

## Development of Diffusion-Precipitation Method to Determine AVS Concentrations in Freshwater Sediments

Ki Hoon Song

Department of Oceanography, Korea Naval Academy

**Abstract** - A diffusion-precipitation method was developed to determine acid volatile sulfide (AVS) concentrations in freshwater sediments. This method uses silver nitrate as a sulfide trap solution and the concentration of trapped sulfide is determined gravimetrically. The proposed diffusion-precipitation method is more rapid and less expensive than previously developed purge-and-trap methods. Spiked sodium sulfide recoveries using this method (97 ~ 120%) were similar with a previously developed diffusion-absorption method (93.8 ~ 115%) and about 20% greater than a previously developed purge-and-trap method (74.6 ~ 105%). Detection limit of this method ( $0.1 \mu\text{mole S g}^{-1}$ ) was comparable with that of diffusion-absorption method ( $0.06 \mu\text{mole S g}^{-1}$ ) and purge-and-trap method ( $0.05 \sim 0.5 \mu\text{mole S g}^{-1}$ ).

**Key words** : AVS, SEM, metal, sediment, method, diffusion, precipitation, benthic invertebrates

### INTRODUCTION

Acid volatile sulfide (AVS) is considered to be a major binding phase controlling the bioavailability of some cationic metals (i.e. Ag, Cd, Cu, Ni and Zn) in anoxic sediments (Di Toro *et al.* 1990; Ankley 1996). Amorphous iron monosulfide (i.e. mackinawite and greigite) are thought to be the primary mineral components of AVS in uncontaminated sediments (Cornwell and Morse 1987). AVS and simultaneously extracted metal (SEM) are operationally defined as the sulfides volatilized and metals extracted, respectively, from sediment by the addition of 1 N HCl (Di Toro *et al.* 1990). Based on the AVS normalization model, all sulfide binding sites will be occupied by dissolved metals resulting in increasing metal bioavailability in the pore water at SEM/AVS ratios  $> 1$  (or mole difference is  $> 0$ ), however, all dissolved metals should be bound in sulfide binding sites resulting in reducing metal bioavail-

ability at SEM/AVS ratios  $< 1$  (or mole difference is  $< 0$ ) (Di Toro *et al.* 1990; Song 2002; Song and Breslin 2004). AVS in sediment, therefore, is important to controlling metal accumulation and toxicity in benthic invertebrates.

Determination of AVS typically has been performed using a purge-and-trap method employing HCl to volatilize the AVS and various absorbing media to trap the generated  $\text{H}_2\text{S}$ . The hydrogen sulfide can then be measured using gravimetric techniques (Di Toro *et al.* 1990; Leonard *et al.* 1995), colorimetric analysis (Allen *et al.* 1993), specific-ion electrode analysis (Pesch *et al.* 1995; Boothman and Helmstetter 1995), or gas chromatography with photoionization detection (Casas and Crecelius 1994). The diffusion method, as described by Brouwer and Murphy (1994), employed a  $15 \times 45$  mm vial containing 3.0 mL of SAOB (sulfide antioxidant buffer) inserted inside a 20 mL vial, which was capped and placed on a rotary shaker for 60 min at 150 rpm. The sulfide in the SAOB was measured with a sulfide ion electrode. This diffusion method was modified from the original method developed by Hsieh and Yang (1989), who acidified 10 g of wet sediment, trapped

\* Corresponding author: Ki Hoon Song, Tel. 055-549-1416, Fax. 055-542-0033, E-mail. songkh37@hanmail.net

the evolved hydrogen sulfide in Zn acetate inside a closed container, and then used an iodometric titration for sulfide quantification.

Recently, Leonard *et al.* (1996a) modified the method of Brouwer and Murphy (1994) as follows: a 30 mL vial was glued with silicon adhesive sealant to the inside of a 500 mL glass jar which contained 5 g of wet sediment and 50 mL of 1 N HCl. The 10 mL of SAOB solution was placed in the 30 mL vial, 25 mm above the bottom of the glass jar, to allow better mixing through magnetic stirring of the sediments. The diffusion methods have some important advantages compared to the purge-and-trap method including: 1) the method enables many more samples to be analyzed in a day and thus time is saved (i.e. about 50 samples per day); 2) reduced cost of supplies and chemicals; 3) the experimental apparatus is simpler and easier to set up; and 4) the recoveries and detection limits of AVS are higher because AVS is analyzed within a closed system.

In this study a simple AVS determination method was developed from a modification of the diffusion–absorption method of Leonard *et al.* (1996a). Silver nitrate ( $\text{AgNO}_3$ ) was used instead of SAOB solution as a sulfide trap solution and analyzed AVS concentrations using a gravimetric method instead of an ion-specific sulfide electrode in this study. This method was referred as a diffusion–precipitation method to distinguish it from the diffusion–absorption methods developed by Brouwer and Murphy (1994) and Leonard *et al.* (1996a). Sulfide recovery and the detection limit of the diffusion–precipitation method were examined using sodium sulfide ( $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ ) and compared with previously developed diffusion–absorption and purge-and-trap methods.

## METHOD AND MATERIALS

The diffusion–precipitation method utilizes HCl to volatilize the AVS and trap the  $\text{Ag}_2\text{S}$  in an  $\text{AgNO}_3$  solution in a closed system. Three to five grams of wet sediment which were collected from Lake Ontario using grab sampler placed on a 500 mL glass jar (Song and Breslin 1998) (Fig. 1).

Wet sediment (5 g) was dried at  $65^\circ\text{C}$  for 24 hours to obtain sediment water content. Ten mL of 0.1 mM  $\text{AgNO}_3$  solution was poured into a 30 mL beaker. To allow the

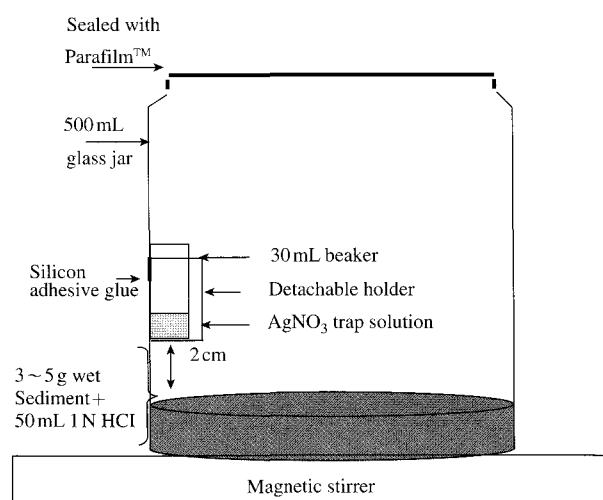


Fig. 1. Schematic diagram of the diffusion–precipitation method apparatus.

beaker to be removed after the experiment, the beaker was inserted in a polyethylene detachable holder that was glued with silicon adhesive sealant inside the glass jar and placed 2 cm above a sediment surface (Fig. 1). After pouring 50 mL of 1 N HCl, the glass jar was immediately and tightly wrapped with Parafilm™ to prevent the escape of  $\text{H}_2\text{S}$  gas, covered whole glass jar to prevent photo-reduction of Ag and stirred on a magnetic stirrer for appropriate time.

The 30 mL beaker containing the trapped  $\text{Ag}_2\text{S}$  was then removed from the detachable holder. The precipitated  $\text{Ag}_2\text{S}$  was filtered using a pre-weighted polycarbonate filter ( $0.45 \mu\text{m}$ ). Sulfide recovery and the detection limit of the diffusion–precipitation method were examined using sodium sulfide ( $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ ) and compared with previously developed diffusion–absorption and purge-and-trap methods. Sulfide recoveries were examined using various sodium sulfide ( $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ ) concentrations ( $2 \sim 20 \mu\text{mol}$ ) and  $\text{AgNO}_3$  concentrations ( $4 \sim 100 \text{mmol L}^{-1}$ ). Sulfide recovery was also examined as a function of time.

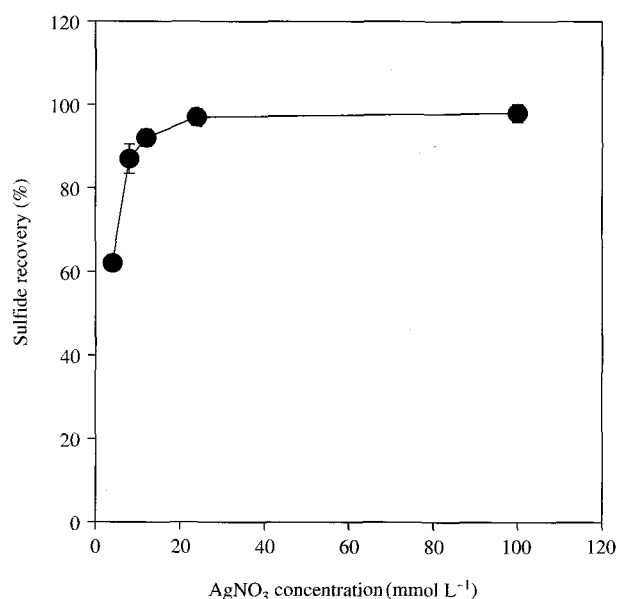
## RESULTS AND DISCUSSION

### 1. Determination of optimal conditions

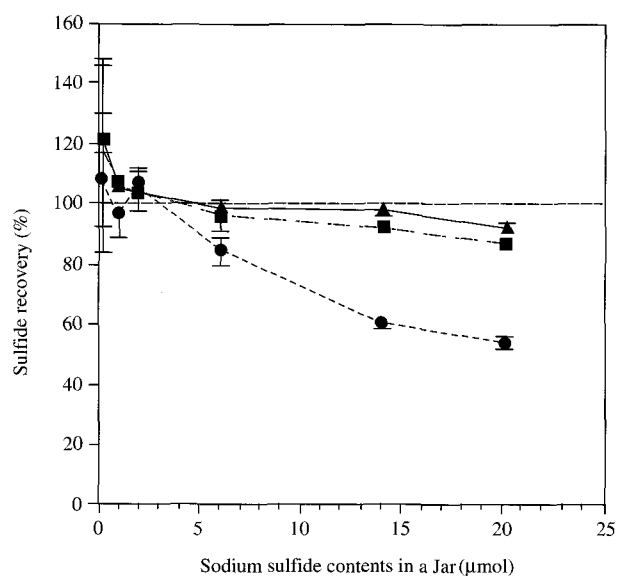
#### 1) Concentration of $\text{AgNO}_3$ trap solution and sulfide recovery

Fourteen micromoles ( $14 \mu\text{mol}$ ) of sodium sulfide ( $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ ) and 50 mL of 1 N HCl were placed into a 500 mL jar to examine sulfide recovery as a function of  $\text{AgNO}_3$  concentration. Ten milliliters (10 mL) of  $\text{AgNO}_3$

trap solution was placed into a 30 mL beaker in the detachable holder. The  $\text{AgNO}_3$  concentrations examined ranged from 4 to 100  $\text{mmol L}^{-1}$ . Results showed that sulfide recoveries increased from 62% to 97% with increasing  $\text{AgNO}_3$  concentrations (Fig. 2). Sulfide recovery did not



**Fig. 2.** Sulfide recovery (%) as a function of  $\text{AgNO}_3$  concentrations (10 mL) in conditions of 14  $\mu\text{mol}$  sodium sulfide and 1 hour diffusion time.



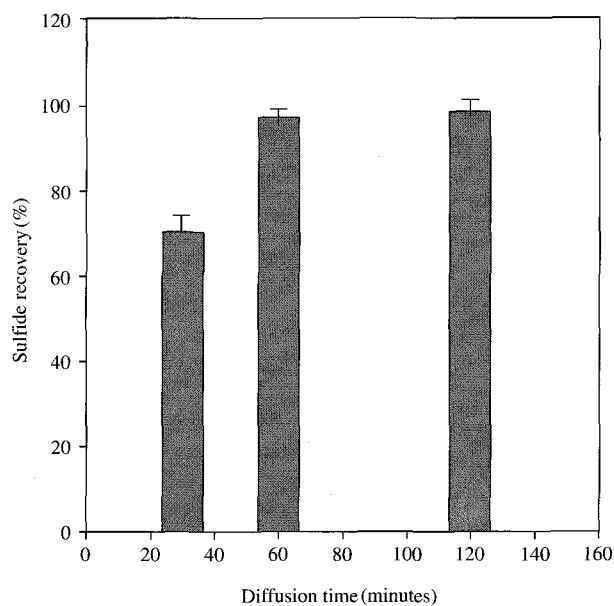
**Fig. 3.** Sulfide recovery (%) in various  $\text{AgNO}_3$  trap solutions ( $--\bullet--$ : 4  $\text{mmol L}^{-1}$ ,  $--\blacksquare--$ : 12  $\text{mmol L}^{-1}$ ,  $-\blacktriangle-$ : 25  $\text{mmol L}^{-1}$ ) as a function of sodium sulfide concentration for 1 hour diffusion time.

change significantly at  $\text{AgNO}_3$  concentrations greater than 25  $\text{mmol L}^{-1}$  (Fig. 2).

For various sodium sulfide concentrations (0.2~20  $\mu\text{mol}$ ) the sulfide recovery ranged from 54~107% and 87~120% in 10 mL of 4 and 12  $\text{mmol L}^{-1}$   $\text{AgNO}_3$  trap solutions, respectively, for a 1 hour diffusion time (Fig. 3). However, sulfide recoveries were more increased to 97~120% in 10 mL of 25  $\text{mmol L}^{-1}$   $\text{AgNO}_3$  trap solution for a 1 hour diffusion time (Fig. 3). In general, AVS concentrations in freshwater sediments are below 13  $\mu\text{mol S g}^{-1}$  (corresponding with approximately 20  $\mu\text{mol}$  of trapped sulfide in the  $\text{AgNO}_3$  solution). Therefore, this method can be used to determine AVS concentrations in freshwater sediments with greater than 97% recoveries using a 10 mL 25  $\text{mmol L}^{-1}$   $\text{AgNO}_3$  solution.

## 2) Diffusion time

An appropriate diffusion time of sulfide trap was determined in fixed conditions of a 14  $\mu\text{mol}$  sodium sulfide solution and 10 mL of a 25  $\text{mmol L}^{-1}$   $\text{AgNO}_3$  trap solution. Results showed that sulfide recovery varied from 70% at a 30 minute diffusion time to over 97% at a 1 hour diffusion time (Fig. 4). Sulfide recoveries were not significantly different after a 1 hour diffusion time (Fig. 4). These results suggest that a 1 hour diffusion time is sufficient to trap all



**Fig. 4.** Sulfide recovery (%) as a function of diffusion time in conditions of a 14  $\mu\text{mol}$  sodium sulfide solution and a 25  $\text{mmol L}^{-1}$   $\text{AgNO}_3$  trap solution.

**Table 1.** Comparison of sulfide recoveries (%) and detection limits (%) between some typical AVS determination methods and Diffusion–Precipitation method in this study

Analytical method	Detection method	Sediment amount (g)	Na <sub>2</sub> S recovery (%)	Detection limits (μmol S g <sup>-1</sup> )	Reference
Purge–and–trap	Gravimetric	10~15	95~103	0.5	Di Toro <i>et al.</i> 1990
		15~20	74.6	–	Liber <i>et al.</i> 1996
		10	87	0.05	Peterson <i>et al.</i> 1996
		10	72~81	–	Carlson <i>et al.</i> 1991
		10	87	0.05	Leonard <i>et al.</i> 1996b
	Colorimetric	2~7	90	–	Chen and Mayer 1999
		10	90	0.01	Allen <i>et al.</i> 1993
		10	94	–	Hare <i>et al.</i> 1994
	Diffusion absorption (SAOB)	Ion–Electrode	5	109~115	0.06
1			93.8	–	Brouwer and Murphy 1994
Diffusion precipitation (AgNO <sub>3</sub> )	Gravimetric	2~5	97~120	0.1	This study

generated hydrogen sulfide in the conditions.

### 3) Method detection limits

Method detection limits were determined using 10 mL of a 4~25 mmol L<sup>-1</sup> AgNO<sub>3</sub> trap solutions for a 1 hour diffusion time. Under these conditions, approximately 0.2 μmol of sulfide was determined with a recovery ranging from 97~120% (Fig. 3). These recoveries correspond to a detection limit of approximately 0.1 μmol S g<sup>-1</sup> based on 5 g of wet sediment. Precipitation of AgCl(s) was not detected in the trap solution when 50 mL of a 1 N HCl solution was examined without sodium sulfide.

## 2. Comparison of recoveries and detection limits with other methods

The range of sulfide recoveries using the diffusion–precipitation method (97~120%) were greater than the purge–and–trap method combined with gravimetric (74.6~103%) and colorimetric (90~94%) analysis (Table 1). However, the range of sulfide recoveries using the diffusion–precipitation method was comparable with the diffusion–absorption method (93.8~115%) (Table 1). The detection limit of the diffusion–precipitation method (0.1 μmol S g<sup>-1</sup>) was similar with the detection limit of the diffusion–absorption method (0.06 μmol S g<sup>-1</sup>) and also comparable with that of the purge–and–trap method (0.05~0.5 μmol S g<sup>-1</sup>) based on the amounts of wet sediment examined (Table 1). Basically, the diffusion–precipitation method was a combination of the previously developed purge–and–trap and the diffusion–absorption methods.

Therefore, the sulfide recovery and detection limit of the

diffusion–precipitation method should be within the range of the purge–and–trap and diffusion–absorption methods. Previously developed purge and–trap systems were purged with oxygen–free nitrogen before acidification of the sediment (Di Toro *et al.* 1990; Leonard *et al.* 1995). However, Brouwer and Murphy (1994) observed no significant difference in the quantity of AVS obtained with or without a nitrogen purge. The diffusion of the H<sub>2</sub>S released from the sediment and absorption on the buffer solution (SAOB) likely proceeds much more rapidly than the oxidation of H<sub>2</sub>S by oxygen in the gaseous state (Brouwer and Murphy 1994; Leonard *et al.* 1996a). Similarly, the high recovery (97~120%) of sulfide by the diffusion–precipitation method also suggests that the precipitation of diffused H<sub>2</sub>S as Ag<sub>2</sub>S is also more rapid than the oxidation of H<sub>2</sub>S by oxygen in the gaseous state in the apparatus. Therefore, a nitrogen atmosphere was not necessary in the diffusion–precipitation method to measure AVS concentrations.

## CONCLUSION

In this study a simple diffusion–precipitation method was developed to determine acid volatile sulfide (AVS) concentrations in freshwater sediments from a modification of the previously developed diffusion–absorption method. Silver nitrate (AgNO<sub>3</sub>) was used as a sulfide trap solution and AVS concentrations were analyzed gravimetrically. Recoveries of sodium sulfide (Na<sub>2</sub>S · 9 H<sub>2</sub>O) in this method were similar with a previously developed diffusion–absor-

ption method and about 20% greater than a purge-and-trap method. Detection limit of this method was comparable with that of other methods. In addition, the diffusion-precipitation method is more rapid and less expensive than purge-and-trap methods.

## REFERENCES

- Allen HE, G Fu and B Deng. 1993. Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) for estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.* 12:1441-1453.
- Ankley GT. 1996. Evaluation of metal/acid-volatile sulfide relationships in the prediction of metal bioaccumulation by benthic macroinvertebrates. *Environ. Toxicol. Chem.* 15:2138-2146.
- Boothman WS and A Helmstetter. 1995. Vertical and seasonal variability of acid volatile sulfides in marine sediments. Final Research Report. U.S. Environmental Protection Agency, Narragansett, RI.
- Brouwer H and TP Murphy. 1994. Diffusion method for the determination of acid-volatile sulfides (AVS) in sediment. *Environ. Toxicol. Chem.* 13:1273-1275.
- Carlson AR, GL Phipps, VR Mattson, PA Kosian and AM Cotter. 1991. The role of acid-volatile sulfide in determining cadmium bioavailability and toxicity in freshwater sediments. *Environ. Toxicol. Chem.* 10:1309-1319.
- Casas AM and EA Crecelius. 1994. Relationship between acid volatile sulfide and the toxicity of zinc lead, and copper in marine sediments. *Environ. Toxicol. Chem.* 13:529-536.
- Chen Z and LM Mayer. 1999. Assessment of sedimentary Cu availability: A comparison of biomimetic and AVS approaches. *Environ. Sci. Technol.* 33:650-652.
- Cornwell JC and JW Morse. 1987. The characterization of iron sulfide minerals in anoxic marine sediments. *Mar. Chem.* 22:193-206.
- Di Toro DM, JD Mahony, DJ Hansen, KJ Scott, MB Hicks, SM Mayr and MS Redmond. 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environ. Toxicol. Chem.* 9:1487-1502.
- Hare L, R Carignan and MA Huerta-Diaz. 1994. A field experimental study of metal toxicity and accumulation by benthic invertebrates: Implications for acid-volatile sulfide (AVS) model. *Limnol. Oceanogr.* 39:1653-1668.
- Hsieh YP and CH Yang. 1989. Diffusion methods for the determination of reduced inorganic sulfur species in sediments. *Limnol. Oceanogr.* 34:1126-1130.
- Leonard EN, VR Mattson and GT Ankley. 1995. Horizon-specific oxidation of acid-volatile sulfide in relation to the toxicity of cadmium spiked into a freshwater sediment. *Arch. Environ. Contam. Toxicol.* 28:78-84.
- Leonard EN, AM Cotter and GT Ankley. 1996a. Modified diffusion method for analysis of acid volatile sulfides and simultaneously extracted metals in freshwater sediments. *Environ. Toxicol. Chem.* 15:1479-1481.
- Leonard EN, GT Ankley and RA Hoke. 1996b. Evaluation of metals in marine and freshwater surficial sediments from the Environmental Monitoring and Assessment Program relative to proposed sediment quality criteria for metals. *Environ. Toxicol. Chem.* 15:2221-2232.
- Liber K, DJ Call, TP Markee, KL Schumde, MD Balcer, FW Whiteman and GT Ankley. 1996. Effects of acid-volatile sulfide on zinc bioavailability and toxicity to benthic macroinvertebrates in spiked-sediment field experiments. *Environ. Toxicol. Chem.* 15:2113-2125.
- Peterson GS, GT Ankley and EN Leonard. 1996. Effect of bioturbation of metal-sulfide oxidation in surficial freshwater sediments. *Environ. Toxicol. Chem.* 15:2147-2155.
- Pesch CE, DJ Hansen, W Boothman, W Berry and JD Mahony. 1995. The role of acid volatile sulfide in determining bioavailability of cadmium and nickel from contaminated sediments: Experiments with *Neanthes arenaceodentata* (Polychaeta: Nereidae). *Environ. Toxicol. Chem.* 14:129-141.
- Song KH. 2002. 6. Prediction of sediment-bound metal bioavailability in benthic organisms: Acid volatile sulfide (AVS) approaches. *Kor. J. Environ. Biol.* 20:101-108.
- Song KH and VT Breslin. 1998. Accumulation of contaminant metals in the amphipod *Diporeia* spp. in western Lake Ontario. *J. Great Lakes Res.* 12:949-961.
- Song KH and VT Breslin. 2004. Influence of AVS on the partitioning of bioavailable Zn to various binding phases in sediments. *J. Kor. Soc. Oceano.* 39:243-250.

Manuscript Received: October 26, 2005

Revision Accepted: November 14, 2005

Responsible Editorial Member: In Young Chung (NIER)