

CHROM. 19 433

## DETERMINATION OF SULPHIDE IN SEA-WATER BY CAPILLARY ISOTACHOPHORESIS

KEIICHI FUKUSHI\*

*Kobe University of Mercantile Marine, Fukae, Higashinada, Kobe 658 (Japan)*

and

KAZUO HIIRO

*Government Industrial Research Institute, Osaka, Midorigaoka, Ikeda, Osaka 563 (Japan)*

(Received December 29th, 1986)

---

### SUMMARY

A new analytical procedure for sulphide in sea-water was developed using capillary isotachophoresis and a tubular microporous polytetrafluoroethylene membrane for preliminary enrichment. Hydrogen sulphide generated by adding sulphuric acid to the sea-water samples was allowed to permeate through the membrane and dissolved in sodium hydroxide solution. Barium cation-exchange resin was then added to the sodium hydroxide solution to remove the carbon dioxide dissolved. A linear calibration graph was obtained for artificial sea-water samples containing up to 2.0 mg/l of sulphide. The method was applied to the determination of sulphide in surface and bottom sea-water samples.

---

### INTRODUCTION

It is important to determine the concentration of sulphide in environmental waters in relation to water pollution. For example, it is said that hydrogen sulphide is generated upon eutrophication of sea-water<sup>1</sup>. In addition, cloudiness in sea-water or underground water is considered to be caused by the presence of sulphide<sup>2,3</sup>.

Methylene blue spectrophotometry<sup>4–6</sup> and iodine titration<sup>6</sup> are generally used for the determination of sulphide ion in aqueous solutions. Goda *et al.*<sup>7,8</sup> determined sulphide ion in artificial aqueous samples and in deposits on the seabed by fluorescence analysis utilizing the fluorescence quenching of mercuriofluoresceinates. However, these methods may lack sensitivity and be affected by interfering substances.

Baadenhuijsen and Seuren-Jacobs<sup>9</sup> determined the total carbon dioxide in plasma by use of a silicone-rubber membrane. Microporous polytetrafluoroethylene (PTFE) membranes were utilized recently for the determination of nitrate ion<sup>10</sup> and ammonia<sup>11–16</sup> in environmental waters, blood and urine and of free chlorine<sup>17</sup> in tap-water. The PTFE membrane appears to be useful for the separation and enrichment of volatile compounds in aqueous solutions containing large amounts of non-volatile interfering substances<sup>18</sup>. Kobos *et al.*<sup>18</sup> examined the selectivity character-

istics of potentiometric carbon dioxide sensors with various gas membrane materials in the context of various organic and inorganic acid interferences. It was reported that the response for hydrogen sulphide as well as that for carbon dioxide was linear.

We have studied the applications of capillary isotachopheresis to the analysis of sea-water<sup>19-22</sup>. There has been no report concerning the isotachophoretic determination of sulphide in sea-water. For this purpose it is necessary to separate sulphide from the large amounts of coexisting chloride, sulphate, bromide, etc., and to enrich prior to the isotachophoretic measurement. Therefore, in the present study, a pre-treatment utilizing a tubular microporous PTFE membrane was applied to the isotachophoretic determination of sulphide in sea-water and the optimum analytical conditions were established. The method was also applied to the determination of sulphide in surface and bottom sea-water samples.

## EXPERIMENTAL

### Apparatus

A Shimadzu Model IP-2A isotachophoretic analyzer equipped with a potential gradient detector was used. The main column was a fluorinated ethylene-propylene (FEP) copolymer tube (15 cm × 0.5 mm I.D.), and the precolumns were PTFE tubes (10-30 cm × 1.0 mm I.D.). The membrane separation unit (Kimoto Electric) is shown in Fig. 1: the inner part comprised a tubular microporous PTFE membrane, maximum pore size 2.0 μm, 20 cm × 2.0 mm I.D. and 2.8 mm O.D. (Japan Goretex), and the outer part of a glass tube (5.0 mm I.D., 6.0 mm O.D.). The flow system is shown in Fig. 2. The separation unit was immersed in a Tokyo-rikakikai Model SB-35 water-bath. The inner part was filled with sodium hydroxide solution, and the sample solution to which sulphuric acid had been added was circulated through the outer part using an Atto Model SJ-1220 peristaltic pump. A Hamilton Model 1710-N or 1725-N microsyringe was used for the injection of samples. A Denkikagaku-keiki Model HPH-22 pH meter, a Yellow Springs Instrument Model 33 salinometer and a Model 58 DO meter were used for the measurements of pH, salinity and dissolved oxygen (DO) of sea-water samples, respectively. A reagent bottle with a thin rope and a Rigosha Vandorn water sampler (2 l) were used for sampling of surface and bottom sea-waters, respectively. Sea-water samples were taken in narrow-mouthed bottles (100 ml) fitted with ground stoppers cut at an angle of 45°. Distilled, deionized water was obtained from a Yamato-kagaku Model WA-22 automatic water distillation apparatus and a Nihon Millipore-kogyo Milli-QII system.

### Reagents

All solutions were prepared using analytical-reagent grade chemicals. Standard

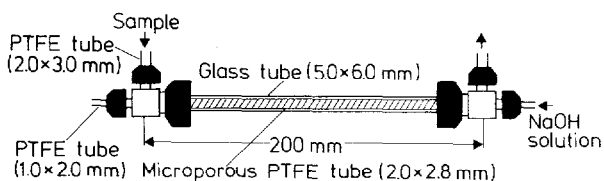


Fig. 1. Schematic diagram of separation unit.

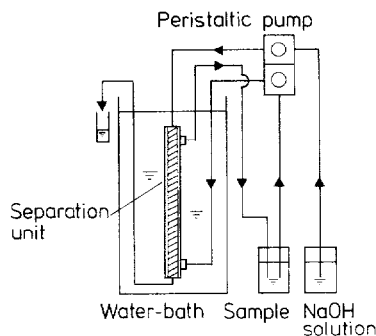


Fig. 2. Schematic diagram of flow system.

solutions of sulphide were prepared by dissolving sodium sulphide (Wako) in oxygen-free water prepared by boiling distilled, deionized water for 30 min<sup>5,23</sup>. The water was quickly cooled to avoid absorption of air. The standard solutions were prepared immediately before use.

The barium cation-exchange resin was prepared as follows: 200 ml of 0.1 *M* barium chloride solution were added to 75 ml of Dowex 50W-X8 (200–400 mesh) cation-exchange resin in the sodium form and stirred for 15 min; the supernatant solution was discarded, and the resin was treated with 200 ml of distilled, deionized water in a similar manner. These treatments were twice repeated. Finally, the resin was washed with distilled, deionized water on a filter-paper and stored in this water. The preparation of artificial sea-water was based on the method described in ref. 24.

### Procedure

Sea-water samples were analyzed by the following procedure as soon as possible after collection. To generate hydrogen sulphide, 0.5 ml of 9 *M* sulphuric acid were added to 45 ml of sample filtered through a 0.45- $\mu\text{m}$  membrane filter. The total volume was adjusted to 50 ml with oxygen-free water. A 10-ml volume of this solution was circulated through the outer part of the separation unit for 10 min at a flow-rate of 9.0 ml/min, as shown in Fig. 2. Hydrogen sulphide permeated through the tubular microporous PTFE membrane and dissolved in  $1.0 \cdot 10^{-2}$  *M* sodium hydroxide solution placed in the inner part. The temperature of the water-bath was 40°C. Large amounts of carbon dioxide in the sea-water samples also permeated through the PTFE membrane and dissolved in the sodium hydroxide solution. As carbon dioxide interfered with the isotachopheretic measurement of sulphide, it was removed as barium carbonate by adding 0.5 g of barium cation-exchange resin to the sodium hydroxide solution: the solution was shaken for 3 min, then filtered under reduced pressure. A 150- $\mu\text{l}$  portion of the resulting solution was injected into the isotachopheresis apparatus. The leading electrolyte was 5 mM sodium hydroxide and 0.1% hydroxypropyl methylcellulose (HPMC), and the terminating electrolyte was 10 mM sodium acetate. The migration current was initially set at 150  $\mu\text{A}$  for 15 min and then reduced to 50  $\mu\text{A}$ .

## RESULTS AND DISCUSSION

*Leading electrolyte*

The following leading electrolytes were examined for the determination of sulphide using a 10-cm PTFE tube: (I) 5 mM hydrochloric acid and 0.1% HPMC, adjusted to pH 10.5 with 2-amino-2-methyl-1-propanol; (II) 5 mM sodium hydroxide solution; (III) 5 mM sodium hydroxide and 0.1% HPMC. Both PTFE and FEP tubes were exchanged for new tubes when the leading electrolyte (II) was used, because isotachophoretic separation was generally affected by the HPMC that adhered to the tube walls<sup>2,5</sup>. A 100- $\mu$ l volume of a standard solution containing 2.0 mg/l sulphide was injected into the isotachopheresis apparatus. The leading electrolyte (III) was selected for subsequent experiments, as sulphide could be detected most successfully.

*Volume of sulphuric acid*

The volume of 9 M sulphuric acid added to the artificial sea-water sample containing 5.0 mg/l sulphide was varied in the range 0.1–1.5 ml. A 100- $\mu$ l portion of the solution treated according to the proposed method was injected into the isotachopheresis apparatus equipped with a 25-cm PTFE tube. The zone length of sulphide in the isotachopherogram was almost constant when the volume of sulphuric acid was more than 0.5 ml, as shown in Fig. 3. Therefore, 0.5 ml of 9 M sulphuric acid were selected and the subsequent mixture was diluted to 50 ml.

*Concentration of sodium hydroxide solution*

The concentration of sodium hydroxide solution in the inner part of the separation unit was varied in the range  $0.5 \cdot 10^{-2}$ – $1.25 \cdot 10^{-2}$  M. The zone length of sulphide greatly increased with increasing sodium hydroxide concentration as shown in Fig. 4. When  $1.25 \cdot 10^{-2}$  M sodium hydroxide solution was used, the length was slightly longer than that using  $1.0 \cdot 10^{-2}$  M solution. On the other hand, the longer time for the isotachophoretic measurement in the former case was due to the excess of hydroxide ion in the treated solution. Therefore,  $1.0 \cdot 10^{-2}$  M was adopted as the optimum concentration of the sodium hydroxide solution.

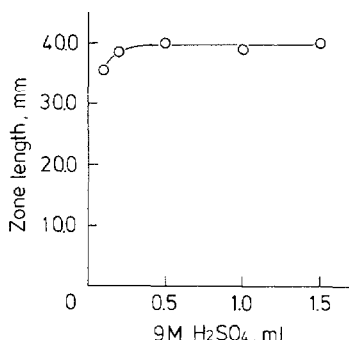


Fig. 3. Effect of the volume of 9 M sulphuric acid solution.

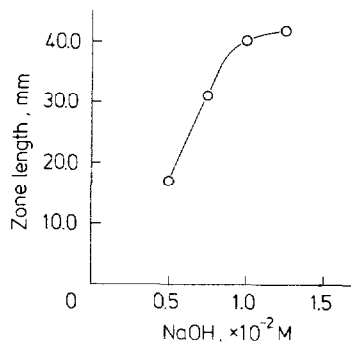


Fig. 4. Effect of the concentration of sodium hydroxide solution.

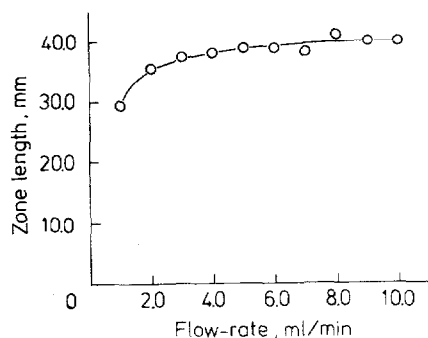


Fig. 5. Effect of the flow-rate of sample solution.

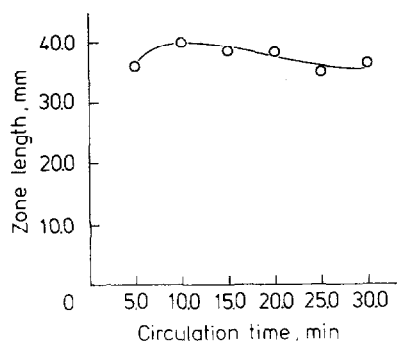


Fig. 6. Effect of the circulation time of sample solution.

#### *Circulating flow-rate of sample solution*

The flow-rate of sample solution circulating through the outer part of the separation unit was varied in the range 1.0–10.0 ml/min. The zone length of sulphide gradually increased with increasing flow-rate, as shown in Fig. 5. It was almost constant when the flow-rate was more than 9.0 ml/min. Therefore, 9.0 ml/min was adopted as the circulating flow-rate of sample solution.

#### *Circulation time of sample solution*

The circulation time of sample solution was varied in the range 5–30 min. The zone length of sulphide gradually decreased with increasing circulation time as shown in Fig. 6. This decrease was considered to be due to the slight oxidation of sulphide over periods longer than 15 min. Therefore, 10 min was adopted as the circulation time of sample solution.

#### *Temperature of water-bath*

The temperature of the water-bath in which the separation unit was immersed was varied in the range 30–50°C. The zone length of sulphide was almost constant

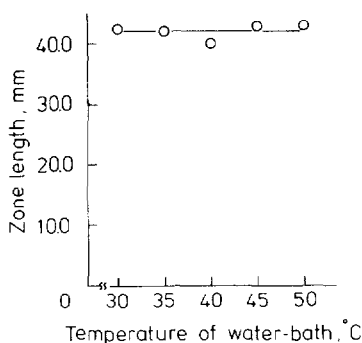


Fig. 7. Effect of the water-bath temperature.

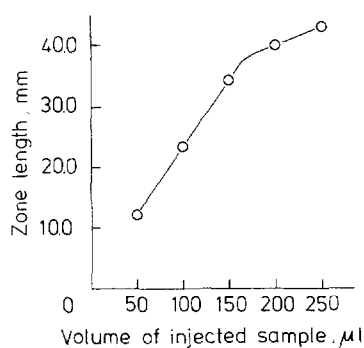


Fig. 8. Effect of the volume of sample injected into the isotachopheresis apparatus.

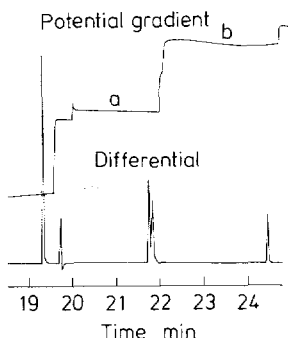


Fig. 9. Isotachopherogram of an artificial sea-water sample treated according to the proposed method. a,  $\text{HS}^-$ ; b,  $\text{CO}_3^{2-}$ .

over the whole range, as shown in Fig. 7. This constancy was considered to be due to the poor solubility of hydrogen sulphide, *i.e.*, 2.014, 1.664 and 1.376  $\text{cm}^3/\text{cm}^3$  of water at 30, 40 and 50°C, respectively<sup>26,27</sup>. A temperature of 40°C was adopted as the temperature adjustment was easier at this temperature.

#### Volume of injected sample

The volume of sample injected into the isotachopheresis apparatus was varied in the range 50–250  $\mu\text{l}$ . The zone length increased in proportion to the volume up to

TABLE I

#### ANALYTICAL RESULTS FOR SULPHIDE IN SEA-WATER SAMPLES

Sampling date: September 16–19, 1986; KUMM = Kobe University of Mercantile Marine; ND = Not detected in isotachopherogram.

Sampling site	Depth (m)	Temp. (°C)	pH	Salinity (‰)	DO (mg/l)	Sulphide		
						Added (mg/l)	Found (mg/l)	Error (%)
Pond of KUMM	0	25.4	8.18	27.0	8.83	—	ND	—
Pond of KUMM	5.0	24.9	7.84	28.9	4.46	—	ND	—
Nishinomiya harbour	0	24.9	8.76	24.3	10.51	—	ND	—
Nishinomiya harbour	3.0	25.4	7.82	28.9	3.11	—	1.6	—
Maya pier	0	24.4	7.95	23.4	6.57	—	ND	—
Maya pier	4.0	24.6	7.83	27.4	4.71	—	ND	—
Port of Kobe	0	24.1	7.95	29.0	5.39	—	ND	—
Port of Kobe	4.5	24.1	7.96	29.0	5.08	—	ND	—
Rokko island	0	24.5	7.80	28.1	4.83	—	ND	—
Rokko island						0.50	0.49	−2.0
Rokko island						1.0	1.1	+10
Rokko island						1.5	1.6	+6.7
Rokko island	5.5	24.2	7.80	29.1	3.32	—	0.10	—
Port of Amagasaki	4.5	24.5	7.53	23.8	1.72	—	ND	—
Koshien ferry terminal	4.0	24.4	7.63	28.6	3.38	—	ND	—

150  $\mu\text{l}$ , as shown in Fig. 8. Therefore, 150  $\mu\text{l}$  was adopted as the volume of sample injected.

#### Calibration graph

A linear calibration graph was obtained for artificial sea-water samples containing up to 2.0 mg/l of sulphide. The regression equation was  $y = 13.7x - 0.083$ , where  $x$  is the concentration of sulphide (mg/l) and  $y$  is the zone length (mm) at a recording speed of 20 mm/min. The correlation coefficient was 1.000. The relative standard deviation of the method was obtained by calculating the zone length per 1.0 mg/l at each point on the calibration graph. It was found to be 0.028 ( $n = 5$ ). The determination limit of sulphide was  $7.3 \cdot 10^{-3}$  mg/l, corresponding to a zone length of 0.1 mm. The recovery of sulphide was  $42 \pm 2\%$  which might be accounted for the fact that the permeability of volatile compounds depends on the characteristic membrane parameters such as pore size, thickness, homogeneity and contact area<sup>27</sup>. Fig. 9 shows the isotachopherogram of 100  $\mu\text{l}$  of an artificial sea-water sample containing 5.0 mg/l of sulphide.

#### Analysis of sea-water samples

The proposed method was applied to the determination of sulphide in surface and bottom sea-water samples collected around the coastal area of Osaka Bay between Port of Amagasaki and Port of Kobe on September 16–19, 1986. Sulphide was not detected in these samples except in the bottom sea-waters of Nishinomiya harbour and Rokko island, as shown in Table I. The very high concentration of sulphide in bottom sea-water of Nishinomiya harbour was considered to be due to hydrogen sulphide generated in deposits in the enclosed area. Amounts of 0.50–1.5 mg/l of sulphide were added to surface sea-water samples from Rokko island and analyzed by the method described. The error was less than  $\pm 10\%$ .

#### ACKNOWLEDGEMENTS

The authors express their gratitude to Drs. E. Sekido, Y. Masuda and T. Tanaka for their kind encouragement and suggestions, to Kimoto Electric Co. for providing the membrane separation unit and to K. Hisatani for his experimental help.

#### REFERENCES

- 1 E. Sasaki, *Boshoku Gijutsu*, 34 (1985) 427.
- 2 K. Hirose, K. Yoshida, M. Ohshima, I. Suzuki and T. Sekine, *Annual Report of Kawasaki City Research Institute for Public Hazards*, Vol. 10, 1983, p. 75.
- 3 M. Koshimizu, *Report of Kawasaki City Research Institute for Public Hazards*, 1975.
- 4 *Testing Methods for Industrial Water*, JIS K 0101-1986, Japanese Standards Association, Tokyo, 1986, p. 152.
- 5 S. Fonselius, in K. Grasshoff (Editor), *Methods of Seawater Analysis*, Verlag Chemie, Weinheim, 1976, p. 71.
- 6 S. Fonselius, *Mar. Pollut. Bull.*, 12 (1981) 187.
- 7 S. Goda, K. Morishige, N. Yamada, M. Okatake and Y. Nishikawa, *Bunseki Kagaku*, 35 (1986) 80.
- 8 M. Okatake, S. Goda, K. Morishige, T. Shigematsu and Y. Nishikawa, *35th Annual Meeting of the Japan Society for Analytical Chemistry, Okayama, October 11–14, 1986*, Abstracts, p. 481.
- 9 H. Baadenhuijsen and H. E. H. Seuren-Jacobs, *Clin. Chem.*, 25 (1979) 443.

- 10 T. Kimoto, *43rd Symposium of the Japan Society for Analytical Chemistry, Yamagata, June 17–18, 1982*, Abstracts, p. 57.
- 11 T. Aoki, S. Uemura and M. Munemori, *Anal. Chem.*, 55 (1983) 1620.
- 12 T. Kimoto and Y. Mitani, *17th Symposium of the Japan Society on Water Pollution Research, Tokyo, March 22–24, 1983*, Abstracts, p. 269.
- 13 T. Aoki, S. Uemura and M. Munemori, *Bunseki Kagaku*, 33 (1984) 505.
- 14 T. Tanaka, A. Kawahara, S. Wakida and K. Hiuro, *Kankyo Gijutsu*, 15 (1986) 46.
- 15 R. Nakata and H. Sakashita, *35th Annual Meeting of the Japan Society for Analytical Chemistry, Okayama, October 11–14, 1986*, Abstracts, p. 556.
- 16 T. Kuwaki, S. Motomizu and K. Toei, *35th Annual Meeting of the Japan Society for Analytical Chemistry, Okayama, October 11–14, 1986*, Abstracts, p. 560.
- 17 T. Aoki and M. Munemori, *Anal. Chem.*, 55 (1983) 209.
- 18 R. K. Kobos, S. J. Parks and M. E. Meyerhoff, *Anal. Chem.*, 54 (1982) 1976.
- 19 K. Fukushi and K. Hiuro, *Bunseki Kagaku*, 34 (1985) 21.
- 20 K. Fukushi and K. Hiuro, *Bunseki Kagaku*, 34 (1985) 205.
- 21 K. Fukushi and K. Hiuro, *Fresenius' Z. Anal. Chem.*, 323 (1986) 44.
- 22 K. Fukushi and K. Hiuro, *Anal. Sci.*, 2 (1986) 219.
- 23 T. Yagi, K. Kojima and T. Haruki, *J. Chromatogr.*, 292 (1984) 273.
- 24 *Testing Method for Rust-Preventing Characteristics of Lubricating Oil*, JIS K 2510–1980, Japanese Standards Association, Tokyo, 1980, p. 8.
- 25 T. Hine, *3rd Isotachopheresis Symposium, Osaka, December 14, 1983*, Abstracts, p. 5.
- 26 *Kagaku Binran*, the Chemical Society of Japan, Tokyo, 1984, p. 159.
- 27 W. E. van der Linden, *Anal. Chim. Acta*, 151 (1983) 359.