



In-situ measurement of the dissolved S^{2-} in seafloor diffuse flow system: sensor preparation and calibration*

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Abstract: The preparation approach and calibration result of an improved type of ion selective electrode (ISE), which is used to measure the total dissolved S^{2-} , are introduced in this paper. The improved Ag/Ag₂S electrode uses silver wire as the substrate, which is surrounded by electric polymer containing superfine silver powder. After the stabilization of the epoxy-resin, Ag₂S layer was formed by chemical reaction with 0.2 mol/L (NH₄)₂S solution for 5 min. With Ag/AgCl as reference electrode, the Ag/Ag₂S electrode can be used to measure dissolved S^{2-} . The correlation between the measured potentials and the logarithm of dissolved S^{2-} is found to be linear, within range of the concentration of dissolved S^{2-} from 10^{-2} ~ 10^{-7} mol/L. The slope of the regression line between measured potential and logarithm of dissolved S^{2-} is about -27.7, which agrees well with the theoretical Nernst value -29.6. Furthermore, the performance of the improved Ag/Ag₂S electrode, such as the response time, sensitivity and stability, greatly outweighs the conventional Ag/Ag₂S electrode.

Key words: Solid Ag/Ag₂S electrode, Preparation approach, Performance

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INTRODUCTION

More and more data documents indicate the differences in physical and chemical characteristics between the diffuse flow fluids from hydrothermal vents and the seawater around since the 1990s (Rubin, 1997). The high temperature hydrothermal fluids, of approximately 350~400 °C, contain high concentration H₂ and H₂S (Ding and Seyfried, 1995; 1996; Ding *et al.*, 2001). Furthermore, these species may also keep relatively high concentration in the diffuse plume area. For example, the diameter of the diffuse plume in Gorda Ridge of East Pacific Ocean is of approximately 15 km (Zhao and Song, 2000). Investigation on the East Pacific and Atlantic Mid-Ocean Ridge suggests the existence of other dissolved gases in the diffuse plume, such as CH₄, CO₂ and He (Em-

bley *et al.*, 1998; Ishibashi *et al.*, 2002).

Concentration of dissolved H₂S is found to be from 0.18 to 4.0 mmol/L for seafloor hydrothermal fluid (Foustoukos and Seyfried, 2005), and from 89 μmol/L to 0.06 mmol/kg solution for diffuse flow system (Embley *et al.*, 1998; Seyfried *et al.*, 2007). H₂S is of major importance in constraining the biological community around the hydrothermal vents. The consumption of H₂S in tubeworm dominated community was suggested to be related to the metabolism of the animals (le Bris *et al.*, 2003), while the concentration of dissolved H₂S may also be affected by some special types of tubeworms (Urcuyo *et al.*, 2003). Furthermore, the spatial and temporal variability of the H₂S concentration was also found to be influenced by magma and earthquake activities along the East Pacific Ridge (EPR) (Seewald *et al.*, 2003). Accordingly, the dissolved H₂S and other type of dissolve sulfur ions are important parameters to recognize the geomicrobiologic environment (Huber and

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Stetter, 1998).

The conventional method to measure the dissolved sulfide in fluid is to analyze the sample in lab after sampling. The drawback of this approach is the potential possibility of missing or changing of the sample's composition. Furthermore, it precludes a long-term continuous monitoring capability. Thus, the approaches of in-situ measurement greatly outweigh the conventional indirect methods (Eroglu *et al.*, 2000).

Although some amperometric microsensors have been used for in-situ measuring oxygen and sulfide concentration in marine sediments (de Beer *et al.*, 2005), most of the potentiometric electrodes with glass or plastic shell and liquid internal electrolyte are vulnerable to the high pressure in deep seafloor. Efforts on adapting for in situ use Ag/Ag₂S electrode have been devoted for recent decades (Beukema, 1991; Revsbech *et al.*, 1983). Solid Ag/Ag₂S electrode of 'coated wire-type' was poor in performance as pointed out by Müller and Stierli (1999), such as slow response, low sensitivity, and short life-time. To overcome these defects they introduced an Ag/Ag₂S electrode made of silver containing epoxy resin, and approved its applicability for in-situ measurement on sulfide concentration gradients in lake sediments. The electrode was housed in a polyethylene microcapillary tip with Cu wire as signal conductor, which may not be suitable for use in deep ocean thermal system. An improved approach to prepare the Ag/Ag₂S electrode is introduced in this paper and the performance of the newly prepared electrode measured in laboratory is reported.

EXPERIMENT

Preparation of the electrodes

Ag wire (outer diameter (OD) 0.6 mm) was cleaned with acetone following by 2 mol/L HNO₃. The cleaned Ag wire was then rinsed with distilled water and dried at 60 °C for approximately 1 h. Conductive resin (PAD-54, Shanghai Research Institute of Synthetic Resins), which is a mixture of sub-micron Ag powder and epoxy, was applied to the tip a few millimeters from one end of the Ag wire, which was then oven-heated at 150 °C for 2 h. The resin covered Ag wire was then immersed in a 0.2

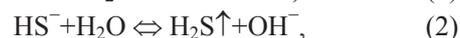
mol/L (NH₄)₂S solution for 5 min to form the Ag₂S layer. The rest of the Ag wire was covered with heat-shrinkable PTFE tubes. Before use, the improved type of Ag/Ag₂S electrode should be immersed in distilled water for more than 3 h.

In order to compare the performance of the improved Ag/Ag₂S electrode with the conventional Ag/Ag₂S electrode, the conventional type of Ag/Ag₂S electrode was also prepared in lab. The differences between the improved and conventional preparation methods were that in conventional approach Ag wire was directly put into 0.2 mol/L (NH₄)₂S solution to form sensitive Ag₂S layer, without conductive resin as medium.

Ag/AgCl electrode made by Department of Geology and Geophysics, University of Minnesota, USA was used as reference. Its structure is similar to commercial calomel electrode, but housed in a PEEK tube instead of glass one, with semipermeable PTFE membrane at the end and filled with 3.5 wt% NaCl solution inside. This reference electrode is robust to tolerate the high pressure in seafloor.

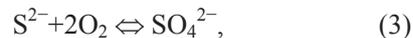
Preparation of Na₂S solution

Two drawback factors should be considered during the procedure of preparing Na₂S fluid. Firstly, the volatilization characteristics of H₂S, formed by reactions of the sulfur anion with water are as follows:



where H₂S is a type of gas with strong volatility in room and acidic conditions, and could escape from fluids easily.

Furthermore, S²⁻ can easily be oxidized:



where the oxidation product, SO₄²⁻, cannot be detected by the Ag/Ag₂S electrode.

Thus, SAOB (sulfur antioxidant buffer) obtained from Thermo Orion, pH=12.6, was used to dissolve Na₂S to avoid volatilization and oxidation of free sulfide anion. The SAOB is mainly composed of NaOH, EDTA and ascorbic acid, in which NaOH can keep the system sufficiently alkaline, so that H₂S could not be formed and evaporated; Vc (ascorbic acid)

as deoxidant can remove dissolved oxygen in solution, keeping S^{2-} from being oxidized; EDTA as inhibitor can restrain the interference from metal ions (Wu, 1994). Meanwhile, 2 mol/L Na_2S was diluted with standard SAOB to produce 2×10^{-2} molality Na_2S solution. The other Na_2S solutions of different concentrations are produced following the same procedure. In order to simulate the constraints imposed by the seawater composition, standard solutions are added with 3.5 wt% NaCl. All chemical agents are of analytical purity. A series of fluids of different concentrations are shown in Table 1 and Fig. 1.

Table 1 Required time for equilibrium between electrodes and solution (responding time)

S^{2-} (mol/L)	Required time	
	CH1 (conventional electrode)	CH2 (improved electrode)
2×10^{-2}	<10 s	<10 s
2×10^{-3}	<10 s	<10 s
2×10^{-4}	3.0 min	0.5 min
2×10^{-5}	6.0 min	2.5 min
1×10^{-5}	9.5 min	3.0 min
5×10^{-6}	N/A	3.5 min
2.5×10^{-6}	N/A	5.5 min
1.25×10^{-6}	N/A	5.5 min
1.25×10^{-7}	N/A	16 min

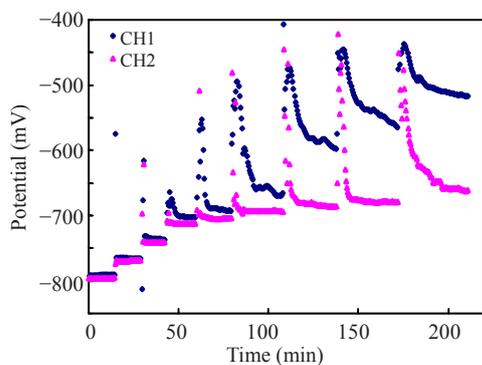


Fig.1 Electrode response versus scanning time. From left to right, Na_2S solution is: 2×10^{-2} , 2×10^{-3} , 2×10^{-4} , 2×10^{-5} , 1×10^{-5} , 5×10^{-6} , 2.5×10^{-6} , 1.25×10^{-6} , 1.25×10^{-7} mol/L, respectively

Experimental procedure

The potential of the Ag_2S electrode and $Ag/AgCl$ electrode was measured using a Keithley 6517A potentiometer. The improved and conventional Ag/Ag_2S electrodes were connected on channel 1 (CH1) and channel 2 (CH2), respectively. They shared the same $Ag/AgCl$ reference electrode and were bounded to-

gether to avoid the potential spatial concentration discrepancy. The fluid was not stirred during the experimental procedure, so that the response time to build up equilibrium between the sensor and the measured fluid should be considered as the longest one. The S^{2-} response test of the Ag/Ag_2S electrode was carried out from highly concentrated Na_2S fluids to lower concentrated ones. The standard series of fluids with different concentrations of S^{2-} were all measured in this way. They were also measured by a commercial Ag/Ag_2S electrode (#AGS150X, Van London-pHoenix) for comparison.

The influence of temperature on the Ag/Ag_2S electrode was examined from 0 to 80 °C. The fluid temperature was monitored by standard thermocouple. The standard fluids were firstly cooled in refrigerator to achieve 0 °C. During measuring, the solution was kept in cold-water bath to reduce the ascending rate of temperature. When the measured fluid temperature reached room temperature, the water bath was removed and the solution was warmed by hot plate. The measured S^{2-} respond signals were recorded in millivolt (mV).

RESULTS AND DISCUSSION

Response time

The monitored potentials revealed general rapid responses to S^{2-} concentration change (Fig.1). The small disturbance of response signal was caused by displacement from one fluid to another.

After a short-term interval of instability, stable reading at the corresponding S^{2-} concentration was observed, which indicated that electrochemical equilibrium between electrode and solution was achieved. It can be observed that the response time for the electrode to achieve equilibrium is related to the Na_2S concentration of measured fluid. For example, measured potential reaches its equilibrium status within 10 s, when Na_2S concentration is higher than 10^{-3} mol/L, while it prolonged the response time significantly at lower Na_2S concentrations, especially at Na_2S concentration of approximately 10^{-7} mol/L (Table 1). If the solution was stirred with a magnetic stirrer, responding time of the electrode in low concentration solution was shortened apparently.

The comparison of measured response time of

the improved and conventional Ag/Ag₂S electrodes indicate that the improved Ag/Ag₂S electrode (CH2) responds more rapidly than the conventional one (CH1) in quiescent solution. Furthermore, the improved Ag/Ag₂S electrode (CH2) extended the measured concentration to as low as 1.25×10^{-7} mol/L. Compared with the detection limits of the conventional Ag/Ag₂S electrode 10^{-5} mol/L, the improved electrode extended the detection limits by more than 2 log units.

Linearity range

To assess the validity of Ag/Ag₂S electrode, the slope of the line depicting changes in measured potential with corresponding changes of logarithm Na₂S concentration was compared with theoretical Nernst slope predictions. Signal intensity of each point is an average of the last 8 min measured potentials of a platform in the scanning curve as shown in Fig.1. Good linear correlations were observed with the improved Ag/Ag₂S electrode between measured potentials and $\log(S^{2-})$ over the entire range from 10^{-2} to 10^{-7} mol/L (Fig.2), while the conventional Ag/Ag₂S electrode only exhibits good linear relationship above measured Na₂S concentration over 10^{-5} mol/L. When the Na₂S concentration is lower than 10^{-5} mol/L, the potential value of the conventional Ag/Ag₂S electrode was apparently deviated from linearity.

The slope of the regression line of potential vs S^{2-} correlation with improved Ag/Ag₂S electrode, -27.7 , fits with the theoretical Nernst values, -29.6 , at room temperature. The equation of the regression line is: $Y = -27.7X - 842.8$, $R^2 = 0.9966$, where Y is the potential (mV) and X is $\log(S^{2-})$. For the conventional Ag/Ag₂S electrode, linear response was also found when the Na₂S concentration is above 10^{-5} mol/L, with the equation: $Y = -30.42X - 845.11$, $R^2 = 0.9963$. Furthermore, it was apparent that deviation extent increases significantly with lowering the concentration of detected Na₂S solutions after the concentration below 10^{-5} mol/L. Therefore, conventional and improved Ag/Ag₂S electrodes are both applicable to measure the S^{2-} . The improved preparation approach helps to extend the detection limit of S^{2-} from original 10^{-5} to 10^{-7} mol/L, which increases the detection limit by 2 log units magnitude. In comparison, the commercial Ag/Ag₂S electrode also shows linear response in the range from 10^{-2} to 10^{-7} mol/L. The equation of the regression line is: $Y = -29.04X - 984.12$, $R^2 = 0.999$.

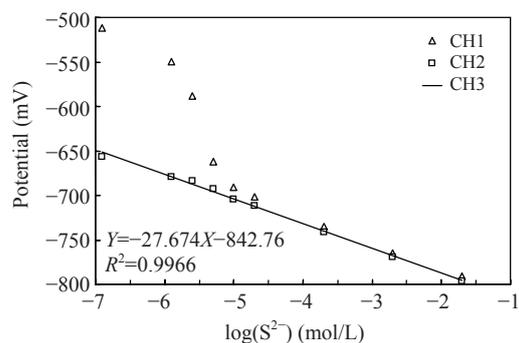


Fig.2 Relationship of response signal and Na₂S concentration

Influence of temperature on response

The effect of temperature variation from 0 to 80 °C on the response of Ag/Ag₂S electrode was examined. In general, measured potentials of both improved and conventional Ag/Ag₂S electrodes were not affected significantly within the temperature increasing from 0 to 80 °C in a series of S^{2-} solutions with concentrations of 2×10^{-3} to 2×10^{-6} mol/L (Fig.3). When TDS (total dissolved sulfur) concentration was as high as 2×10^{-2} mol/L (the lowest curve in Fig.3a), however, there was a negative linear correlation between the measured signals (Y , in mV) and the temperature (X , in °C): $Y = -0.2961X - 805.16$, $R^2 = 0.9729$. For the conventional Ag/Ag₂S electrode, however, measured potentials fluctuated apparently at temperature below 25 °C, which is quite possibly caused by its poor performance at this condition instead of a real temperature dependent effect.

To discuss temperature influence in detail, both electrode potential (E°) and the slope (S) were calculated from measured data in Fig.3 from the formula $E = E^\circ + S \log(S^{2-})$. Here E is the potential between the working and reference electrodes, and S is the slope. Temperature dependences of the conventional (Conv) and improved (Imp) Ag/Ag₂S electrodes are projected on Figs.4a and 4b. For the improved Ag/Ag₂S electrode, both E° and S were correlated with temperature and agreed with Nernst law, so variation of signal intensity with temperature was predictable and can be corrected while characterization data are available. Variation of E° and S with temperature of the conventional Ag/Ag₂S electrode was rather vague, depart from Nernst law, especially when temperature was lower than 25 °C.

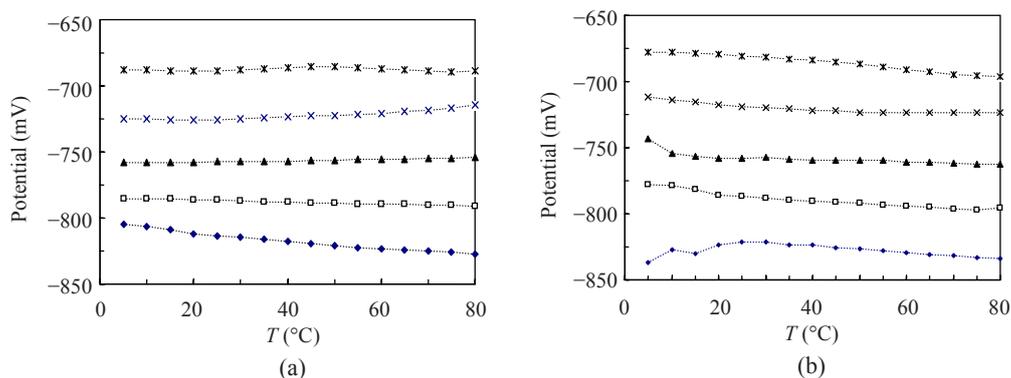


Fig.3 Relationship between measured potentials with ascending temperature in standard solution series (from bottom upward: 2×10^{-2} , 2×10^{-3} , 2×10^{-4} , 2×10^{-5} , 2×10^{-6} mol/L). (a) Improved Ag/Ag₂S electrode; (b) Conventional Ag/Ag₂S electrode

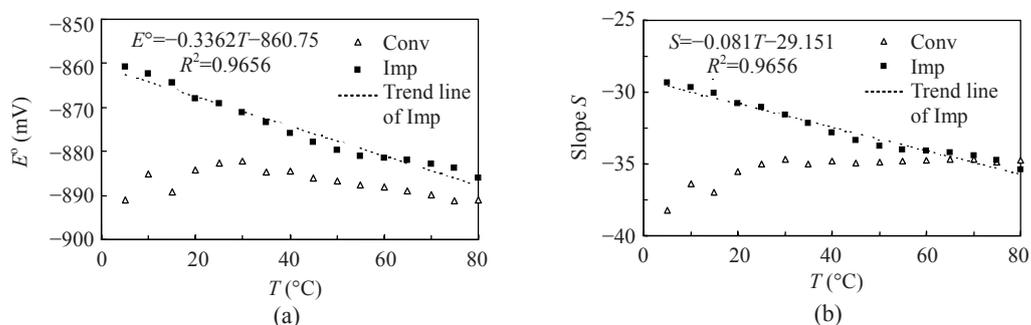


Fig.4 Variation of (a) electrode potential (E^0) and (b) slope (S) with temperature of the conventional (Conv) and improved (Imp) Ag/Ag₂S electrode

CONCLUSION

A new type of solid Ag/Ag₂S electrode with Ag powder containing resin middle layer was prepared and its performance was demonstrated. Compared to the conventional Ag/Ag₂S electrode, the improved Ag/Ag₂S electrode was observed to have better performance in the following aspects:

(1) Shorter response time. Time required for the improved Ag/Ag₂S electrode to build up equilibrium between the measured substance and the sensing layer on the electrodes was apparently shorter than the conventional Ag/Ag₂S electrode, especially at lower concentrated S²⁻ solutions.

(2) Higher detection sensitivity. The detection limit of the improved Ag/Ag₂S electrode was extended from the previous 10^{-5} to 10^{-7} mol/L.

(3) Better performance in low temperature. Stable potentials were obtained by the improved Ag/Ag₂S electrode at temperature even below 25 °C while the fluctuation of measured potentials by the

conventional Ag/Ag₂S electrode was obvious especially at temperature below 25 °C.

References

- Beukema, V.P.T., 1991. In-situ characterization of sediments measurement of oxygen and sulfide profiles with novel combined needle electrode. *Limnol. Oceanogr.*, **36**(7):1476-1480.
- de Beer, D., Wenzhofer, F., Ferdelman, T.G., Boehme, S.E., Huettel, M., van Beusekom, J.E.E., Bottcher, M.E., Musat, N., Dubilier, N., 2005. Transport and mineralization rates in North Sea sandy intertidal sediments, Sylt-Romo Basin, Wadden Sea. *Limnol. Oceanogr.*, **50**(1):113-127.
- Ding, K., Seyfried, W.E.Jr., 1995. In-situ measurement of dissolved H₂ in aqueous fluid at elevated temperatures and pressures. *Geochimica et Cosmochimica Acta*, **59**(22):4769-4773. [doi:10.1016/0016-7037(95)00319-3]
- Ding, K., Seyfried, W.E.Jr., 1996. Direct pH measurement of NaCl-bearing fluid with an in situ sensor at 400 °C and 40 megapascals. *Science*, **272**(5268):1634-1636. [doi:10.1126/science.272.5268.1634]
- Ding, K., Seyfried, W.E.Jr., Tivey, M.K., Bradley, A.M., 2001. In-situ measurement of dissolved H₂ and H₂S in high temperature hydrothermal vent fluids at the Main En-

- deavour field, Juan de Fuca Ridge. *Earth and Planetary Science Letters*, **186**(3-4):417-425. [doi:10.1016/S0012-821X(01)00257-6]
- Embley, R.W., Lupton, J.E., Massoth, G., Urabe, T., Tunnicliffe, V., Butterfield, D.A., Shilbata, T., Okanao, O., Kinoshita, M., Fujioka, K., 1998. Geological, chemical, and biological evidence for recent volcanism at 17.5°S: East Pacific Rise. *Earth and Planetary Science Letters*, **163**(1-4): 131-147. [doi:10.1016/S0012-821X(98)00181-2]
- Eroglu, A.E., Volkan, M., Ataman, O.Y., 2000. Fiber optic sensors using novel substrates for hydrogen sulfide determination by solid surface fluorescence. *Talanta*, **53**(1): 89-101. [doi:10.1016/S0039-9140(00)00377-5]
- Foustoukos, D.I., Seyfried, W.E.Jr., 2005. Redox and pH constraints in the seafloor root zone of the TAG hydrothermal system, 268 N Mid-Atlantic Ridge. *Earth and Planetary Science Letters*, **235**(3-4):497-510. [doi:10.1016/j.epsl.2005.04.042]
- Huber, H., Stetter, K.O., 1998. Hyperthermophiles and their possible potential in biotechnology. *Journal of Biotechnology*, **64**(1):39-52. [doi:10.1016/S0168-1656(98)00102-3]
- Ishibashi, J., Sato, M., Sano, Y., Wakita, H., Gamo, T., Shanks, W.C., 2002. Helium and carbon gas geochemistry of pore fluids from the sediment-rich hydrothermal system in Escanaba Trough. *Applied Geochemistry*, **17**(11):1457-1466. [doi:10.1016/S0883-2927(02)00112-9]
- le Bris, N., Sarradin, P.M., Caprais, J.C., 2003. Contrasted sulphide chemistries in the environment of 13°N EPR vent fauna. *Deep Sea Research Part I: Oceanographic Research Papers*, **50**(6):737-747. [doi:10.1016/S0967-0637(03)00051-7]
- Müller, B., Stierli, R., 1999. In situ determination of sulfide profiles in sediment porewaters with a miniaturized Ag/Ag₂S electrode. *Analytica Chimica Acta*, **401**(1-2): 257-264. [doi:10.1016/S0003-2670(99)00490-0]
- Revsbech, N.P., Blackburn, T.H., Cohen, Y., 1983. Microelectrode studies of the photosynthesis and O₂, H₂S and pH profiles of a microbial mat. *Limnol. Oceanogr.*, **28**:1062-1074.
- Rubin, K., 1997. Degassing of metals and metalloids from erupting seamount and mid-ocean ridge volcanoes: Observation and predictions. *Geochimica et Cosmochimica Acta*, **61**(17):3525-3542. [doi:10.1016/S0016-7037(97)00179-8]
- Seewald, J., Cruse, A., Saccocia, P., 2003. Aqueous volatiles in hydrothermal fluids from the Main Endeavour Field, northern Juan de Fuca Ridge: temporal variability following earthquake activity. *Earth and Planetary Science Letters*, **216**(4):575-590. [doi:10.1016/S0012-821X(03)00543-0]
- Seyfried, W.E.Jr., Foustoukos D.I., Fu, Q., 2007. Redox evolution and mass transfer during serpentinization: An experimental and theoretical study at 200 °C, 500 bar with implications for ultramafic-hosted hydrothermal systems at Mid-Ocean Ridges. *Geochimica et Cosmochimica Acta*, **71**(15):3872-3886. [doi:10.1016/j.gca.2007.05.015]
- Urcuyo, I.A., Massoth, G.J., Julian, D., Fisher, C.R., 2003. Habitat, growth and physiological ecology of a basaltic community of *Ridgeia piscesae* from the Juan de Fuca Ridge. *Deep Sea Research Part I: Oceanographic Research Papers*, **50**(6):763-780. [doi:10.1016/S0967-0637(03)00061-X]
- Wu, G.L., 1994. Cathodic stripping analysis of sulfide in marine sediments. *Marine Environmental Science*, **13**(1):64-68.
- Zhao, W.D., Song, J.M., 2000. Progress in the development of marine chemical sensors. *Oceanologia et Limnologia Sinica*, **31**(4):453-459.