Evidence for the Occasional Appearance of Molecular Iodine in Sea Water

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EVIDENCE FOR THE OCCASIONAL APPEARANCE OF MOLECULAR IODINE IN SEA WATER

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By application of an extraction-derivatization approach, the presence of molecular iodine in concentrations of about 10^{-9} mol/L was detected in some surface samples from the Adriatic Sea. It is proposed that the concentration of molecular iodine is caused by sun irradiation, and most probably by the reaction of ozone with iodide.

KEY WORDS: Molecular iodine, Adriatic Sea, sea water, extraction voltammetry, iodoform.

INTRODUCTION

Iodine is an important microconstituent of sea water which is present in a number of different oxidation states and species[1]. The average concentration of total iodine in sea water is 50–70 µg/L[2-5]. Its thermodynamically stable ionic form in the oxic sea water is iodate which appears in an average concentration of 25–65 µg/L[2,5-7]. A product of biological activities in the sea water is iodide. Its concentration is highest at the surface and in the euphotic zone: 6–30 µg/L[2,3,6-9]. "Organic iodine" is that fraction of total iodine which contains different organic compounds of iodine which are not volatile[3,4,7,8,10,11]. It was detected in concentrations between 0.6 and 9 µg/L[3,4,7,10]. Among the volatile organic species of iodine is CH_3I which is produced by algae[12-14]. The concentration of volatile iodine compounds in sea water is very low (2.6 ng/L[14]), but in the atmosphere it is significant[12,15,16]. In aerosols above the sea surface, there were 5–6 ng/L of iodine, in the rain, the Figures are between 0.3 and 4 µg/L of iodine[15].

Molecular iodine, I_2, is believed to be unstable in sea water[4,7,10,17-22]. It may be produced by photochemical oxidation of iodide in surface waters:
$$4I^- + O_2 + 2H_2O \xrightarrow{h\nu} 2I_2 + 4OH^-$$ [1,22], but it reacts quickly with the organic matter in sea water to form organic iodides[1,4,20-22]. Molecular iodine was recorded at the oxic/anoxic boundary in a stratified lake[23]. There it appears in the reactions of HS^- with IO_3^- [19], or of Fe^{3+} with I^- [23]. Thus, the presence and concentration of molecular iodine in sea water depend on many factors such as biological activity, irradiation by sun light, concentrations of oxygen or sulfides, convection conditions, temperature and interactions

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with the atmosphere and dissolved organic matter. Therefore, its determination is a demanding task.

Recently, we have shown that the derivatization of molecular iodine to iodoform is a reaction which is applicable to the trace determination of molecular iodine[24]. Here, we report first measurements which prove the presence of molecular iodine in sea water under certain special conditions.

EXPERIMENTAL

A field study was undertaken at different localities near Šibenik (Croatia) during August 6 to 26 1994 (see Figure 1). All localities were in shallow, inshore water (10–200 cm) over the stony bottom. The samples were collected from the upper surface of the sea (upper 2–5 cm layer) and also from a depth of one meter. The samples were taken into clean, dark glass bottles which were rinsed with the sea water. The extractions into benzene were performed 15–30 minutes after sampling.

150 mL of the sample solution were extracted with 5 mL benzene for 10 minutes. To the extract, there were added 2.5 mL of a 0.1 M ethanolic potassium hydroxide solution, 7 mL ethanol and 2.5 mL of a 1 M ethanolic acetic acid solution. The resulting solution was transferred into the electrochemical cell.

All measurements were performed with a Princeton Applied Research Model 174A polarographic analyser equipped with a Hewlett Packard 7045 X-Y-Recorder and an EG&G PARC Model 303A SMDE with a saturated calomel electrode as reference electrode and a platinum wire counter-electrode. The oxygen was removed from the solution by passing through it oxygen-free nitrogen for 12 minutes. The differential pulse voltammograms were recorded with the following set of parameters: initial potential 0.00 V vs. SCE, modulation amplitude 50 mV, scan range 1.50 V, drop time 0.5 s, scan rate 5 mV/s. A deposition time of 10 s and a deposition potential of 0.00 V vs. SCE were used for the adsorptive preconcentration of iodoform at the electrode surface.

RESULTS

Recently, we have shown that the derivatization of molecular iodine to iodoform is a reaction which is applicable to the trace determination of molecular iodine[24]. This so-called *iodoform reaction* allows a complete conversion of iodine into iodoform and iodide according to the following equation:

$$4I_2 + 6OH^- + CH_3CH_2OH \rightarrow 5I^- + HCOO^- + CHI_3 + 5H_2O \qquad (1)$$

To perform this reaction, molecular iodine is extracted into benzene. Then the extract is mixed with a solution of KOH in ethanol. The iodoform reaction is rather rapid, so that this mixture can be neutralized with acetic acid after 10 minutes. The neutralization is necessary to allow an adsorptive stripping determination of the formed iodoform at the mercury drop electrode. This means that iodoform is preliminarily enriched by adsorption on the surface of the mercury drop. Then follows a cathodic scan during which iodoform is reduced to diiodomethane according to the equation:

$$CHI_3 + H^+ + 2e^- \rightleftharpoons CH_2I_2 + I^- \qquad (2)$$
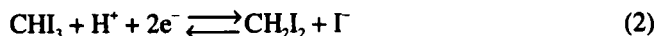
Figure 2 shows differential pulse voltammograms of iodoform obtained as a result of the derivatization of iodine extracted either from the artificial sea water (curve 1) or from the
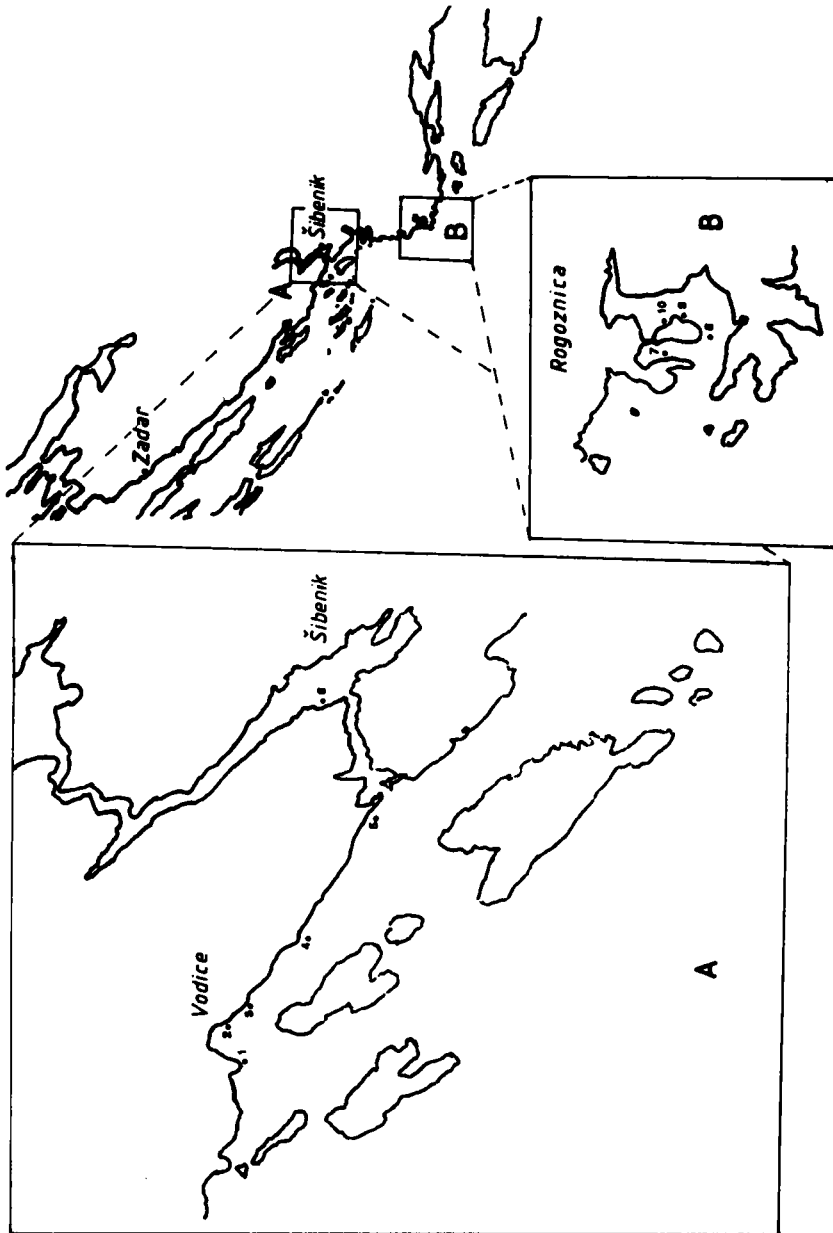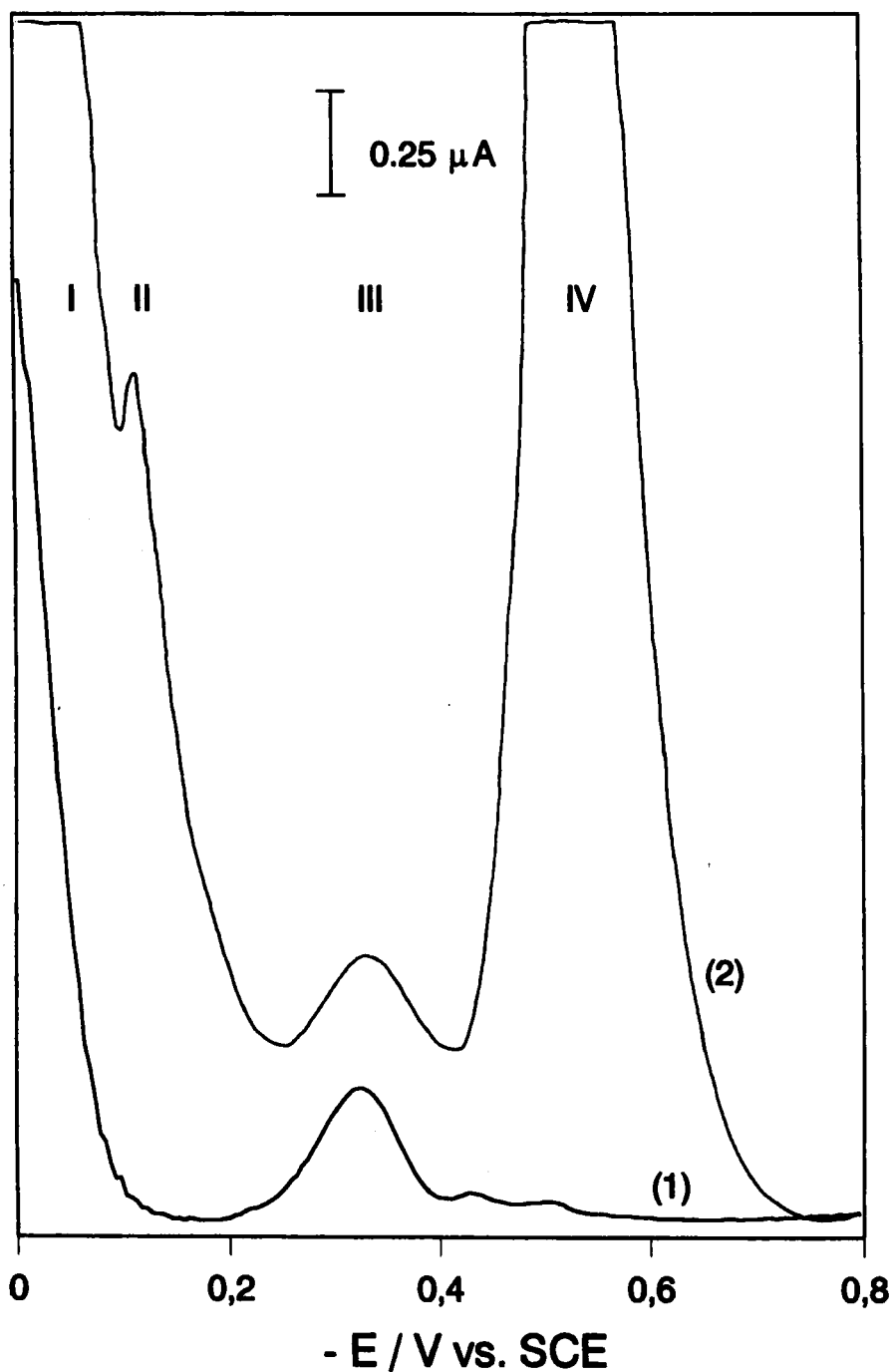
Figure 1   Adriatic coast near Šibenik and localities of sampling.

Figure 2 Differential pulse voltammograms of iodoform after derivatization of iodine. Iodine was extracted from artificial sea water containing $3.5 \cdot 10^{-9}$ mol/L iodine (1) or from a real sea water sample containing $2.7 \cdot 10^{-9}$ mol/L iodine (2) (sampling point 7).

sea water sample (curve 2). Three high peaks (I, II and IV) can be noted on the curve 2. They are probably caused by the reduction of some unknown derivatives of chlorine, bromine and sulphur compounds which are extracted from the sample or which are dissolved as impurities in benzene (peak IV). Peak III corresponds to the reduction of iodoform. Because of the peaks II and IV, the limit of detection of iodine is $1 \cdot 10^{-9}$ mol/L.

The concentration of iodine is determined by using the calibration graph which is obtained for each sample separately by the standard addition method. Because sea water is a very reactive medium with respect to iodine, it was impossible to make standard additions of iodine to the sea water sample itself. Therefore standard additions of I_2 have been made to the benzene extract before derivatization. Because of the stoichiometry of reaction[1] and of the volume ratio in the extraction step the concentration extrapolated from the calibration curve is by a factor of 8.8 higher than in the sea sample.

As to the surface samples, it was possible to measure molecular iodine in three samples in the following concentrations: $1.3 \cdot 10^{-9}$ mol/L, $2.7 \cdot 10^{-9}$ mol/L (sampling point 7) and $1 \cdot 10^{-8}$ mol/L (sampling point 1). An example of the response is shown in Figure 3. The relative standard deviation (r.s.d.) of the analytical method, without sampling, is 10%. Because of the inhomogeneity of the samples, no r.s.d. can be given for the sea water samples. These positive samples were collected under conditions of strong sun irradiation and a quiet sea. In all other samples[30] it was not possible to measure molecular iodine. Thus it can be concluded that its concentration was definitely below the detection limit of the method, i.e. below $1 \cdot 10^{-9}$ mol/L.

DISCUSSION

Before the application of this method to the sea water samples it was necessary to show that molecular iodine is the only iodine species which undergoes the iodoform reaction. Since it is well-known that neither iodide nor iodate are able to form iodoform, the only compounds which had to be studied are the organic iodine compounds. Experiments with different concentrations of methyl iodide proved that this compound is unable to form iodoform. Of course, from a theoretical point of view, we can easily say that this is impossible. But one can always argue that methyl iodide may rapidly decompose with the formation of molecular iodine, which then can be derivatized to iodoform. Obviously, this pathway cannot be observed, neither in artificial solutions nor in simulated sea water. Diiodomethane is known to be a very unstable compound which rapidly decomposes with formation of molecular iodine. This reaction is already observable when a solution of diiodomethane in benzene proceeds for some minutes or hours. Consequently, we observed the formation of iodoform upon addition of a diiodomethane solution to the alkaline ethanol. The adsorptive stripping voltammograms are almost identical with those of iodoform, although slight deviations in peak potential are observed. This might be due to the presence of the product of electrode reaction (2) in a considerable concentration together with formed iodoform. The iodoform reaction (1) is strongly driven to the right side by the presence of KOH. This will cause an additional increase of the decomposition of diiodomethane. From these experiments follows that the formation of iodoform after extraction of sea water with benzene may in principle be caused by the presence of diiodomethane. Until now it could never be shown that diiodomethane is present in sea water in measurable concentration. This is also very reasonable because of the high reactivity of CH_2I_2 and the very low probability that iodination of methane or other precursors will exceed the monoiodinated state.
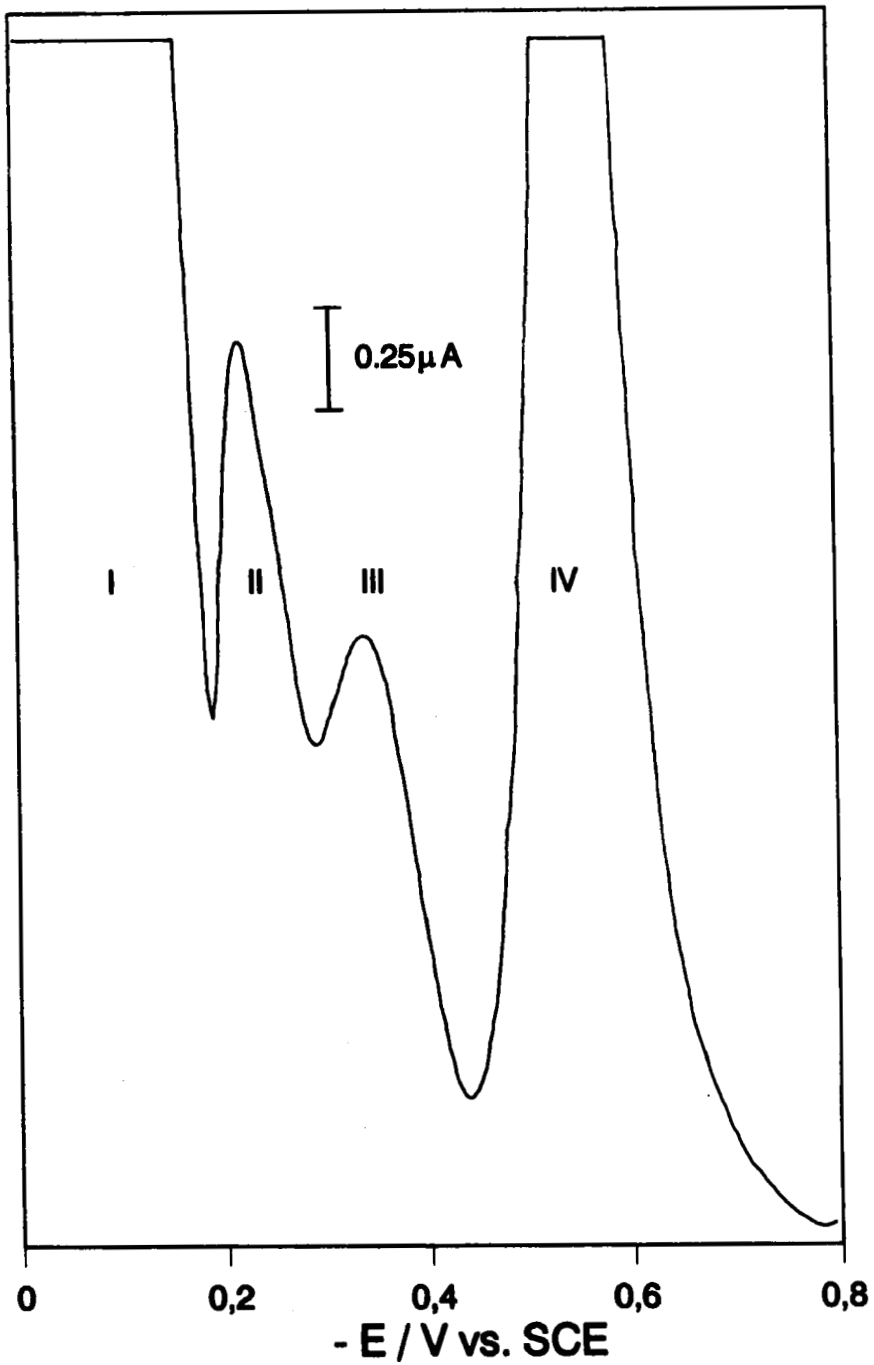
Figure 3 Differential pulse voltammogram of the sample which contained iodine in a concentration of $1 \cdot 10^{-8}$ mol/L.

The most probable source of molecular iodine in sea water is the reaction of photochemically formed ozone with iodide. To test this reaction under real conditions we added iodide to 1.5 L sea water and left this in a big glass beaker to stand in the sun light for 16 hours. The iodide concentration was chosen in great excess ($1 \cdot 10^{-5}$ mol/L) of the normal concentration in sea water. Following this natural irradiation we determined a concentration of molecular iodine of $1.4 \cdot 10^{-8}$ mol/L. This is one promille of the initial iodide concentration in the beaker. Considering a hundred times lower average concentration of iodide in the sea water, this reaction may produce about 10^{-10} mol/L of molecular iodine. Higher concentrations can be ascribed to local inhomogeneities in the sea. Although the sun irradiation and the quietness of sea water seems to be of importance for the detection of molecular iodine, it was observed that there are cases in which both conditions were fulfilled but iodine could not be found. Since molecular iodine is a reactive species it is very probable that its fate depends to a large extent on the presence of other reaction partners, e.g. certain organic compounds.

The concentration of molecular iodine certainly depends on irradiation intensity and is strongly influenced by convection within the water and also by the rate of transfer of molecular iodine from water to air. Additionally one has to take into account biological activities and the presence of different concentrations of organic compounds. For a quantitative understanding of the fate of iodine species, it would be necessary to follow the concentrations of all species over a long period with different weather conditions etc..

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