

Development of an On-site Simplified Determination Method for Hydrogen Sulfide in Marine Sediment Pore Water Using a Shipboard Ion Electrode with Consideration of Hydrogen Sulfide Oxidation Rate

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Abstract—An on-site simplified determination method for hydrogen sulfide (H₂S) in marine sediment pore water using an ion electrode was proposed. The H₂S loss attributed to its oxidation was corrected by estimating an initial rate constant for H₂S oxidation. The H₂S oxidation rate constant used in this study was dependent on initial concentration of H₂S and salinity, while water temperature and pH did not affect the rate constant. The horizontal distribution of H₂S concentration in the sediment pore water collected from the northern headwaters of Hiroshima Bay was investigated using this proposed method. The concentration ranged *ca.* 0.1 to 28 mg-S L⁻¹. For the H₂S analyses, it is advisable to note total time required for sampling and measurement to compensate for H₂S oxidation, or determine H₂S concentration immediately after sampling using the detection tube method.

Keywords: detection tube, ion electrode, hydrogen sulfide, oxidation, sediment

INTRODUCTION

Hydrogen sulfide is mainly produced through the reduction of sulfate by sulfate-reducing bacteria under reduced conditions. Generally, marine sediments accumulated on the bottom of enclosed or semi-enclosed water bodies located adjacent to large metropolitan areas are affected by significant terrigenous organic matter loads. Since the oxidative decomposition of organic matter consumes dissolved oxygen within the water column, high levels of hydrogen sulfide can sometimes be observed in pore water of the marine sediments (Asaoka

et al., 2009). Hydrogen sulfide sometimes has negative impact on aquaculture activities. In Japan, sulfide compounds in marine sediments are regulated at less than 0.2 mg g^{-1} under the aquaculture criteria so as to support sustainable aquaculture activities.

The sulfide contents in marine sediments have been evaluated by measuring acid volatile sulfide (AVS) which is conventionally defined as those sediment sulfides including some metal sulfides that are volatile in acid solution (Howard and Evans, 1993; Rickard and Morse, 2005). In fact, it has been argued that AVS does not reflect the concentration of hydrogen sulfide that is fatal to cultured aquatic organisms. Hydrogen sulfide has conventionally been detected using the methylene blue method, flow injection coupled with spectrometry, gas chromatography and so on (Williams, 1979; Kuban *et al.*, 1992; Radford and Cutter, 1993). However, these methods are not always suitable for on-site analysis. Potentiometry and stripping chronopotentiometry have also been used for the determination of hydrogen sulfide (Ma *et al.*, 1994; García *et al.*, 1999; Manova *et al.*, 2007). However, these have not been tested for determining hydrogen sulfide in seawater. To provide reliable, fast and easy on-site analyses such as on a shipboard laboratory with limited time and space constraints, it is desirable to develop a simplified H_2S determination procedure.

The purpose of this study is to evaluate an on-site, simplified analytical method for determining hydrogen sulfide in marine sediment pore water using a selective ion electrode.

METHOD

Sampling and analyses

Sediment samples were collected at Hiroshima Bay on October 5 to 8th, 2010 using a core sampler ($\phi 4.8 \text{ cm}$, 60 cm long) deployed from the Toyoshio-Maru, a training and research vessel of Hiroshima University (Fig. 1). In this study, the core collected from 5–10 cm depth was used for this analysis because the surface core (0–5 cm) was significantly affected by the overlying waters. After centrifugation (3,000 rpm for 10 min) to obtain pore water of the sediment sample, the concentration of hydrogen sulfide was measured using an ion electrode (Ag/AgCl type; S-2021, DKK-TOA Co.) attached with a portable ion meter (IM-32P, DKK-TOA Co.). For cross checking, the H_2S concentration value measured by an ion electrode was compared to the values obtained by a detection tube for dissolved sulfide ion (200SA or 200SB; Komyo Rikagaku Kougyo). The detection tube was calibrated beforehand by H_2S standard solution prepared by dissolving an aliquot of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Nacalai Tesque) in 3% NaCl solution to correct a salinity error. The ion electrode was also calibrated by H_2S standard seawater solution prepared by dissolving an aliquot of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Nacalai Tesque) to seawater collected from Hiroshima Bay.

The procedure of H_2S measurement using the ion electrode was as follows; 10 mL of sediment pore water sample was collected in a 50 mL plastic bottle. Ascorbic acid (0.385 g) was added to the pore water sample and the pH was

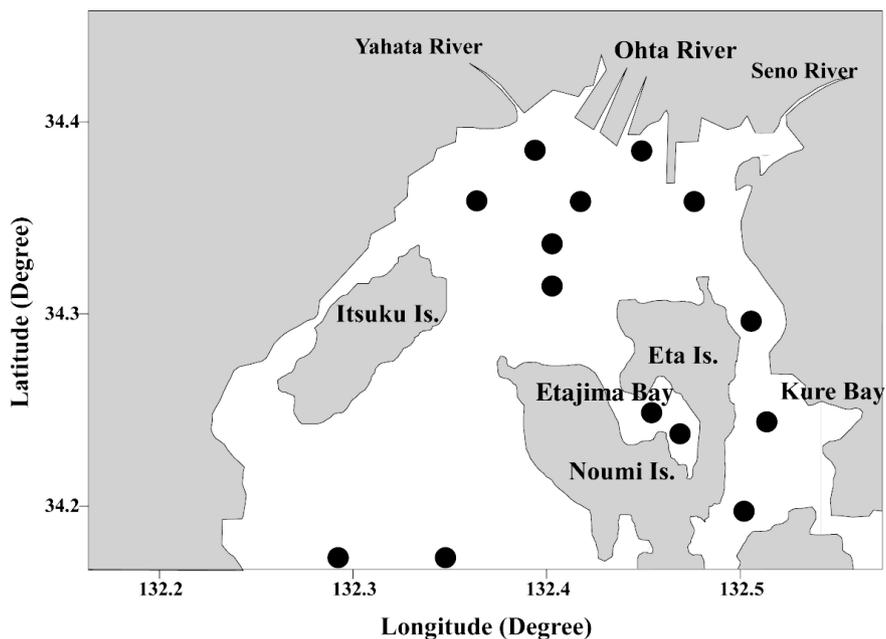


Fig. 1. Sampling stations in the northern headwaters of Hiroshima Bay.

adjusted to 13 by adding NaOH solution. Thereafter, the ion electrode was inserted into the plastic bottle. The concentration of H_2S was measured with the plastic bottle shaken moderately. Although the accompanying instruction for the ion electrode required the use of a magnetic stirrer for H_2S measurement, manual bottle shaking was used instead because pore water volume collected was too little to make the use of a magnetic stirrer feasible.

Determination of H_2S oxidation rate

Oxidation rate of H_2S was determined under various adjusted parameter values within normal coastal conditions. Adjustments of the initial concentration, pH, water temperature, salinity and DO concentrations were introduced within ranges of 5–20 mg-S L^{-1} , 6–8.5, 15–38°C, 0–3‰ and aerobic or anaerobic, respectively. The time course of H_2S concentration of the 10 mL solution was monitored by a detection tube (200SA or 200SB: Komyo Rikagaku Kougyo). The first order rate constants were calculated by the following equation (Eq. (1))

$$[C_t] = [C_0]e^{-kt}. \quad (1)$$

Where, $[C_t]$: concentration of hydrogen sulfide at time t (mg-S L^{-1}), $[C_0]$: initial concentration of hydrogen sulfide (mg-S L^{-1}), t : time (min), and k : first order rate constant (min^{-1}).

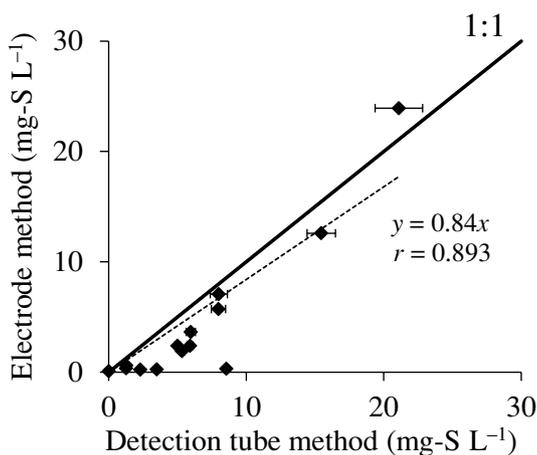


Fig. 2. H_2S concentration in the sediment pore water determined using the detection tube and ion electrode methods without data correction.

RESULTS AND DISCUSSION

The H_2S concentrations in sediment pore water determined by the ion electrode were much smaller than those measured by the detection tubes (Fig. 2). The detection tube took under 3 min to determine the concentrations of H_2S , while the ion electrode took *ca.* 20 min. The latter method required more time compared to the detection tube method because more time was needed in adding ascorbic acid and adjusting sample pH.

The time course of H_2S concentrations (initial concentration: 10 and 20 mg-S L^{-1} , pH = 7, 25°C, salinity: 3%) was monitored under aerobic and anaerobic (N_2 gas atmosphere) conditions. Under aerobic condition, the H_2S concentration decreased by 34 and 19% for initial concentrations of 10 and 20 mg-S L^{-1} , respectively for 30 min. On the other hand, the concentration did not significantly change between initial and 30 min thereafter under anaerobic condition, indicating that hydrogen sulfide might have been oxidized and lost under aerobic condition. Therefore, it is necessary for on-site H_2S analyses using the ion electrode method to correct for the oxidation loss of H_2S .

The H_2S oxidation rate, specifically the observed decreasing rate, was significantly dependent on the initial concentration of H_2S and salinity (Figs. 3 and 4). The rate constants ranged between 0.0069–0.0151 min^{-1} , 0.0066–0.0123 min^{-1} , respectively. Since the seawater contains electron acceptors such as NO_3^- , Mn(IV), and Fe(III) which play important roles in the oxidation of H_2S (Yao and Millero, 1996; Zopfi *et al.*, 2001), it is reasonable that the H_2S oxidation rate in 3% seawater is higher compared to that of pure water (Fig. 4). Water temperature (15–38°C), pH (6–8.5) did not affect the rate constants within 0.0123–0.0134 min^{-1} .

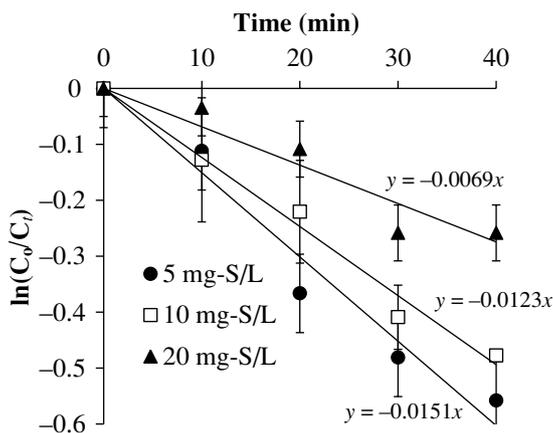


Fig. 3. Effect of initial H_2S concentration on the H_2S oxidation rate.

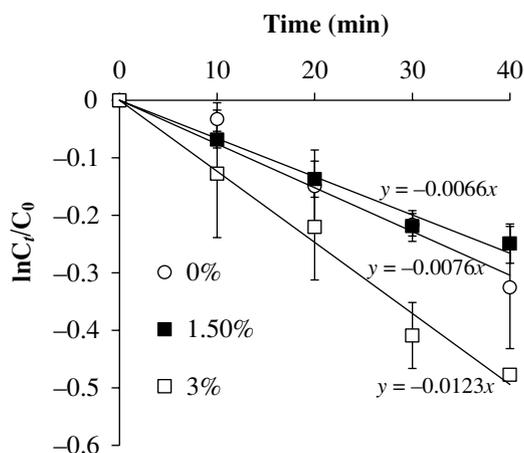


Fig. 4. Effect of salinity on the H_2S oxidation rate.

As previously mentioned, the H_2S oxidation rate was dependent on the initial concentration of H_2S and salinity. Since salinity in the field study area was almost 3%, the salinity was fixed to 3% in latter discussions. Although we cannot determine H_2S initial concentrations (Eq. (1)), we can estimate H_2S concentration at arbitrary time (t), i.e., we have to determine the initial H_2S oxidation rates while considering H_2S concentration dependence. As shown in Fig. 5, H_2S concentration at time (t) after sampling was conveniently well proportional to the initial H_2S oxidation rate constants (k^{-1}). As a result, we can estimate initial H_2S concentration following Eq. (1) using initial H_2S oxidation rate constants (k^{-1}), time after

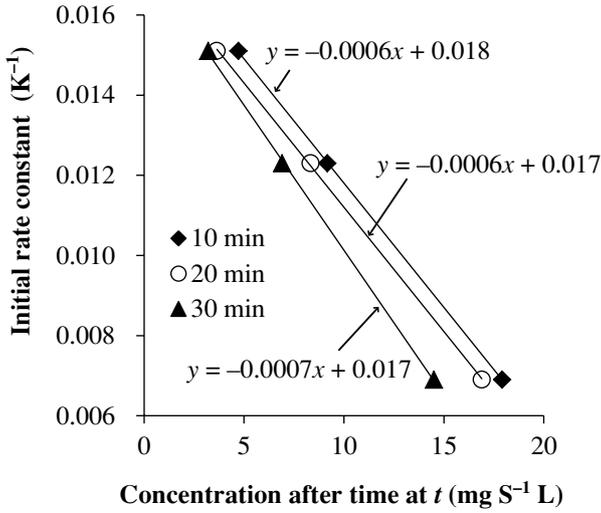


Fig. 5. Relationship between H₂S concentration at time (*t*) and initial H₂S oxidation rate constants.

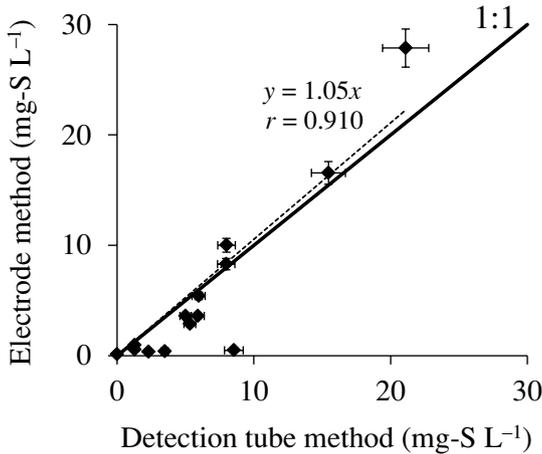


Fig. 6. H₂S concentration in the sediment pore water determined using the detection tube and ion electrode methods corrected by the proposed method.

sampling (*t*), and H₂S concentration at time *t*.

The corrected H₂S concentrations obtained by the ion electrode were very close to values measured by the detection tube (Fig. 6). A slope of least square equation between the ion electrode and detection tube was almost 1 after data correction (Fig. 6), while it was 0.8 before data correction. Although accuracy can

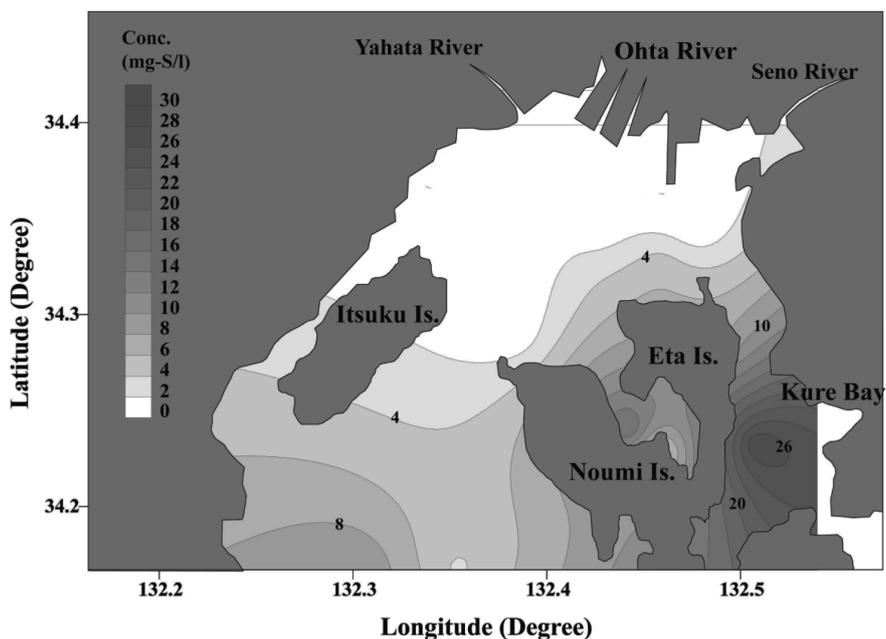


Fig. 7. Horizontal distribution of H₂S concentration in the sediment pore water from the northern headwaters of Hiroshima Bay.

be improved while performing this proposed method, the pore water samples with H₂S concentration lower than 0.5 mg-S L⁻¹ yielded unreliable results which may be attributed to their higher H₂S oxidation rates compared to those seen in Fig. 5.

Finally, the horizontal distribution of H₂S concentration in the pore water of the sediment collected from the northern headwaters of Hiroshima Bay was investigated (Fig. 7). The concentration ranged from 0.1 to 28 mg-S L⁻¹. Especially, the highest levels of H₂S were observed in Etajima Bay where extensive oyster culture is conducted and in Kure Bay which is surrounded by industrial areas.

CONCLUSIONS AND SUGGESTIONS

An on-site simplified method for the determination of hydrogen sulfide in marine sediment pore water was developed using an ion electrode with consideration of hydrogen sulfide oxidation rate and calculated initial H₂S oxidation rate constant. The H₂S oxidation rate was dependent on the initial concentration of H₂S and salinity, while water temperature and pH did not affect the rate constants. It is advisable to note the total time required for sampling and measurement to compensate for H₂S oxidation, or determine H₂S concentration immediately after sampling using detection tube method to increase the accuracy of the test results.

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