, 1992a). Total iodine (i.e. iodide plus iodate) is determined by cathodic stripping square wave voltammetry (Wong and Zhang, 1992b). Total iodine (i.e. iodide, iodate and organic iodine) is determined by differential pulse polarography (Butler and Smith, 1980; Takayanagi and Wong, 1986). The procedure for sample preservation is based on the results of Wong (1973).

Iodide is deposited onto the mercury electrode at -0.15 V (*vs* SCE) as Hg_2I_2. This compound is reduced at more negative potential with a negative-scanning square wave potential. The reduction current forms a peak at about -0.33 V. The peak current is proportional to the concentration of iodide in sample. Triton X-100 is added to the sample to enhance the mercury electrode's sensitivity to iodide.

Iodate is reduced at mercury electrode with a negative-scanning differential pulse potential. The reduction current forms a peak at about -1.1 V (*vs* SCE). The peak current is proportional to the concentration of iodate. Interference from zinc is eliminated by adding EDTA to complex zinc.

Iodate is reduced to iodide by adding sulfite and adjusting the sample's pH to 1-1.5. After iodate is reduced to iodide, the sample's pH is adjusted back to 8-9 with ammonium hydroxide. Then, total iodine (i.e. iodide plus iodate) is determined as iodide.

Iodide is oxidized to iodate by sodium hypochlorite. Organic iodine in seawater may also be oxidized to iodate. The excess of oxidizing agent is destroyed later with sodium sulfite. Total iodine (i.e. iodide, iodate, and organic iodine) is determined as iodate.

Dissolved oxygen in the sample may be removed with sodium sulfite.

1.0 SAFETY

Laboratory glassware, acids, oxidizing agents, mercury as well as other potentially hazardous chemicals are required for this procedure. The use of safety glasses or goggles is mandatory. The transfer of large volumes of concentrated acids should be handled in fume hoods. Caution should be taken to prevent mercury from being dumped into a sink.

2.0 PROCEDURE

2.1 PREPARATION OF LABWARE

1. Filters are washed with distilled de-ionized water before use.
2. Sample bottles and labware are cleaned with laboratory detergent, rinsed with distilled de-ionized water, leached with 10% hydrochloric acid for at least 24 hours, and then rinsed with a copious amount of distilled de-ionized water. Labware should be rinsed with distilled de-ionized water before and after use. They should be filled with distilled de-ionized water when not in use if applicable, and should be reserved exclusively for the iodine work.
3. Polarographic cells are rinsed with distilled de-ionized water before and after use. When sodium sulfite is used to remove dissolved oxygen, the sample's pH may increase and precipitation may occur on the cell wall. Dilute acid (e.g. 1 M HCl) is used to wash the precipitation. The cell should be rinsed well with distilled de-ionized water

2.2 Materials

2.2.1 Chemicals

1. Potassium iodate (KIO_3, MW 214.00) - reagent grade, no further purification.
2. Potassium iodide (KI, MW 166.00) - reagent grade, no further purification.
3. Sodium sulfite - reagent grade, no further purification.
4. Triton X-100 (MW 628, FisherBiotech BP151-100)- reagent grade.
5. Di-sodium ethylene diamine tetraacetate ($Na_2EDTA.2H_2O$, MW 372.2) - reagent grade, no further purification.
6. Sodium hypochlorite (4 to 6% NaOCl) - purified grade, no further purification.
7. Sulfuric acid (H_2SO_4, 36 N, 96%)- reagent grade.
8. Ammonium hydroxide(NH_3H_2O, 15 M, 28-30%) - reagent grade.
9. Argon gas - at least commercial grade, 99.99% pure.
10. Pyrogallol (1,2,3-trihydroxybenzene) - at least purified grade, no further purification.
11. Potassium hydroxide - at least technical grade, no further purification.
12. Salts for making artificial seawater - reagent grade.

2.2.2 Reagents

Distilled de-ionized water is used in making reagents.

1. Standard solutions of iodate

Primary standard of iodate (10 mM): Dry potassium iodate at 80°C for over night. Cool it in a desiccator. Add 2.140 g of iodate to a 1-l volumetric flask. Dissolve to the mark. Store in a refrigerator. Stable at least for 12 months.

Secondary standard of iodate (600 μM): Get small

amount of primary standard out of the refrigerator, let it reach to room temperature before use. Pipet 3 ml of primary standard (10 mM) to a 50-ml volumetric flask and dilute to mark to make the secondary standard.

Working standard of iodate (24 μM): Pipet 2 ml of secondary standard to a 50-ml volumetric flask and dilute to mark to make the working standard.

$[IO_3^-]$ = (3 ml×10 mM/50 ml)×(2 ml/50 ml) = 24 μM (The exact concentration depends on the calibrated volume of pipette).

2. Standard solutions of iodide

Primary standard of iodide (10 mM): Dry potassium iodide at 80°C for over night. Cool it in desiccator. Add 1.660 g of iodide to a 1-l volumetric flask. Dissolve to the mark. Store in a refrigerator. Stable for several months.

Secondary standard of iodate (200 μM): Get small amount of primary standard out of the refrigerator, let it reach to room temperature before use. Pipet 1 ml of primary standard (10 mM) to a 50-ml volumetric flask and dilute to mark to make the secondary standard.

Working standard of iodide (2 μM): Pipet 1 ml of secondary standard to a 100-ml volumetric flask and dilute to mark to make the working standard.

$[I^-]$ = (1 ml×10 mM/50 ml)×(1 ml/100 ml) = 2 μM (The exact concentration depends on the calibrated volume of pipette).

3. Sodium sulfite (1 M): Add 1.26 g of sodium sulfite to a 20-ml vial, dissolve it to a 10-ml mark. The concentration is not crucial, but the spiked volume to a sample is needed in later calculation. Made before use.
4. Triton (0.2%): Dissolve 0.2 ml of pure Triton in a 100-ml volumetric flask. Store in refrigerator. Stable for a long time. Keep small amount in a vial for routine use.
5. Na_2EDTA (0.1 M): Add 3.72 g of EDTA to a 100-ml volumetric flask and dissolve to mark. Stable for a long time.
6. NaOCl (0.6 - 1.0%): Pipet 1 ml of 4-6% NaOCl to a 20-ml vial, add 5 ml of distilled de-ionized water, mix. Made before use.
7. Sulfuric acid (2 N): Add 800 ml of distilled de-ionized water to a 1-l volumetric flask and place it in a water bath. Slowly add 56 ml (in graduated cylinder) of concentrated sulfuric acid with constant stirring. Cool and dilute to the mark. 2 N sulfuric acid is used to adjust the pH of sample when measuring total iodine in CSSWV mode. To the sample (5 ml of distilled de-ionized water + 0.5 or 1 ml of seawater + 0.2 ml of 1 M sodium sulfite), 1 ml of this 2 N sulfuric acid should reduce the pH to less than 1.2, but not less than 0.8.
8. Ammonium hydroxide (1+4 or 1+5, v/v): Add 100 ml of distilled de-ionized water to a 250-ml volumetric flask. Add 50 ml of concentrated ammonium hydroxide. Dilute to the mark. Ammonium hydroxide is used to adjust the pH of

sample when measuring total iodine in CSSWV mode. To the sample (5 ml of distilled de-ionized water + 0.5 or 1 ml of seawater + 0.2 ml of 1 M sodium sulfite + 1 ml of 2 N sulfuric acid), 1 ml of this ammonium hydroxide should bring the pH of sample back to between 7.5 and 9.

9. ISA (Ionic strength adjustor): Artificial seawater (ASW) is used as ISA. When making ASW (e.g. the recipe of Lyman and Fleming, 1940), magnesium, calcium and strontium are substituted with an equimolar amount of sodium in order to avoid the precipitation at high pH.

10. Alkaline pyrogallol

Oxygen-free water: Boil 2 l of distilled deionized water in an Erlenmeyer flask for 20 minutes while bubbling Ar gas through it. Allow the water to cool under Ar gas. Stopper the flask and store the water under Ar gas.

Pyrogallol solution (15%): Transfer 30 g of pyrogallol to a 300 ml Erlenmeyer flask. Add 150 ml of oxygen-free water with a graduated cylinder. Swirl the solution to allow the solids to dissolve. Add 50 ml of oxygen-free water. Mix the solution and stopper the flask.

Potassium hydroxide (30%): Transfer 120 g of potassium hydroxide to a 500 ml Erlenmeyer flask. Add 400 ml of oxygen-free water with a graduated cylinder. Swirl the solution to allow all the solids to dissolve. Store in a stoppered flask.

Alkaline pyrogallol (1:3 solution): To a 500 ml Erlenmeyer flask, add 100 ml of 15% pyrogallol solution and 300 ml of 30% potassium hydroxide. Swirl the solution and store under Ar gas in a stoppered flask.

2.3 EQUIPMENT

1. A PAR Model 384-4B polarographic analyzer system equipped with a PAR Model 303A Static Mercury Drop Electrode (SMDE) is used.

Electrodes: Rinse with distilled de-ionized water before and after use. Precipitation on the electrodes may occur when sodium sulfite is used to remove dissolved oxygen and the performance of electrodes may deteriorate. For example, the mercury drop does not hang on the tip of electrode. Dilute acid is used to wash the electrodes. The electrodes should be rinsed and soaked with distilled de-ionized water to remove acid, sulfite, and iodide. Blank should be checked before the determination of iodide.

2.4 SAMPLE COLLECTION AND PRESERVATION

1. Mount a Gelman A/E 147 mm glass fiber filter (nominal 1 μM size) onto a filter holder.
2. Wash the filter with distilled de-ionized water and discard the filtrate.

3. Filter the sample through the filter.
4. Discard approximately the first 200 ml of the filtered sample.
5. Rinse the sample bottle at least three times with the filtered sample and then fill 80% of the sample bottle (The sample volume is about 250 ml).
6. Quickly freeze the sample or at least keep it chilled or refrigerated until the sample can be frozen (Immediate freezing is preferred).
7. Unfiltered water may be taken as sample.

2.5 DETERMINATION OF IODINE SPECIES IN NATURAL WATERS

2.5.1 Preliminary step

Turn on Model 384B. Wait for the message of **WAIT-C1**, and **MODEL 384B POLAROGRAPHIC ANALYZER F0:C1**. Turn on 303 Electrode. Turn on the recorder. Push SMALL of the recorder.

Check/fill the salt bridge with saturated KCl. Check the pen. Get record papers ready for use. Get Ar gas ready for purging. If the commercial grade Ar gas contains trace amounts of oxygen, pass the gas through an alkaline pyrogallol trap and a water trap. The alkaline pyrogallol trap removes oxygen more efficiently at higher temperature (e.g. 60°C). Use a full cell of water, soak and wash the electrodes.

2.5.2 Determination of iodide by cathodic stripping square wave voltammetry

1. Set the drop size of the 303 Electrode to large. Push DISPENSE to make tens of drops. Check the knocking force.
2. Set the following parameters: deposition potential, -0.15 V *vs* SCE; final potential, -0.6 V; deposition time, 60 seconds; equilibrium time, 5 seconds; scan increment, 2 mV; pulse height, 20 mV; frequency, 100 Hz; mode, SWV.
3. To a polarographic cell (GLASS cell!) with a stirring bar in it, pipet 10 ml of diluted sample[1].

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[1] The linear range for the determination of iodide in CSSWV mode is from several nM to 120-140 nM. The concentrations of iodide in open ocean water are from several nM (deep water) to 200 nM (surface water). The original samples need to be diluted so that the unknown concentrations of iodide in the diluted samples are less than 70 nM. The final concentrations of iodide in the diluted samples (unknown plus two spikes) would be within that linear range (e.g. 70 + 25 + 25 = 120 nM).

Samples can be diluted by using volumetric flasks. There are other ways to do the sample dilution. For example, pipet 10 ml of distilled de-ionized water with 10-ml pipet to the

4. Add 0.05 ml of 0.2% Triton.
5. Add 0.2 ml of 1 M sodium sulfite. Wait for several minutes to let sulfite to react with dissolved oxygen[2].
6. Place the cell onto the electrode. Place the stirrer. Set the stirrer to auto.
7. Purge the cell with Ar gas for 30 seconds. Protect the cell with Ar gas.
8. Run the scan.
9. Spike 0.1 ml of working standard of iodide (2 μM) with a calibrated pipette.
10. Run the scan.
11. Repeat spike and run one more time.
12. Repeat steps 3 through 11 for more samples.
13. At step 3, pipet 10 ml of distilled de-ionized water as a blank sample for the determination of blank.

2.5.3 Determination of iodate by differential pulse polarography

1. Set the drop size of the 303 Electrode to medium. Push DISPENSE to make tens of drops. Check the knocking force.
2. Set the following parameters: initial potential, -0.5 V *vs* SCE; final potential, -1.5 V; equilibrium time, 5 seconds; drop time, 1 second; scan increment, 6 mV; pulse height, 60 mV; mode, differential pulse polarography.
3. To a polarographic cell, pipet 5 ml of sample.
4. Add 0.01 ml of 0.1 M Na_2EDTA.
5. Add 0.1 ml of 1 M sodium sulfite. Seal the cell with PARAFILM. Swirl the cell a little bit. Wait for several hours to let sulfite to react with dissolved oxygen[3].

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cell, pipet out 2 ml of distilled de-ionized water from the cell with 1-ml Eppendorf pipette, then add 2 ml of sample water. The calibrated volumes of the pipets are used in later calculation, but normally the volume error introduced in this way of dilution is minor compared to the instrument error.

[2] The reaction between sulfite and dissolved oxygen is faster at higher salinity. In seawater (salinity = 35), sulfite removes dissolved oxygen in less than 1 minute. In a diluted sample (i.e. low salinity), it takes longer time for sulfite to remove dissolved oxygen.

[3] Without the presence of EDTA, sulfite removes dissolved oxygen in less than 1 minute. With the presence of EDTA, the reaction between sulfite and dissolved oxygen is greatly reduced. It takes 4 hours for sulfite to remove dissolved oxygen chemically. Ar gas of very high purity may still need to purge the sample to remove dissolved oxygen physically. The interference of dissolved oxygen may still be inevitable for the determination of iodate in an estuarine water in which the concentration of iodate may be close to zero.

6. Place the cell onto the electrode.
7. Purge the cell with Ar gas for 1 to 2 minutes. Protect the cell with Ar gas.
8. Run the scan.
9. Spike 0.05 ml of working standard of iodate (24 μM) with a calibrated pipette.
10. Purge for 30 seconds. Run the scan.
11. Repeat spike, purge and run one more time.
12. Repeat steps 3 through 11 for more samples.

13. At step 3, pipet 5 ml of ISA (artificial seawater) as a blank sample for the determination of blank.

2.5.4 Determination of total iodine (iodide plus iodate) by cathodic stripping square wave voltammetry

1. Set the drop size of the 303 Electrode to large. Push DISPENSE to make tens of drops. Check the knocking force.
2. Set the following parameters: deposition potential, -0.15 V *vs* SCE; final potential, -0.6 V; deposition time, 60 seconds; equilibrium time, 5 seconds; scan increment, 2 mV; pulse height, 20 mV; frequency, 100 Hz; mode, SWV.
3. To a polarographic cell (GLASS cell!) with a stirring bar in it, pipet 5 ml of distilled de-ionized water. Add 0.5 ml of seawater.
4. Add 0.05 ml of 0.2% Triton.
5. Add 0.2 ml of 1 M sodium sulfite.
6. Place the cell onto the electrode. Place the stirrer.
7. Pipet 1 ml of 2 N sulfuric acid. Stir for 30-40 seconds.
8. Pipet 1 ml of 1+4 ammonium hydroxide. Mix 10 seconds. Set the stirrer to auto.
9. Purge the cell with Ar gas for 1 to 2 minutes. Protect the cell with Ar gas.
10. Run the scan.
11. Spike 0.1 ml of working standard of iodide (2 μM) with a calibrated pipette.
12. Run the scan.
13. Repeat spike and run one more time.
14. Repeat steps 3 through 13 for more samples.

15. At step 3, pipet 5.5 ml of distilled de-ionized water as a blank sample for the determination of blank.

2.5.5 Determination of total iodine (iodide, iodate and organic iodine) by differential pulse polarography

1. Set the drop size of the 303 Electrode to medium. Push DISPENSE to make tens of drops. Check the knocking force.
2. Set the following parameters: initial potential, -0.5 V *vs* SCE; final potential, -1.5 V; equilibrium time, 5 seconds; drop time, 1 second; scan increment, 6 mV; pulse height, 60 mV; mode, differential pulse polarography.
3. To a polarographic cell, pipet 5 ml of sample.

4. Add 0.05 ml of 0.6% NaOCl. Allow the mixture to stand at room temperature for 30 minutes to let NaOCl to oxidize iodide and organic iodine to iodate.
5. Go to step 5 - 11 of section 2.5.3.

6. Repeat steps 3 through 5 for more samples.

7. At step 3, pipet 5 ml of ISA (artificial seawater) as a blank sample for the determination of blank.

2.5.6 CALIBRATION

A calibration curve is constructed for each sample by internal standard additions. The potassium iodate and potassium iodide used for the preparation of the standard solution, being reagent grade, are of the highest purity, exceeding 99.9% pure.

2.5.7 TREATMENT OF RAW DATA

1. Primary formula: The peak current is proportional to the concentration of iodine species in the sample, then:

$$CM = B \times C \ ;$$

where: CM: peak current (nA);
B: constant (nA/nM);
C: concentration of iodine species (nM).

2. Formula 1: For the standard addition method:

$$CM_j = B \times \frac{V_{sam} \times C_{sam} + (j-1) \times V_{std} \times C_{std}}{V_{sam} + (j-1) \times V_{std} + V_{oth}} \ ;$$

where: CM_j: peak current of the j-th measurement (nA);
V_{sam}: volume of sample (ml);
C_{sam}: concentration of iodine in sample (nM);
V_{std}: volume of spiked standard (ml);
C_{std}: concentration of iodine in standard (nM);
V_{oth}: volume of all other added solutions;
in the case of total iodine in CSSWV mode:

$$V_{oth} = V_{Triton} + V_{Na_2SO_3} + V_{H_2SO_4} + V_{NH_3H_2O} \ ;$$

in the case of iodate in DPP mode:

$$V_{oth} = V_{EDTA} + V_{Na_2SO_3} \ ;$$

etc.

3. Formula 2:

$$CM_j \times (V_{sam} + (j-1) \times V_{std} + V_{oth}) = B \times V_{sam} \times C_{sam} + B \times (j-1) \times V_{std} \times C_{std};$$

or:

$$Y_j = A + B \times X_j \ ;$$

$$Y_j = CM_j \times (V_{sam} + (j-1) \times V_{std} + V_{oth}) \ ;$$

$$X_j = (j-1) \times V_{std} \times C_{std} \ ;$$

$$A = B \times V_{sam} \times C_{sam} \ .$$

4. Formula 3:

$$C_{sam} = \frac{A}{B \times V_{sam}} \ .$$

A and B can be obtained through linear least-square regression method.

5. Example: Determination of iodide. Three runs.

CM1 = 100 nA; CM2 = 200 nA; CM3 = 300 nA.
V_{sam} = 10 ml; V_{oth} = 0.05+0.2 = 0.25 ml;
V_{std} = 0.1 ml; C_{std} = 2000 nM.

		j = 1	2	3
$Y_j=CM_j*(10+(j-1)*0.1+0.25)$	= CM_j *	10.25	10.35	10.45
Y_j	=	1025	2070	3135
X_j = (j-1) * 0.1 * 2000	=	0	200	400

$Y_j = 1021.67 + 5.275 * X_j$;

$C_{sam} = 1021.67 / (5.275 * 10) = 19.4$ nM.

Appendix C: The determination of iodide in artificial seawater

The concentration of iodide in artificial seawater is measured electrometrically with an Orion iodide-specific electrode (Orion 945300).

The response of iodide electrode, i.e. the potential, is linearly related to the logarithm of concentration of iodide. Based on the specification of the electrode, the linear range is from 10^{-6} to 10^{-1} M of iodide in 0.1 M of sodium nitrate. In artificial seawater, the linear range is at least from 10 μM to 0.44 mM of iodide (Fig. C-1).

The standard solution of iodide is added to a medium of 0.1 M sodium nitrate twice consecutively. Two measurements of potential are carried out at these two known concentrations of iodide. The sample then is added to the medium of sodium nitrate. The third measurement of potential is carried out. Based on the first two measurements, the slope of the electrode is established. Based on the last two measurements, the concentration of iodide in the sample is calculated.

1.0 PROCEDURE

1.1 PREPARATION OF LABWARES

Sample bottles and labwares are cleaned with laboratory detergent, rinsed with distilled de-ionized water, leached with 10% hydrochloric acid for at least 24 hours, and then rinsed with a copious amount of distilled de-ionized water.

1.2 Materials

1.2.1 Chemicals

1. Potassium iodide (KI, MW 166.00) - reagent grade, no further purification.
2. Sodium nitrate ($NaNO_3$, MW 84.99) - reagent grade, no further purification.
3. Salts for making artificial seawater - reagent grade.

1.2.2 Reagents

Distilled de-ionized water is used in making reagents.

1. Standard solutions of iodide

   Primary standard of iodide (10 mM): Dry potassium iodide at 80°C for over night. Cool it in desiccator. Add 1.660 g of iodide to a 1-l volumetric flask. Dissolve to the mark. Store in a refrigerator. Stable for several months.

Working standard of iodide in artificial seawater (0.5 mM): Get small amount of primary standard out of the refrigerator, let it reach to room temperature before use. Pipet 2.5 ml of primary standard (10 mM) to a 50-ml volumetric flask and dilute to mark with artificial seawater to make the working standard.

2. Sodium nitrate (0.1 M)
Transfer 8.50 g of sodium nitrate to a 1-l volumetric flask. Dissolve the solids in 800 ml of distilled de-ionized water and then dilute to mark.
3. Artificial seawater
The artificial seawater is made on the recipe of Lyman and Fleming (1940).

1.3 EQUIPMENT

An Orion Model 94-53 iodide electrode, and Orion Model 90-02 double junction reference electrode, and an Orion Model 701A Digital Ionolyzer are used.

1.4 SAMPLE COLLECTION

Collect sample in a glass bottle.

1.5 DETERMINATION OF IODIDE

1. Pipet 10 ml of 0.1 M sodium nitrate to a 20-ml glass vial.
2. Insert the electrodes into the nitrate solution. Stir the solution.
3. Spike 1 ml of working standard of iodide (0.5 mM).
4. Stir 30 seconds. Read the potential as mV1.
5. Spike 1 ml of working standard of iodide (0.5 mM).
6. Stir 30 seconds. Read the potential as mV2.
7. Add 1 ml of sample.
8. Stir 30 seconds. Read the potential as mV3.
9. Repeat steps 3 through 8 for more samples.

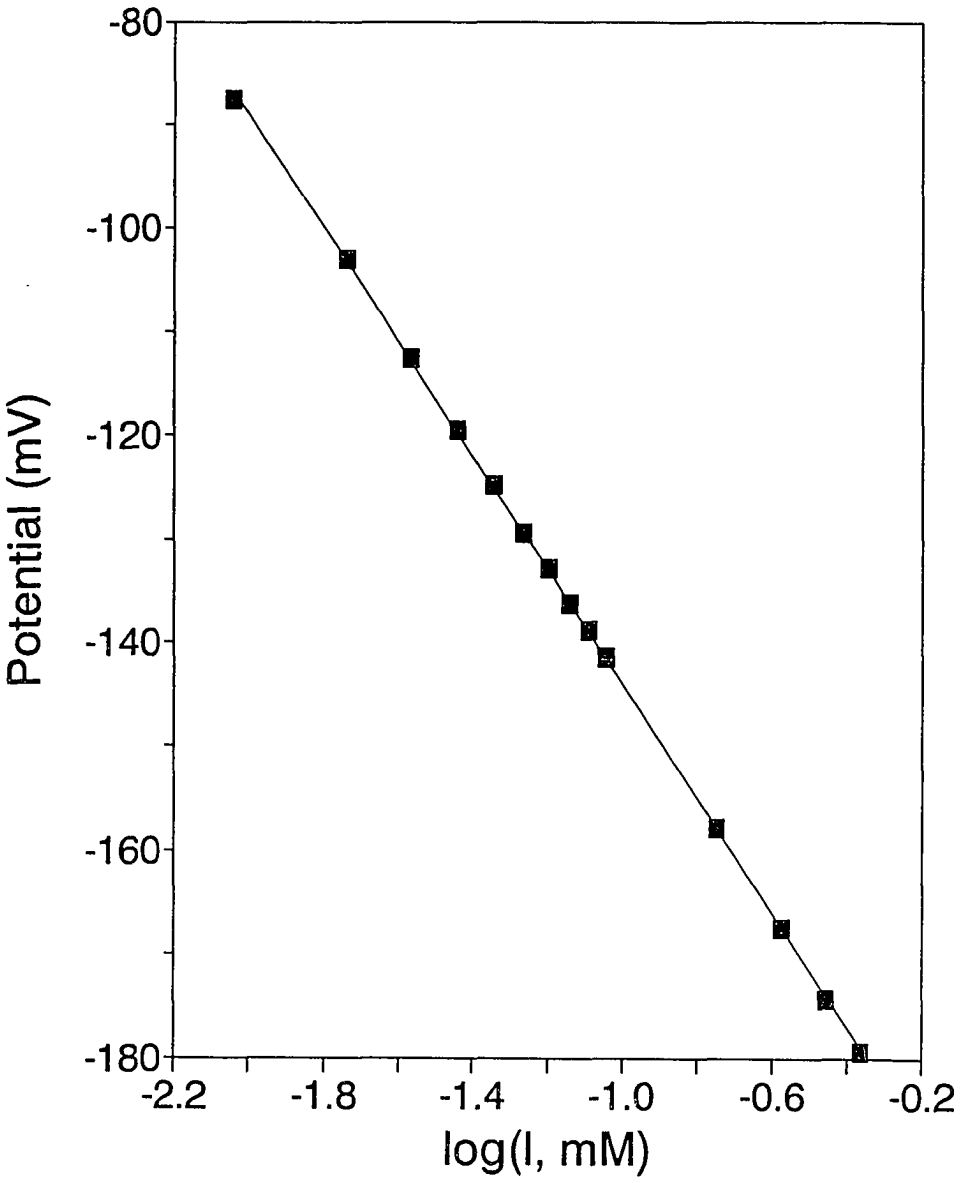

Fig. C-1
The response of iodide-selective electrode to the concentration of iodide in log(I)

2.0 TREATMENT OF RAW DATA

1. The concentration of iodide in the sample is calculated in the following way (See 3.0 for the derivation):

$$N=\left(\frac{2\times(V_{std}+V_{ori})}{2\times V_{std}+V_{ori}}\right)^{\frac{mV3-mV2}{mV2-mV1}}; \qquad (1)$$

$$C_{sam}=\frac{2\times V_{std}\times C_{std}}{V_{sam}}\times\left(\frac{2\times V_{std}+V_{ori}+V_{sam}}{2\times V_{std}+V_{ori}}\times N-1\right); \qquad (2)$$

where
mV1: 1st reading of potential;
mV2: 2nd reading of potential;
mV3: 3rd reading of potential;
V_{ori}: volume of solution of sodium nitrate, ml;
V_{std}: volume of working standard of iodide, ml;
V_{sam}: volume of sample, ml;
C_{std}: concentration of iodide in working standard, mM;
C_{sam}: concentration of iodide in sample, mM.

2. When V_{ori} is 10 ml, V_{std} 1 ml, V_{sam} 1 ml, and C_{std} 0.5 mM, the equations become:

$$N=\left(\frac{11}{6}\right)^{\frac{mV3-mV2}{mV2-mV1}}; \qquad (3)$$

$$C_{sam}=\frac{13}{12}\times N-1\ . \qquad (4)$$

3. The precision is better than 3% at 80 μM level of iodide in the medium of sodium nitrate, or about 1 mM of iodide in the original sample.

3.0 DERIVATION OF EQUATIONS 1 AND 2 IN SECTION 2.0

1. When the response of iodide electrode is linearly correlated to the logarithm of activity of iodide, the response is:

$$mV=-S\times\log A+b;$$

where
mV: potential of iodide electrode, mV;
S: slope;
A: activity of iodide;
b: intercept.

2. To a solution whose volume is V_{ori} and activity of iodide is 0, spike V_{std} ml of standard solution of iodide. The potential of iodide electrode is mV1:

$$mV1=-S\times\log\frac{V_{std}A_{std}}{V_{std}+V_{ori}}+b;$$

where A_{std}: activity of iodide in the standard solution.

Spike V_{std} ml of standard solution of iodide again. The potential is mV2:

$$mV2=-S\times\log\frac{2V_{std}A_{std}}{2V_{std}+V_{ori}}+b.$$

Then add V_{sam} ml of sample. The potential will be mV3:

$$mV3=-S\times\log\frac{2V_{std}A_{std}+V_{sam}A_{sam}}{2V_{std}+V_{ori}+V_{sam}}+b;$$

where A_{sam}: activity of iodide in the sample.

3.

$$mV3-mV2=-S\times[\log\frac{2V_{std}A_{std}+V_{sam}A_{sam}}{2V_{std}+V_{ori}+V_{sam}}-\log\frac{2V_{std}A_{std}}{2V_{std}+V_{ori}}].$$

$$mV2-mV1=-S[\log\frac{2V_{std}A_{std}}{2V_{std}+V_{ori}}-\log\frac{V_{std}A_{std}}{V_{std}+V_{ori}}].$$

$$\frac{mV3-mV2}{mV2-mV1}=\frac{\log(\frac{2V_{std}A_{std}+V_{sam}A_{sam}}{2V_{std}+V_{ori}+V_{sam}}\times\frac{2V_{std}+V_{ori}}{2V_{std}A_{std}})}{\log\frac{2(V_{std}+V_{ori})}{2V_{std}+V_{ori}}}.$$

$$\frac{mV3-mV2}{mV2-mV1}\times\log\frac{2(V_{std}+V_{ori})}{2V_{std}+V_{ori}}=\log(\frac{2V_{std}A_{std}+V_{sam}A_{sam}}{2V_{std}+V_{ori}+V_{sam}}\times\frac{2V_{std}+V_{ori}}{2V_{std}A_{std}}).$$

$$(\frac{2(V_{std}+V_{ori})}{2V_{std}+V_{ori}})^{\frac{mV3-mV2}{mV2-mV1}}=\frac{2V_{std}A_{std}+V_{sam}A_{sam}}{2V_{std}+V_{ori}+V_{sam}}\times\frac{2V_{std}+V_{ori}}{2V_{std}A_{std}}.$$

4. Let

$$N=\left(\frac{2\left(V_{std}+V_{ori}\right)}{2V_{std}+V_{ori}}\right)^{\frac{mV3-mV2}{mV2-mV1}};$$

therefore:

$$\frac{2V_{std}+V_{ori}+V_{sam}}{2V_{std}+V_{ori}}\times\left(2V_{std}A_{std}\right)\times N=A_{sam}V_{sam}+2V_{std}A_{std};$$

$$A_{sam}V_{sam}=2V_{std}A_{std}\times\left(\frac{2V_{std}+V_{ori}+V_{sam}}{2V_{std}+V_{ori}}\times N-1\right);$$

or:

$$A_{sam}=\frac{2V_{std}A_{std}}{V_{sam}}\times\left(\frac{2V_{std}+V_{ori}+V_{sam}}{2V_{std}+V_{ori}}\times N-1\right).$$

5. The activity of iodide is related to the concentration in the following way:

$$A=\gamma\times C;$$

where
A: activity of iodide;
γ: activity coefficient;
C: concentration of iodide.

Therefore:

$$C_{sam}=\frac{2V_{std}C_{std}}{V_{sam}}\times\left(\frac{2V_{std}+V_{ori}+V_{sam}}{2V_{std}+V_{ori}}\times N-1\right).$$

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