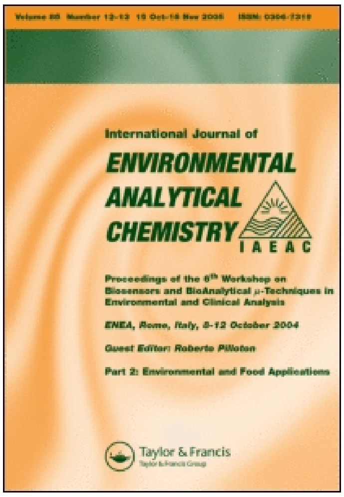

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THE USE OF SILVER ION BUFFERS FOR CALIBRATING A pH_2S ELECTRODE CELL

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A method to calibrate a pH_2S electrode cell is presented. The cell, which consists of a pH glass half cell and a Ag°, Ag_2S half cell, is calibrated in solutions of known hydrogen ion and silver ion activities. The method allows the determination of the concentration of H_2S gas, dissolved in aqueous solutions, with a precision of about ±30% ($p = 0.05$). The method is very easy to work with and therefore ideally suited for calibrating pH_2S electrode cells during routine analysis such as wastewater survey studies or aquaculture monitoring programs.

KEY WORDS: Hydrogen sulfide, pH_2S-electrode, sulfur

INTRODUCTION

Hydrogen sulfide (H_2S) plays a major role in the biogeochemical cycle of sulfur compounds. It is formed microbiologically in anoxic environments such as sediments of lakes and salt marshes. The precursors are more oxidized sulfur compounds like sulfate, elemental sulfur, and thiosulfate[1,2]. Once released from the anoxic environment it may, if still dissolved in water, be chemically oxidized rapidly to sulfate or, if released to the atmosphere, it becomes a relatively stable trace gas in the troposphere[3,4]. Its determination is crucial in any research studying the chemistry and fluxes of reduced sulfur. Additionally, its high chemical reactivity and toxicity makes it a key factor in the management of waste water.

The determination of dissolved H_2S is problematic because a very strict sampling protocol has to be followed to avoid sampling artifacts due to rapid decomposition of H_2S under aerated conditions. For that reason, the potentiometric method to determine dissolved hydrogen sulfide concentrations seems to be very promising. It can be used *in situ* without disturbing the chemical environment of the sample conditions. Also, the possibility to monitor H_2S concentrations continuously in a sediment or waste water, offers the chance to study the concentrations and dynamics of hydrogen sulfide in great detail.

Frevert and Galster[5] introduced a potentiometric electrode cell for the measurement of dissolved hydrogen sulfide concentrations. The combination of the pH glass cell and a silver/silver sulfide cell (Ag°,AgI|0.7 M HI|glass|solution|Ag_2S,Ag°; Ingold, FRG) leads to an H_2S electrode cell of high sensitivity and selectivity[7,8]. It is usually referred to as the pH_2S electrode cell because the potential is a direct linear function of the pH_2S. The pH_2S is, in analogy to the pH, the negative logarithm of the activity of dissolved hydrogen sulfide gas: $pH_2S = -\log_{10}(\gamma \cdot c_{H_2S})$.

The application of the pH_2S electrode cell in routine analysis is limited due to a cumbersome calibration procedure of adding increasing amounts of a sodium sulfide standard solution to a pH buffer[8]: The method requires thorough deaeration of the calibration solutions and iodometric standardization of Na_2S solutions before each calibration and is, therefore, very time consuming. In contrast to this standard addition method, it was suggested to use silver ion buffers at different pH's to establish well defined potentials at both the glass and the Ag°,Ag_2S half cell[9]. Their combined response can be related to H_2S concentrations in solution. The buffer solutions employed in this procedure have the advantage that they can be easily prepared and stored in the laboratory.

In this contribution, we will evaluate the accuracy and precision of the potentiometric determination of H_2S based on silver ion buffer calibration solutions.

THEORETICAL

The pH_2S electrode cell

The proportionality between the electromotive force (emf) of the pH_2S electrode cell and the pH_2S can be derived by combining the electrochemical response of the electrode cell:

$$\text{emf} = E_{\text{glass}} - \frac{F}{2.303 \cdot R \cdot T} \cdot \text{pH} - E^{\circ}_{\text{Ag}^{\circ}, \text{Ag}^{+}} + \frac{F}{2.303 \cdot R \cdot T} \cdot \text{pAg} \qquad (1)$$

emf: electromotive force of the cell/V
E_{glass}: standard potential of the glass half cell/V
F: Faraday constant ($= 9.648456 \cdot 10^4$ A·s·mol^{-1})
R: universal gas constant ($= 8.31441$ kg·m^2·s^{-2}·mol^{-1}·K^{-1})
T: temperature/K
$E^{\circ}_{\text{Ag}^{\circ}, \text{Ag}^{+}}$: standard potential of the silver half cell (0.799 V at 298 K)

With the solubility of Ag_2S,

$$Ag_2S \rightleftharpoons 2Ag^+ + S^{2-},$$

$$K^S_{Ag_2S} = (a_{Ag^+})^2 \cdot a_{S^{2-}} \qquad (2)$$

$K^S_{Ag_2S}$: solubility product of Ag_2S ($= 10^{-51.0}$ $mol^3 \cdot l^{-3}$ at 298 K^{10})

and the dissociation of H_2S

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$\frac{(a_{H^+})^2 \cdot a_{S^{2-}}}{a_{H_2S}} = K^{a,1}_{H_2S} \cdot K^{a,2}_{H_2S} \qquad (3)$$

$K^{a,1}_{H_2S}$: first dissociation constant of H_2S ($= 10^{-7.02}$ $mol \cdot l^{-1}$ at 298 K^{10})

$K^{a,2}_{H_2S}$: second dissociation constant of H_2S ($= 10^{-13.9}$ $mol \cdot l^{-1}$ at 298 K^{10})

the combination of Eqs. 1–3 leads to:

$$\begin{aligned} \text{emf} = {} & E^{\circ}_{glass} - E^{\circ}_{Ag^{\circ}, Ag^+} + 0.5 \cdot \frac{F}{2.303 \cdot R \cdot T} \cdot (pK^S_{Ag_2S} - pK^{a,1}_{H_2S} - pK^{a,2}_{H_2S}) \\ & - \frac{F}{2.303 \cdot R \cdot T} \cdot pH - 0.5 \cdot \frac{F}{2.303 \cdot R \cdot T} \cdot (pH_2S - 2pH) \qquad (4) \end{aligned}$$

or

$$\text{emf} = \tilde{K} - 0.5 \cdot \frac{F}{2.303 \cdot R \cdot T} \cdot pH_2S \qquad (5)$$

with $\tilde{K}$ being defined as:

$$\tilde{K} = E^{\circ}_{glass} - E^{\circ}_{Ag^{\circ}, Ag^+} + 0.5 \cdot \frac{F}{2.303 \cdot R \cdot T} \cdot (pK^S_{Ag_2S} - pK^{a,1}_{H_2S} - pK^{a,2}_{H_2S})$$

However, the two terms $F/2.303 \cdot R \cdot T$ in Eq. 1 may not be identical for an individual pH_2S electrode cell due to deviance of the glass and/or the Ag°,Ag_2S half cell from nernstian behavior. Such non-ideal slopes of half cells occur often and may cause problems in the development of Eq. 5. If either or both of the slopes of the glass half cell (S_{glass}) or of the silver sulfide half cell (S_{Ag°, Ag^+}) differ from the ideal nernstian behavior $F/2.303 \cdot R \cdot T$, Eq. 5 will not be valid and will have to be changed into Eq. 6:

$$\text{emf} = \tilde{K} + (S_{Ag^{\circ}, Ag^+} - S_{glass}) \cdot pH - 0.5 \cdot S_{Ag^{\circ}, Ag^+} \cdot pH_2S \qquad (6)$$

If the individual slopes of the two half cells differ from each other, it follows from these considerations that the potential of the pH_2S electrode cell will also be a function of the pH.

Calibration of the Electrode Cell

The conventional calibration procedure for the pH_2S electrode cell uses Eq. 5 and reads the emf as a function of the pH_2S concentration in the calibration solutions[8]. As mentioned before (and shown in detail in Section 3), the procedure is cumbersome and time consuming. Also it does not provide any information about the individual slopes of the two half cells and thus the pH dependency of the electrode cell potential.

It was shown[7] that proportionality between the emf and the pH_2S also holds in those cases where the total dissolved sulfide concentration is buffered to a very low level by the presence of a metal sulfide Me_mS in excess concentration of the corresponding metal ion Me^{n+}. The emf is proportional to the solubility of a given metal sulfide precipitate according to Eq. 7:

$$pH_2S = pK^{S}_{Me_mS} - pK^{a,1}_{H_2S} - pH^{a,2}_{H_2S} + 2pH - m \cdot pMe^{n+} \tag{7}$$

According to these results, Peiffer *et al.*[9] developed the idea of preparing calibration solutions of known silver ion and hydrogen ion activity. The silver ions would define the potential of the silver/silver sulfide half cell, and therefore the pH_2S of these solutions derived to be

$$pH_2S = pK^{S}_{Ag_2S} - pK^{a,1}_{H_2S} - pK^{a,2}_{H_2S} + 2pH - 2pAg^{+}. \tag{8}$$

The silver ion activity is buffered by precipitating $AgNO_3$ in excess iodide solution, while the proton activity is stabilized by the addition of adequate amounts of HNO_3 to the solutions.

Experimental

We used two pH_2S electrode cells (Ingold, FRG, Model H_2S 25-85-S7) to compare the two different calibration procedures. Both procedures were conducted three times with each electrode cell resulting in a total number of 12 calibrations per electrode cell.

Standard calibration

The standard calibration procedure follows instructions given by Peters *et al.*[8] with some modifications. The emf of the electrode cell immersed in solutions of varying H_2S concentrations was measured using a Corning (USA) ion analyzer Model 250. All solutions and flasks were deaerated in a glove box for at least one hour by bubbling with argon (99.998% purity) or nitrogen (99.995% purity) before use. The calibration was conducted in a gas tight reaction vessel[7,8] which had two ports for standard size (12 mm diameter) electrode cells and one port with a septum. The total volume of the vessel with two electrode cells in it was 167 ml. The calibration solution was 100 ml of a phthalate pH buffer (Orion Research, USA, Low Ionic Strength buffer pH 4.1, diluted 1 + 1), into which increasing amounts of a 0.1 mol·l^{-1} Na$_2$S standard solution were injected. The sulfide solution was made in a glove box under an argon atmosphere from anhydrous Na$_2$S flakes (Alfa Products, USA, No. 65122) which were assumed to be 100% pure[11]. The pH of the calibration solution was monitored after each addition of sulfide solution with a double liquid junction pH combination electrode cell, and, if necessary, adjusted to pH < 5.0 with one drop of concentrated HCl. For pH below 5, the added sulfide was assumed to be H$_2$S, with a solution equilibrium being established between the gas and liquid phase. The concentration in the liquid phase was computed from the gas volume, liquid volume, and the Henry's Law constant for H$_2$S as a function of temperature:

$$c_{H_2S} = S^{2-}_{tot}/(vol_{H_2O} + (vol_{gas}/(vol_{mol} \cdot P_{act} \cdot K^H_{H_2S}))) \tag{9}$$

c_{H_2S}:	H$_2$S concentration in the liquid phase mol·l^{-1}
S^{2-}_{tot}:	total amount of sulfide added mol
vol_{H_2O}:	volume of liquid phase l
vol_{gas}:	volume of gas phase l
vol_{mol}:	specific volume of gas l·mol^{-1} (= 22.4 l·mol^{-1} at standard conditions)
P_{act}:	actual ambient pressure atm
$K^H_{H_2S}$:	Henry's law constant for H$_2$S mol·l^{-1}·atm^{-1}

(For our computations we used the Henry's law constant according to $-\log_{10}(K^H_{H_2S}) = 103.7 - 4455.94/T - 37.1874 \cdot \log_{10}(T) + 0.01426 \cdot T$, and we neglected activity corrections for hydrogen sulfide, i.e., $a_{H_2S} = c_{H_2S}$[12]. The consecutive injection of 10, 100, and 1000 μl Na$_2$S solution resulted in pH$_2$S values (pH$_2$S = $-\log_{10}(a_{H2S})$) of 5.10, 4.06, and 3.06, respectively, for the calibration points a, b, and c. The emf of the pH$_2$S electrode cell was read as a function of the pH$_2$S.

Silver ion buffer calibration (SIC)

The silver ion buffer calibration procedure (SIC) does not use hydrogen sulfide. Therefore, no deaeration of the calibration solutions had to be done. Nitric acid (Titrisol, VWR EM-9964-2, USA) and potassium iodide (Merck, FRG, No. PX1507-3) solutions were mixed in various amounts together with approximately 4 drops of a saturated AgNO$_3$ solution to make solutions of well defined pH and pAg$^+$ conditions. The computations of pH and pAg$^+$ were made using the Davies approximation for ion activity coefficients[13] and solubility and dissociation constants[10]. The pH$_2$S was calculated using Eq. 8. Table 1 shows the amounts of stock solutions applied and the resulting pH, pAg$^+$, and pH$_2$S values for 12 different calibration solutions.

Table 1 Amounts of potassium iodide solution (1 mol·l^{-1}) and nitric acid solution (0.1 mol·l^{-1}) which are diluted to 100 ml to obtain the indicated pH, pAg$^+$, and pH$_2$S values in the silver ion buffer calibration procedure (computed using Eq. 8). The last four columns indicate the resulting concentrations for the I$^-$, H$^+$, ionic strength I (all in units mol·l^{-1}), and the ion activity coefficient or monovalent ions $\gamma_{z=1}$.

Solution No.	*Amounts of*		*Resulting chemical conditions*						
	1 *mol·l^{-1} KI*	0.1 *mol·l^{-1} HNO$_3$*	*pH*	*pAg$^+$*	*pH$_2$S*	c_{I^-}	c_{H^+}	I	$\gamma_{z=1}$
1	10 ml	0.1 ml	4.10	15.10	7.18	0.1	0.0001	0.1001	0.79
2	10 ml	1 ml	3.10	15.10	5.18	0.1	0.001	0.101	0.79
3	10 ml	10 ml	2.10	15.10	3.18	0.1	0.01	0.11	0.79
4	1 ml	0.1 ml	4.05	14.15	8.98	0.01	0.0001	0.101	0.90
5	1 ml	1 ml	3.05	14.15	6.98	0.01	0.001	0.011	0.90
6	1 ml	10 ml	2.06	14.14	5.02	0.01	0.01	0.02	0.88
7	0.1 ml	0.1 ml	4.02	13.18	10.86	0.001	0.0001	0.0011	0.96
8	0.1 ml	1 ml	3.02	13.18	8.86	0.001	0.001	0.002	0.95
9	0.1 ml	10 ml	2.05	13.15	6.98	0.001	0.01	0.011	0.90
10	0.01 ml	0.1 ml	4.00	12.19	12.98	0.0001	0.0001	0.0002	0.98
11	0.01 ml	1 ml	3.02	12.18	10.98	0.0001	0.001	0.0011	0.96
12	0.01 ml	10 ml	2.05	12.15	8.98	0.0001	0.01	0.0101	0.90

Table 2 Emf's (in units mV) of the standard calibration (solutions a, b, c) and silver ion buffers (solutions 1–12, see Table 2) at indicated days of calibrations (1990), and ambient atmospheric conditions.

	Electrode cell no 1			*Electrode cell no* 2		
Day	15 *May*	12 *Jun*	18 *Jun*	02 *Jul*	03 *Jul*	09 *Jul*
T/K	292	295	298	294	294	295
P$_{act}$/atm	0.9901	0.9980	0.9882	0.9891	0.9882	0.9951
Solution No.	*emf/mV*					
a	−102.5	−119.2	−115.6	−136.2	−137.7	−146.6
b	−71.9	−84.1	−80.6	−104.2	−104.1	−113.6
c	−43.1	−54.5	−49.1	−75.6	−73.7	−86.3
1	−169.2	−168.8	−153.4	−202.2	−201.2	−198.1
2	−110.4	−109.3	−103.2	−142.5	−144.1	−139.8
3	−56.3	−58.3	−52.2	−86.6	−85.9	−85.9
4	−224.9	−220.5	−213.8	−251.8	−247.1	−247.0
5	−166.9	−165.9	−156.9	−195.0	−193.3	−196.5
6	−109.3	−114.6	−111.9	−141.8	−140.3	−141.5
7	−279.5	−273.9	−276.0	−299.7	−301.1	−299.4
8	−222.7	−215.7	−217.2	−247.0	−245.6	−241.7
9	−167.0	−164.7	−164.0	−195.8	−195.3	−191.0
10	−336.9	−316.7	−328.5	−354.3	−355.6	−355.0
11	−279.9	−260.2	−271.1	−300.0	−300.7	−303.2
12	−225.1	−209.6	−218.6	−250.1	−250.7	−255.2

Table 3 Slopes of the pH_2S electrode cells as measured by the standard calibration method as well as individual slopes of the half cells computed from the buffer calibration method.

Day	*Electrode cell no* 1			*Electrode cell no* 2		
	15 *May*	12 *Jun*	18 *Jun*	02 *Jul*	03 *Jul*	09 *Jul*
Standard calibration procedure						
slope mV/pH_2S	−29.1	−31.7	−32.6	−29.7	−31.4	−29.6
intercept mV (for $pH_2S = 0$)	46.1	43.3	51.0	15.7	22.7	5.0
regression coefficient r	0.9999	0.9993	0.9998	0.9998	0.9998	0.9991
residual standard deviation mV	0.256	1.73	0.9	0.9	0.8	1.8
Silver ion buffer calibration procedure						
slope mV/pH_2S	−28.9	−26.4	−28.4	−27.2	−27.4	−27.5
intercept (for $pH_2S = 0$)	36.0	21.7	39.0	−4.0	−2.3	−0.6
regression coefficient	0.9997	0.9974	0.9976	0.9995	0.9997	0.9991
residual standard deviation mV	2.0	5.6	5.8	2.6	2.0	3.36
S_{glass} mV/pH	57.8	55.3	54.4	55.4	55.3	54.5
$S_{\text{Ag}^\circ,\text{Ag}^+}$ mV/$p\text{Ag}^+$	59.1	53.0	59.9	55.7	55.6	56.6

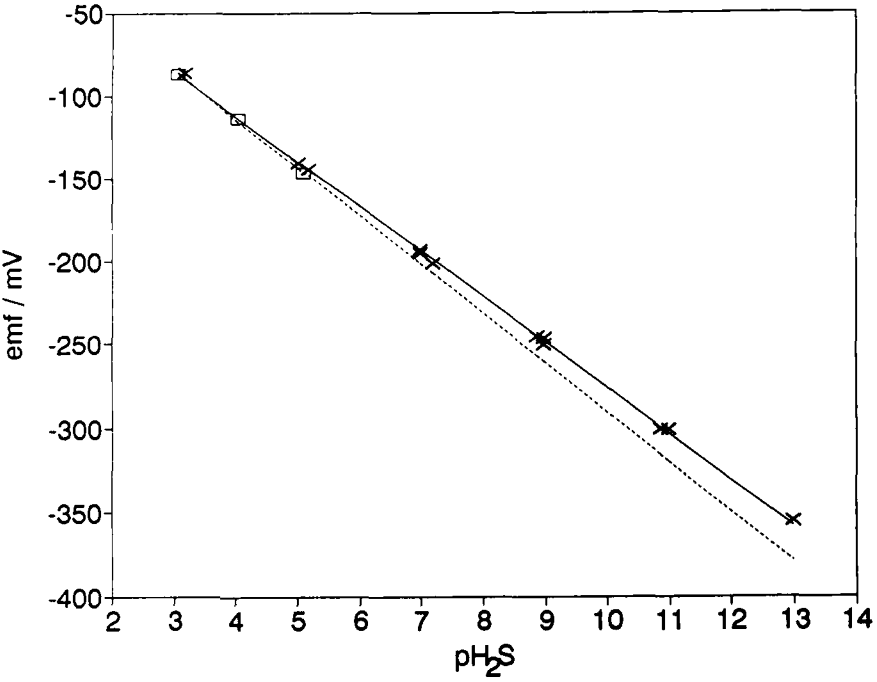

Figure 1 Results of a standard calibration (☐, broken line) and a silver ion buffer calibration (×, full line), as obtained on July 03, 1990 (data from Table 3). Also shown are the regressions for the two calibrations (for statistical data see Table 4).

Results and discussion

The results of the calibration procedures, which were obtained on six different days, are presented in Table 2. Some statistical information for these data is presented in Table 3. The regression lines for each individual calibration procedure are shown with the regression coefficients and residual standard deviations. Also included in Table 3 are the individual slopes for the glass half cell and the silver half cell, calculated from the SIC data. Figure 1 depicts one day of calibration (03 July) and shows the individual results of the two calibration procedures as well as the regression lines.

The individual slopes of the half cell were calculated using an iterative procedure. For the glass half cell, an individual slope was calculated for each silver ion activity in the calibration solutions. For example, a slope of 56.5 mV/pH can be calculated for $pAg^+ = 15.1$ in the calibration procedure No. 1 from the solutions No. 1, 2, and 3 (see Table 1). However, the silver ion activity is not always exactly the same in solutions of different pH (e.g. solutions 8 and 9), so the potential of the silver half cell must have changed, too. Therefore, slight corrections had to be made using an iterative procedure. First, we estimated the potential of the pH_2S electrode cell in a solution of $pH = 2.05$ and $pAg^+ = 13.18$ by adding a potential difference of 1.7 mV to the potential of the pH_2S electrode cell in solution 9. The value of 1.7 mV corresponds to the nernstian response of a silver half cell due to the change of the silver ion activity by 0.03 units. In this case ($pAg^+ = 13.18$, first calibration procedure) the individual slope of the pH electrode cell was calculated as 58.0 mV/pH. Similar corrections result in individual slopes for the pH half cell as 58.1 mV/pH for $pAg^+ = 14.15$ and 58.5 mV/pH for $pAg^+ = 12.19$. The mean value of these four individual slopes is 57.8 mV/pH. After similar corrections, the slope of the silver half cell is calculated as the mean value of three individual slopes for $pH = 4.00$, 3.02, and 2.05, respectively. For this purpose, an ideal nernstian slope of the glass half cell was assumed.

As a second step in the iterative procedure, we used the slopes as computed above instead of the nernstian slope assumption to recalculate a more precise number for the slope of the cells. When the result of such a computation was the same as the starting value (usually after two steps), the computation was aborted and the slopes assumed to be as precisely calculated as possible.

There are deviations between the results of the two calibration methods which will lead to uncertainties in the determination of H_2S concentrations. For example, the slopes, as obtained with the two different calibration procedures, can vary on a single day (e.g., 12 June), as much as 5.3 mV or 17%. Also, we find high residual standard deviations with the standard calibration method. That may, however, be partly due to the fact that we used only 3 datapoints for each calibration with the standard procedure. For the silver ion buffer calibration procedure, which uses 12 points each time, the observed high residual standard deviations indicate that there are consistent uncertainties in the potential reading of the electrode cell in the employed solutions.

To better understand the accuracy of the SIC, we used the regression of the SIC calibration to predict the known pH_2S values of the standard calibration solutions,

Table 4 The pH_2S values of the standard calibration solutions, as they are predicted (Eq. 9), and as they are measured with the pH_2S electrode cell using the silver ion buffer solutions as calibration points of the cell.

Day	*Electrode cell no 1*			*Electrode cell no 2*		
	15 *May*	12 *Jun*	18 *Jun*	02 *Jul*	03 *Jul*	09 *Jul*
Predicted pH_2S	*Measured* pH_2S ± *residual standard deviations*					
5.10	4.79 ± 0.14	5.32 ± 0.38	5.44 ± 0.38	4.85 ± 0.19	4.95 ± 0.14	5.30 ± 0.23
4.06	3.73 ± 0.15	4.00 ± 0.39	4.21 ± 0.40	3.68 ± 0.19	3.72 ± 0.15	4.11 ± 0.24
3.06	2.73 ± 0.15	2.88 ± 0.41	3.10 ± 0.41	2.63 ± 0.20	2.61 ± 0.15	3.11 ± 0.25

i.e. using these solutions as samples. Thus the SIC based calibration curve should predict the pH_2S values of the solutions within a tolerable error, which is calculated as the 95% confidence interval of the regression line at the point of interest.

The results, as presented in Table 4, illustrate that neither the accuracy nor the precision of the pH_2S values obtained by the silver ion buffer calibration is satisfying at the requested level of confidence in all cases. We have, however, to take into consideration that the error is increasing at both ends of the calibration graph. Since we have no reason to assume that the calibration curve is less well defined at lower pH_2S values (higher H_2S activities), a mean error of ± 0.15 pH_2S units can be stated. This error in reading pH_2S values corresponds to an uncertainty of $\pm 29\%$ in determining the concentration of dissolved H_2S.

Slopes of the electrode cells

It should be pointed out here that the regressions of the standard calibration method indicate a hypernernstian slope of the pH_2S cell (>30 mV/pH_2S, see Table 3). This behavior has repeatedly been reported for this type of electrode cell[6,7,8]. We are not aware of any reports of similar behavior by other types of electrodes. It is beyond the scope of this work to discuss the possible reasons. However, the individual slopes of the two half cells, calculated from the silver ion buffer calibration method at the same days of experiments demonstrate nernstian or slightly below nernstian slopes.

Detection limit

It follows from the results of the silver ion calibration that the pH_2S electrode cell reads pH_2S values as high as 13.2 (corresponding to computed H_2S activities below 10^{-13} mol·l^{-1}), if the aqueous solution is buffered with respect to the silver ion activity. Results by Peiffer and Frevert[7] indicate that the linear response of the cell is observable at computed values as high as $pH_2S \approx 18$ in acid solutions. In cases when a solution was not well buffered with respect to silver ions, and H_2S gas was actually present in an oxygen-free solution (e.g., during the standard calibration), we observed a linear response of the electrode cell until pH_2S values as high as 5. Using a very rigorous procedure in the standard calibration method, nernstian behavior of the cell is observable until pH_2S values between 6 and 7 (results not shown in detail here). Hence it is not possible to determine the detection limit of the pH_2S electrode cell, because the range of the linearity of the electrode response is dependent on the geochemical conditions of the solutions under view.

CONCLUSIONS

From the tests of the silver ion buffer calibration method to calibrate a pH_2S electrode cell, we conclude that this method is very rapid and easy to handle. It requires no complicated handling of the calibration solutions, and is, therefore, well suited for various types of applications. For routine analyses, the number of calibration solutions may be reduced in order to further reduce the time required. The use of the calibration solutions No. 6, 9, 10, 11, and 12 (see Table 1), for example, still enables the user to check the individual slopes of the two half cells.

The major drawback of the method is that it allows the determination of the concentration of H_2S with a precision of not better than $\pm 30\%$. This error, however, is partly intrinsic in the fact that the electrode response is a logarithmic measure of the hydrogen sulfide concentration with half nernstian slope (Eq. 5), so that a small error in reading the potentiometric output of the cell will always lead to a large uncertainty in the H_2S concentration.

In summary we can recommend the SIC in all those cases where knowledge of the precise concentration is not of crucial importance and where it may be sufficient to know the order of magnitude of the H_2S concentration. This may be the case in certain technological processes. For example, the H_2S activity may be monitored continuously in wastewater treatment plants as an indicator for strongly anoxic conditions. In aquaculture plants, H_2S is a highly toxic substance and its occurrence has to be recognized as soon as possible. In this case, the pH_2S electrode cell, combined with the silver ion buffer calibration method, may be a very useful tool.

The standard calibration method may, if much attention is paid to the experimental conditions, lead to somewhat better results with respect to precision and accuracy. If possible, calibrations should be made at a pH close to the actual sample pH. We further recommend to enlarge the number of calibration solutions. Instead of varying the total sulfide concentration by a factor of 10, it seems more appropriate to double the concentration at each step of addition. Hypernernstian slopes of the pH_2S electrode cell (see Table 3) have to be taken into consideration as possible causes for artifacts in this case.

If measurements are to be performed with a maximum of achievable precision, e.g. in experimental studies with sulfide as a reactant, none of the above methods will be sufficient. We recommend, in this case, to determine the slope of the pH_2S electrode cell by use of the standard calibration method and to relate measured potentials to potentials corresponding to sulfide standards added to the solution (standard addition method[14]).

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