

Stabilization and Determination of Fe(II) in Seawater and its Concentration in Harimanada

Yoshihiro SUZUKI*, Shigeto NAKABAYASHI*, Kenshi KUMA*
Isao KUDO* and Katsuhiko MATSUNAGA*

Abstract

Fe(II) exists even in oxic seawater as a result of Fe(III) reduction with some organic substances under ultraviolet. However it is very unstable and its concentration is extremely small. After sampling for Fe(II), it must be immediately stabilized until analysis. Fe(II) was stabilized by complex reagent (nitroso-PSAP) and then preconcentrated on a 8-hydroxyquinoline column. After elution with acid, Fe(II) was determined spectrophotometrically. About 0.06 μ M Fe(II) was detected in Harimanada.

1. Introduction

Iron is one of the most important elements for marine algae and macroalgae growth and has two oxidation states in natural waters even under oxic conditions. Fe(II) in river or lake waters complexes with fulvic acid. On the other hand, the existence of Fe(II) in oxic seawater was reported by NAKABAYASHI *et al.* (1989) and KUMA *et al.* (1992). They mentioned that Fe(II) is produced by the reduction of Fe(III) in the presence of hydroxycarboxylic acids under ultraviolet.

8-hydroxyquinoline forms complexes with many metals. By immobilizing it on silicagel, STURGEON *et al.* (1981) used it as a preconcentration column for many metals.

In this paper, fixation of Fe(II) in seawater and its measurement after preconcentration on the column were investigated.

2. Experimental

Reagents

Nitroso-PSAP : 0.302 g of nitroso-5-(N-propyl-N-sulfopropylamine) phenol (PSAP) was dissolved in 100 ml of 0.01 M HCl. PSAP was the most sensitive to Fe(II) and its molar absorptivity is 45,000 $\text{mol}^{-1} \text{l cm}^{-1}$

(SAITO *et al.*, 1981). There is no interference by various ions in seawater and the pH range for maximum color development of PSAP with Fe(II) is 4-10.

Buffer solution (pH9.2) : 214g of NH_4Cl was dissolved in 150 ml concentrated ammonium hydroxide and dilute to 1 l with water.

8-hydroxyquinoline (8-HQ) silicagel column : 8-HQ was immobilized on silicagel (HILL, 1973). Outline of the procedure is as follows : silicagel is treated with 3-aminopropyl triethoxy silane to form aminopropyl silicagel and then 8-HQ is immobilized on aminopropyl silicagel.

Elution of iron from the 8-hydroxyquinoline silicagel column : Acid solution consists of 0.2M HNO_3 and 4M HCl (1 : 1).

Pretreatment of the column

The column treatment was reported by STURGEON *et al.* (1981). The improved column treatment is as follows : About 4 g of 8-HQ silicagel was packed into a ECONO-column ($D=0.7\text{cm}$) on which 500 ml of glass separatory funnel was connected with silicon rubber tubing. The sample was drawn with a Cole Palmer flow pump connected with Tygon tubing to the column with flow rate of about 10 ml min^{-1} (Fig. 1).

Prior to use, 200 ml of the acid solution for elution was passed through the column to clean resin and tube, followed by 100 ml

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*Department of Chemistry, Faculty of Fisheries, Hokkaido University, Hakodate 041, Japan.

of water.

Fixation of Fe(II) in seawater

It has been reported that Fe(II) is oxidized rapidly under oxic seawater (THEIS and SINGER, 1974). In our study, a half-life of Fe(II) oxidation in seawater was several minutes at 20°C, even at 4°C was about 20 min. Thus, for accurate determination of Fe(II) in seawater, it is necessary to stabilize unstable Fe(II) immediately subsequent to collection of the sample. Seawater samples were adjusted to pH 6.0-6.9 with HCl to quench the oxidation of Fe(II) (HONG and

KESTER, 1986). However, this method was not sufficient to quench the Fe(II) oxidation in seawater and furthermore the measurement must be carried out on board.

In this study, PSAP in a neutral solution as a complexing reagent with Fe(II) was added to the seawater sample to stabilize Fe(II).

Analytical procedure

Water sample was taken in a 1 l polyethylene bottle, in which 1 ml of PSAP was already added. The filtered seawater sample (0.45 μm) was drawn through the column at a flow rate of about 10 ml min⁻¹, followed by 100 ml of water. Fe(II) was then eluted from the resin with the acid solution at a flow rate of 5 ml min⁻¹. After discarding 10 ml of residual solution in the column, the following 10 ml of eluate was stored in a 10 ml screw capped polyethylene tube. The column was cleaned by further passage of 40 ml of the acid solution, followed by 50 ml of water to remove excess acid providing a clean column for the next sample.

To 10 ml of eluate, 1 ml of 0.01 M PSAP was added and then adjusted pH about 9 with buffer (pH 9.2). This solution was diluted to 25 ml and the absorbance was measured with a 5 cm cell at 756 nm within 10 min. All treatments were carried out in a clean bench.

3. Results and discussion

Fixation of Fe(II)

To 1 l of filtered seawater, 1 ml of 0.01 M PSAP solution was added, followed by Fe

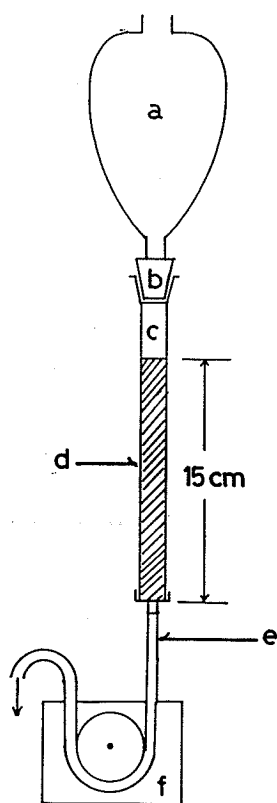


Fig. 1. Preconcentration system.

- a : glass separatory funnel.
- b : silicon rubber.
- c : ECONO column.
- d : 8-hydroxyquinoline silicagel.
- e : Tygon tube.
- f : Cole Pamer flow pump.

Table 1. Stability of Fe(II)-PSAP in seawater.

Sample No.	Fe(II) concentration (μM)	
	t=0 h	t=24 h
1	0.098	0.092
2	0.098	0.090
3	0.096	0.094

Added Fe(II) concentration : 0.1 μM .

(II) standard solution in final concentration of $0.1 \mu\text{M}$. The seawater solutions were passed through the columns after 0 and 24 h and the Fe(II) was determined according to the described procedure. The result in Table 1 shows that above 90% of Fe(II) were measured after 24 h compared to 0 h. Even though PSAP can stabilize Fe(II) after 24 h, the reduction of Fe(III) to Fe(II) must be considered.

It is well known that the complex reagents in an acid solution for the determination of Fe(II) could reduce Fe(III) to Fe(II). (MURRAY and GILL, 1978; MACALADY *et al.*, 1982; Box, 1984). Thus, in this work, neutral PSAP was used in order to prevent the reduction of Fe(III).

To 1 l of filtered seawater with final concentrations of 0.1 and $0.2 \mu\text{M}$ Fe(III), 1 ml of the PSAP was added and allowed to stand in the dark. After standing for 5, 15, and 24 h, their solutions were filtered followed by the determination of Fe(II) by this method.

Fe(II) in both solutions was below detection limit ($0.01 \mu\text{M}$) within 15 h, however, Fe(II) in the solution containing $0.2 \mu\text{M}$ Fe(III) was slightly above detection after 24 h (Fig. 3). From these results, Fe(II) in

seawater with high Fe(III) concentration ($0.2 \mu\text{M}$) must be determined within 15 h subsequent to collection even if neutral PSAP was used.

Working curve and precision

For working curve, Fe(II)-PSAP complex was used. The precision (RSD) was 7% at $0.04 \mu\text{M}$ Fe(II).

The blank was measured by using filtered artificial seawater allowed to stand 1 day after filtration, which means that Fe(II) is oxidized to Fe(III) even if Fe(II) exists in artificial seawater. The absorbance of the blank was 0.023, which is in accord with PSAP only reagent blank.

Recommended sampling

Seawater samples are collected with Go-Flo sampling bottles. Samples are taken immediately from the Go-Flo into 1 liter polyethylene bottles in which 1 ml of 0.01 M PASP was already spiked. Samples are stored in black packages and analyzed within 15 h.

Application to Harimanada

Fig. 2 shows the sampling stations in Harimanada. Samples were taken and ana-

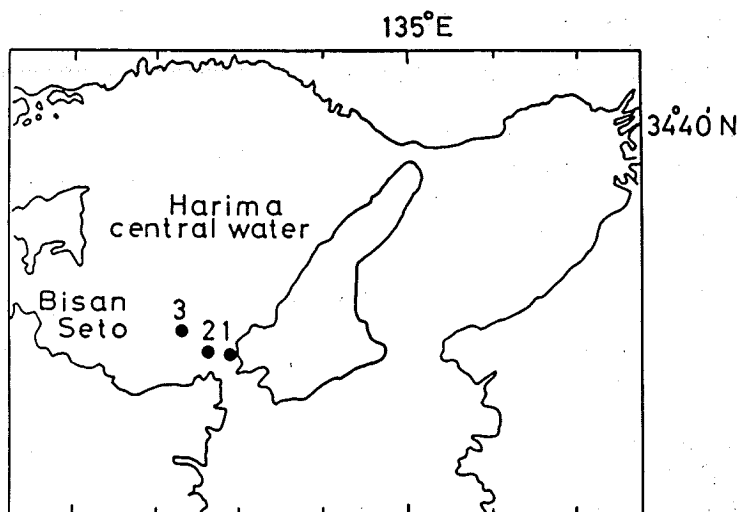


Fig. 2. Sampling stations.

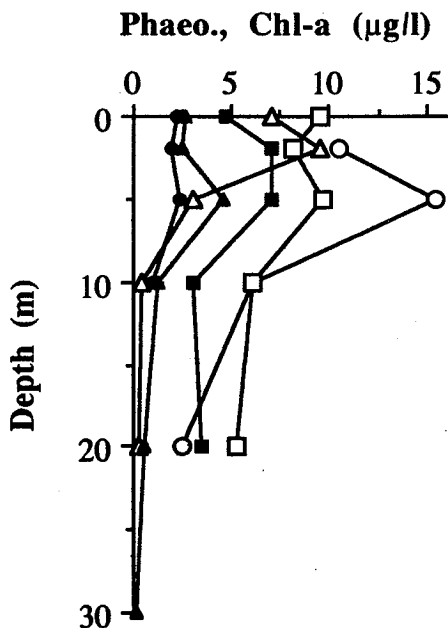


Fig. 3. Vertical distributions of chlorophyll-*a* and phaeophytin in Harimanada, on 3 Aug., 1988.

St. 1. ○ : Chlorophyll-*a*, ● : Phaeophytin.
 St. 2. △ : Chlorophyll-*a*, ▲ : Phaeophytin.
 St. 3. □ : Chlorophyll-*a*, ■ : Phaeophytin.

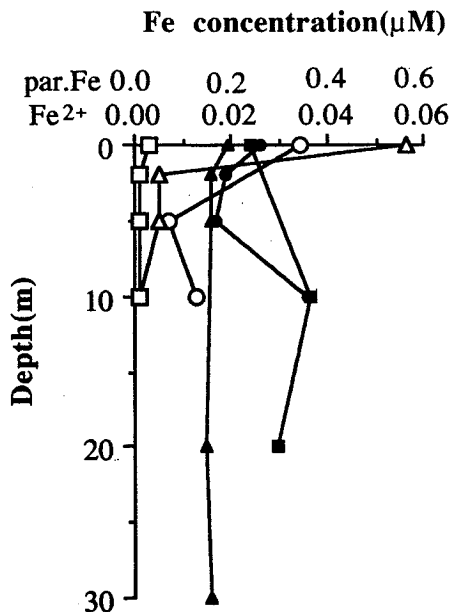


Fig. 4. Vertical distributions of particulate Fe and Fe (II) in Harimanada, on 3 Aug., 1988.

St. 1. ○ : Fe(II), ● : particulate Fe.
 St. 2. △ : Fe(II), ▲ : particulate Fe.
 St. 3. □ : Fe(II), ■ : particulate Fe.

lyzed according to the recommended sampling and the analytical procedure on 3 Aug., 1988, respectively. The vertical profiles of chlorophyll-*a* and phaeophytin, and particulate Fe and Fe(II) were shown in Figs. 3 and 4, respectively. Fe(II) was detected at Sts. 1 and 2, in which high chlorophyll-*a* and low phaeophytin are observed. Fe(II) was not detected in the other station. The reason is assumed to be lack of hydroxycarboxylic acid, which reduce Fe(III) under ultraviolet. The other applications were already reported by NAKABAYASHI *et al.* (1989) and KUMA *et al.* (1992).

4. Acknowledgment

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海水中のFe(II)の定量と播磨灘におけるその濃度

鈴木 祥広*・中林 成人*・久万 健志*
工藤 勲*・松永 勝彦*

酸化環境下における海水中でも、ヒドロキシカルボン酸等が共存するとFe(III)から還元で生じたFe(II)が存在する。しかし、Fe(II)は極めて不安定で、しかも低濃度で存在するため、このFe(II)を安定に保持するために、キレート試薬nitroso-PSAPを用いて安定化することを試みた結果、試水にこのキレート剤を加え、暗所で保存すれば少なくとも24時間は安定であることが

わかった。但し、Fe(III)が0.2 μM存在する場合には、試薬自身がFe(III)を還元するため、15時間以内に分析を行わなければならない。この試水を8-ヒドロキシキノリンシリカゲルカラムを用いて濃縮し、酸で溶離後、吸光度計によりFe(II)を分析する方法を確立した。本法を用い、播磨灘での観測を行ったところ、0.06 μM程度のFe(II)が検出された。

*北海道大学水産学部 〒041 函館市港町3-1-1