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PORE WATER SAMPLING METHOD FOR SULFIDE MEASURING IN SEDIMENT

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The concentration of sulfide contained in the bottom sediment is a crucial indicator of environmental pollution in enclosed coastal seas. Acid-volatile sulfide (AVS) is widely used as an index of sulfide concentration in Japan. However, AVS contains a large amount of sparingly soluble bound sulfides that have little effect on living organisms. Therefore, its accuracy as an environmental index for evaluating the effect on living organisms is considered low. However, there are few measurement examples of dissolved sulfide (hereafter abbreviated as DS) because it is difficult to collect and analyze many samples in a short time. We devised a method to easily collect pore water from sediments and analyze the DS contained in pore water. The accuracy of this analysis method was examined and it was confirmed that sufficiently practical measured values could be obtained. By comparing DS with conventional AVS at the survey site of Hakata Wan enclosed coastal sea using this method, it was found that the DS concentration is a highly independent index different from AVS and is an effective index for evaluating environmental pollution.

Key Words: *dissolved sulfides, sediment, pore water, AVS*

1. INTRODUCTION

Sulfides, including hydrogen sulfide and sulfide ions, are produced by sulfate-reducing bacteria in sediments found in eutrophic environments lacking oxygen.[1)] The amount of these compounds is considered an important indicator of environmental degradation. In the field of aquatic environments related to fisheries, acid-volatile sulfide (AVS) is commonly used as a measure of sulfides and is also listed as a standard value for water used in fisheries.[2)] However, it is important to note that the majority of AVS consists of bonded sulfides derived from iron sulfide and other substances. It has been pointed out that such bonded sulfides have an extremely low solubility product[3)] and are almost insoluble in water, making them inappropriate as a measure to assess their impact on biological habitats.[4)] Conversely, there is a paucity of data on the measurement of DS in sediments, despite the awareness of the need for such measurements. The reason is that conventional methods of analyzing DS, such as the official method (JIS K 0102),[5)] are not suitable for processing a large number of samples due to the complexity of the equipment configuration and procedures. The authors developed a method for measuring DS in sediments that does not require special techniques and provides results quickly in the field, and made measurements at a number of sites, mainly in Hakata Bay. The purpose of this study is to evaluate this method and to examine the difference between conventional AVS and dissolved sulfide.

2. MATERIALS AND METHODS

(1) Collection of pore water from sediments

a) Pore water-collecting pipette (Patent No. 6467577)

A filtration section was fabricated by treating JIS No.5C quantitative filter paper with water-repellent

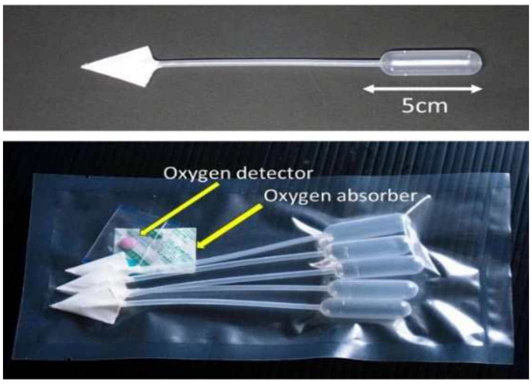

Fig.1 Pore water-collecting pipette.

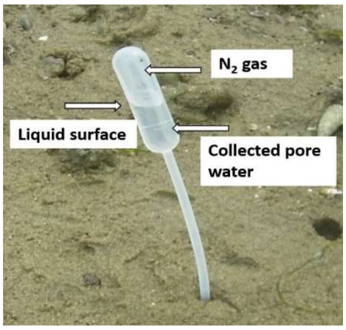

Fig.2 Usage on tidal flat.

treatment and shaping it into an arrowhead shape. The filtration section was then attached to the tip of a disposable polyethylene pipette (**Fig.1** upper).

The pipettes were filled with nitrogen gas internally and subsequently sealed in gas-barrier bag with an oxygen absorber. To minimize the effects of atmospheric oxygen, the package was opened immediately before use (**Fig.1** lower). The anoxic condition of the pipettes was confirmed by enclosing an oxygen detector (sensitivity of 0.1% O_2) (**Fig.1** lower).

b) Features of the pipette

The suction force of 70 to 100 hPa is low enough to prevent clogging. This feature allows pore water to be filtered from difficult-to-filtrate sediments such as sludge in a relatively short period of time.

c) Method of use

To collect filtered pore water, filter paper section was inserted into the target sediments and negative pressure was applied by crushing the dropper section **(Fig.2)**. This pipette may experience difficulty when collecting water from sediments that contain many voids, such as sandy soil. In this case, the authors placed the sample in a container and lightly tapped or otherwise vibrated it to allow the pore water to seep out and then collected it using this pipette. Sample collection takes 1.5mL to 2mL per pipette. The sample is removed by cutting off the filter paper portion of the pipette and measured using an existing analysis kit.

(2) Simplified analytical methods

For the simple analysis method, we used the Kyoritsu Rikagaku Kenkyusho WAK-S kit. The measurement range is 0.1 to 5 ppm, and the device can be used in seawater. This is a variation of the methylene blue method described in JIS K0102.[5)]

The required sample volume is 1.5 ml. The first reagent was added to the sample taken from the pipette and promptly aspirated into the pack containing the coloring reagent to cause a color reaction. Measurements were primarily taken using a colorimetric card, with a spectrophotometer utilized when needed. If the concentration of the sample exceeded the upper limit of measurement, the sample was quantitatively diluted with oxygen-free water to a measurable concentration. The obtained result was then multiplied by the dilution factor. To prevent oxidation by oxygen in the air, the process from sample removal to pack inhalation was completed within 30 seconds.

(3) Accuracy Testing

a) Influence of the use of this pipette

Test solutions of 0.1, 0.5, and 1.0 ppm were prepared by diluting a 1000 ppm sodium sulfide solution adjusted by the iodine titration method with oxygen-free water. The solution was impregnated into analytical quartz sand. The test solution was collected from each impregnated silica sand sample using this pipette and was used as the experimental group, while the test solution itself was used as the comparison group. The samples were subjected to the aforementioned color reaction process and their absorbance was measured at 670 nm on a Shimadzu UVmini-1240 spectrophotometer. Each measurement was repeated eight times to determine the difference between the experimental and control groups.

b) Colorimetric card reading accuracy

Individual differences in reading colorimetric cards used in the simplified method were tested by several people. The solution used was adjusted by diluting the aforementioned sodium sulfide solution. The tests were conducted outdoors under natural light. When the object of measurement displayed the middle density of the colorimetric card tones, the measured value was determined by the average of the values above and below the card. At the Kuromon River measurement site, described below, the absorbance of the same samples was measured with a portable absorbance photometer (Kyoritsu Rikagaku Kenkyusyo Lamda 9000 model) and compared with the colorimetric card readings. Furthermore, the accuracy of the portable absorbance spectrophotometer was evaluated in comparison with a high-precision absorbance spectrometer (Shimadzu UV mini-1240) using a methylene blue solution.

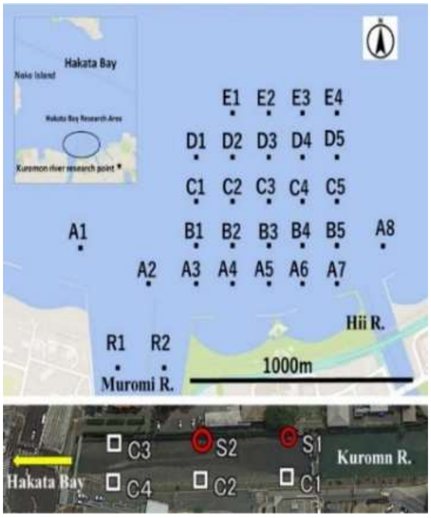

Fig.3 Hakata Bay and Kuromon River research points.

(4) Comparison with existing method

An existing simple analytical method for measuring sulfide in pore water (DS) is the method devised by Sugawara et al.[6] We measured DS at eight sites on tidal flats in Higashi-ku, Fukuoka City, Japan, using this method and the method described by Sugawara et al.[6] and compared the results.

(5) On-site measurement

a) Inner part of Hakata Bay

A total of 74 measurements were taken off Momochihama, Sagara-ku, Fukuoka City in November 2017 and October 2019, 2020 (**Fig.3** top). This area is known for frequent outbreaks of anoxic water.

AVS, mud temperature, and DS were measured. Pore water was collected from a depth of approximately 5cm in the sediment using an Ekman Barge mud sampler (20cm square). AVS was measured using the Hedrotec S330 sulfide kit detector tube method, and moisture content was calculated per gram of dried mud using a 110°C, two-hour drying method. In the October 2020 survey, flame atomic absorption spectrophotometry (Hitachi Z-2000 atomic absorption spectrophotometer) was used to analyze the total iron and investigate its relationship with iron content.

b) Seasonal variation in the Kuromon River

To investigate the seasonal fluctuation of DS, a survey was conducted at six predetermined locations along the Kuromon River. The river flows into Hakata Bay from an artificial lake located in Ohori Park, Chuo-ku, Fukuoka-City (**Fig.3** bottom). Surveys were conducted seven times during the ebb tide of high tide from July 2018 to July 2019. The method described above was used to measure DS and AVS, and seasonal variations in the measured values were compared.

3. RESULTS AND DISCUSSION

(1) Accuracy testing

a) Influence of the use of this pipette

Table 1 displays the absorbance values for both the test and control groups. The concentration in the group that used the pipette varied slightly more than that in the control group at low concentrations, but was almost the same at 1 ppm. The coefficient of variation was less than 0.1 in all cases, and it was concluded that the use of this pipette did not significantly affect the measurement.

b) Colorimetric card reading accuracy

The color tones on the card were visually consistent, and no individual differences were observed (**Fig.4**). In the field samples measured at the Kuromon River, the correlation coefficient was as high as

Table 1 Absorbance values of both groups.

	0.1ppm		0.5ppm		1.0ppm	
	EXPT	CNTR	EXPT	CNTR	EXPT	CNTR
Average	0.17	0.15	0.74	0.66	1.58	1.31
S.D	0.02	0.01	0.05	0.03	0.08	0.08
C.V	0.09	0.05	0.07	0.04	0.05	0.06

Table 2 Coefficient of variation of two devices.

	1ppm	2ppm	4ppm	8ppm
portable	0.17	0.06	0.02	0.01
UV-mini	0.07	0.00	0.01	0.01

Fig.4 Testing with known concentrations of sodium sulfide.

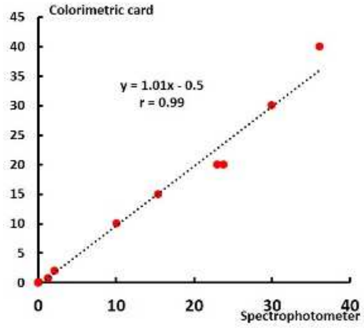

Fig.5 Comparison of colorimetric card and portable spectrophotometer readings.

0.99 when compared using a portable absorbance spectrophotometer and a colorimetric card (**Fig.5**). However, individual differences and the measurement environment can affect colorimetric card readings. For accurate low-concentration sulfide measurements, it is recommended to use an absorbance spectrophotometer to avoid errors. Comparison of the portable absorbance spectrophotometer and the high-precision Shimadzu UVmini-1240 spectrophotometer with methylene blue solution showed relatively large variations at 1 ppm for the portable type (**Table 2**). However, at 2 ppm and above, the coefficient of variation of the portable type was less than 0.6. The lower limit of quantification of this simple kit is 0.1 ppm, indicating that even the portable type can be used without accuracy problems. This is because a 2ppm methylene blue solution corresponds to about 0.15 ppm sulfide, which is near the lower limit of this measurement method.

(2) Comparison with existing method

The results of the DS measurements at the eight sites demonstrated a consistent relationship between the Sugawara method and the method employed in this study, with a correlation coefficient of 0.9 (**Fig.6**). However, some values measured by the method in this study were several times higher than those measured by the Sugawara method. The Sugawara method uses a water-extracted sample as the analysis target, while the present method uses the pore water itself as the analysis target, and the analysis process differs from the Sugawara method. It was expected that different analytical objectives and methods would produce different results to some extent, but the cause of such discrepancies is unknown.

(3) On-site measurement

a) Measurements in the inner part of Hakata Bay

Table 3 displays the measurement results, while

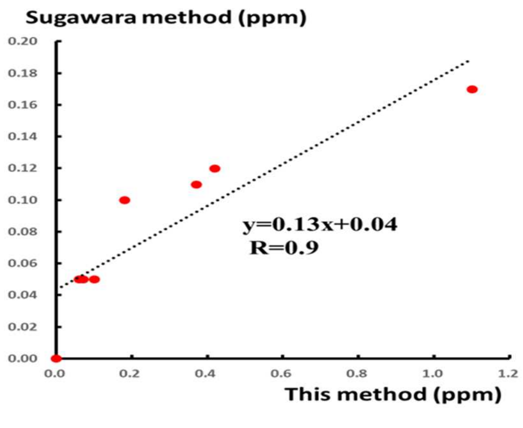

Fig.6 Comparison with Sugawara method.

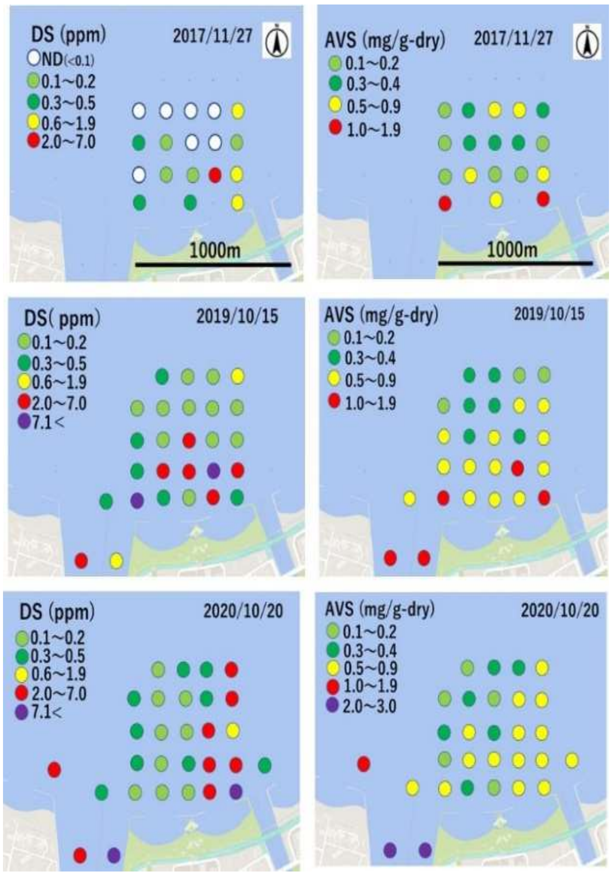

Fig.7 Horizontal distributions of DS and AVS.

Table 3 Measurement results.

survey point	2017/11/27			2019/10/15			2020/10/20			
	DS ppm	AVS mg/g	Temp ℃	DS ppm	AVS mg/g	Temp ℃	DS ppm	AVS mg/g	Temp ℃	Total Iron mg/g
A1	–	–	–	–	–	–	2.0	1.7	21.7	42.7
A2	–	–	–	0.3	0.8	21.9	0.5	0.8	21.8	36.2
A3	0.5	1.6	15.8	10.0	1.5	21.9	0.1	0.7	21.9	40.9
A4	–	–	–	0.5	0.6	21.9	0.1	0.4	21.3	39.5
A5	0.5	0.5	15.5	0.2	0.5	22.1	0.1	0.2	21.2	28.1
A6	–	–	–	2.5	0.7	21.9	4.0	0.6	21.3	39.8
A7	0.7	1.0	16.2	0.5	1.0	22.3	10.0	0.9	21.3	37.6
A8	–	–	–	–	–	–	0.3	0.5	20.9	18.9
B1	ND	0.1	13.5	0.3	0.5	22.2	0.3	0.2	21.4	35.9
B2	0.2	0.6	13.5	2.5	0.5	22.5	0.2	0.5	21.1	42.5
B3	0.1	0.2	14.2	4.0	0.6	22.7	0.3	0.8	20.9	44.6
B4	5.0	0.1	14.2	20.0	1.4	22.5	3.0	0.9	20.9	42.5
B5	1.5	0.8	14.0	2.5	0.6	22.4	2.5	0.7	20.9	31.5
C1	0.3	0.1	15.3	0.4	0.5	22.1	0.3	0.3	21.5	37.2
C2	0.1	0.3	15.2	0.1	0.3	22.2	0.2	0.6	21.3	42.4
C3	ND	0.3	14.8	4.0	0.7	22.5	0.2	0.3	21.2	41.5
C4	ND	0.3	14.6	0.1	0.3	22.4	2.0	0.5	21.1	28.6
C5	0.1	0.2	14.7	0.2	0.6	22.4	1.5	0.8	20.9	35.7
D1	ND	0.1	15.7	0.2	0.2	22.2	0.3	0.2	20.9	36.1
D2	ND	0.3	16.0	0.2	0.3	21.5	0.1	0.3	20.5	34.0
D3	ND	0.9	15.5	0.2	0.4	21.8	0.1	0.2	20.6	28.9
D4	ND	0.5	15.9	0.1	0.5	22.1	0.4	0.6	21.1	41.9
D5	1.3	0.3	15.4	0.2	0.5	21.8	2.5	0.5	21.2	42.1
E1	–	–	–	0.5	0.4	22.1	0.2	0.2	20.9	39.9
E2	–	–	–	0.2	0.4	22.1	0.5	0.3	20.9	38.0
E3	–	–	–	0.1	0.2	22.1	0.5	0.4	21.2	38.4
E4	–	–	–	1.5	0.2	21.9	2.0	0.5	20.6	44.9
R1	–	–	–	5.0	1.6	21.7	7.0	2.0	21.9	39.9
R2	–	–	–	1.0	1.5	22.3	10.0	2.8	21.8	38.0

Fig.7 illustrates the horizontal distributions of DS and AVS. DS tended to be higher in 2017 and 2018 at survey points closer to shore, A1-A8 and B1-B5. In 2020, high concentrations were found in the waterways of the Hii River, specifically in E4, D5, and A7. AVS showed a similar trend, but not as clear as DS.

Sulfate-reducing bacteria are a complex system composed of multiple bacterial species capable of utilizing nearly all organic matter.7) It is suggested that areas with high organic matter, such as the lower reaches of rivers, have higher activity of these bacteria, which may have resulted in the accumulation of high concentrations of DS. In 2017, the mean temperature of the bottom sediment was 15.0°C, a value that was higher than the 22.1°C observed in 2019 and 21.2°C in 2020. The activity of sulfate-reducing bacteria is significantly affected by temperature, as explained below. The elevated number of non-detects observed in 2017 may be attributed to the temporal discrepancy between the measurements and the other two survey periods, with the mud temperature exhibiting a notable decline of approximately 7°C lower.

b) Seasonal variation in the Kuromon River

The concentration fluctuations of DS were almost always linked to the fluctuations of mud temperature in the mean value fluctuations at the measurement points. However, this tendency was rarely observed in the AVS (**Fig.8**). In AVS, as discussed below, the majority of the sulfides are relatively stable bonded sulfides, which may explain why the effect of temperature variation was small. At this research site, seawater from Hakata Bay and freshwater from the upstream mix, caused the bottom mud to become extremely sludgy. Furthermore, during low tide in summer, the surface temperature of the mud that has dried out under direct sunlight rises to nearly 40°C. The optimal temperature for growth of most sulfate-reducing bacteria is 28-30°C or 37°C.8) As a result, sulfate reducing bacteria are more active during the summer and less active during the winter. The concentration of DS is influenced by the activity of sulphate- reducing bacteria, which is in turn affected by the temperature of the mud. This may be the reason for the observed decrease in DS during the winter months. The AVS increased again in July of the following year, indicating that it slowly followed the fluctuations in DS. This indicates that the AVS reflects a relatively long-term pollution situation.

c) Relationship between AVS and DS

Figure 9 shows the correlation between AVS and DS based on 116 analytical data obtained from the Hakata Bay and Kuromon River surveys. There is a significant, but not strong, correlation between AVS and DS concentrations. Calculations of the measurements at 116 points showed that the average percentage of bound sulfide in the AVS was 98.5%, and the remaining 1.5% was DS. The coefficient of variation of AVS was 0.8 and that of DS was 1.8 at 116 points. A possible reason for the large DS variability is that AVS is mostly composed of relatively stable bonded sulfides, while DS is unstable and reflects fluctuations in temperature and organic load.

d) Relationship with iron

In October 2020, the sediments at the Hakata Bay survey station had a total iron content ranging from

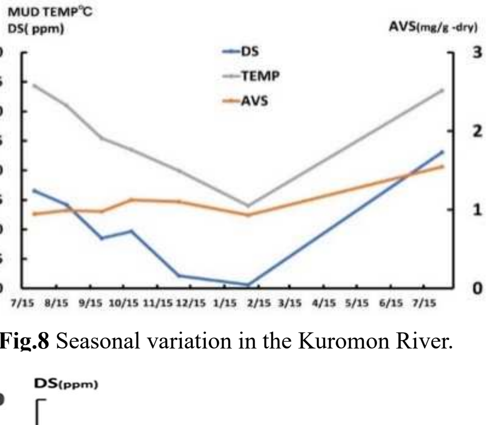

Fig.8 Seasonal variation in the Kuromon River.

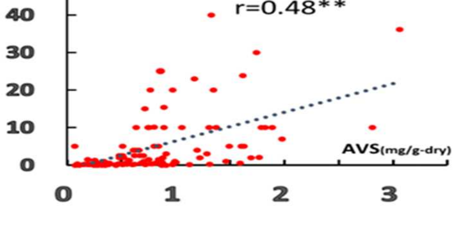

Fig.9 Relationship between AVS and DS.

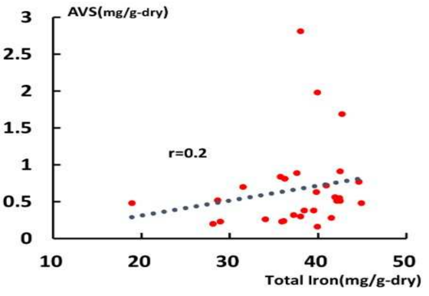

Fig.10 Relationship between AVS and total iron.

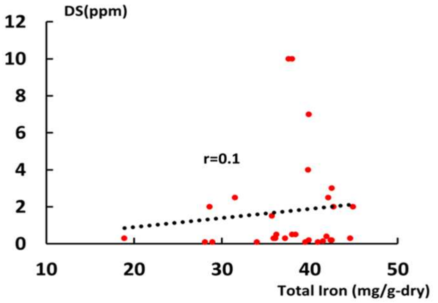

Fig.11 Relationship between DS and total iron.

19 to 45 mg/g-dry, as indicated in **Table 3**. **Figure 10** and **Figure 11** demonstrate that there is no correlation between the total iron content, AVS, and DS.

As previously stated, most of the AVS in this area consists of bound sulfides. Even if we assume that all of the bound sulfides are iron (II) sulfide, the amount of iron present as iron (II) sulfide is only about 3% of the total iron content. Total iron includes iron unrelated to sulfides, but the presence of iron disulfide cannot be ignored. Iron (II) sulfide is converted to iron disulfide in nature and accumulates in the environment.9),10) When evaluating AVS, it is important to pay attention to the chemical species of iron sulfides since iron disulfide is not detected as an AVS due to its insolubility.11)

4. CONCLUSION

In Tokyo Bay, it has been observed that anoxic water mass and blue tide occurrences are closely related to DS trends in seabed sediments, while AVS is reported to be less correlated.4) DS is an unstable compound, forming in hypoxic environments and easily oxidized and eliminated in the presence of oxygen. Its measured value is considered an indicator of short-term environmental conditions. It has been suggested that it is best to avoid actively substituting AVS for DS variability.12) One of the problems with this method is the inadequate evaluation of direct analysis of pore water that may contain unknown interfering substances. Based on the results of the numerous measurements we have carried out to date, it is considered that there are few interfering components causing significant errors. The method will continue to be refined in order to enhance its reliability. Improvements are being made to the method, such as fixing samples as zinc sulfide or other sulfides.

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