

Determination of Total Dissolved Sulfide in the pH Range 7.5 to 11.5 by Ion Selective Electrodes

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A total dissolved sulfide meter was designed and tested over the concentration range 10^{-5} to 10^{-1} mol/L. The instrument applies a sulfide ion activity electrode and a pH glass electrode, whose potentials are measured against a double junction reference electrode. The potentials are processed by an electronic analog circuit to obtain an output voltage that is proportional to total dissolved sulfide. The proposed instrument—adjustment procedure eliminates mutual dependence of the adjusted controls. The total dissolved sulfide readings of the instrument were found to be pH independent over the pH range pH 7.5 to pH 11.5.

The importance of sulfide compounds in biological processes has been widely demonstrated (1, 2) and it is well-known that the generation of sulfide is linked to a number of vital, chemical, physical, and biochemical processes (3).

The classical analytical methods for sulfide determination like the Methylene Blue or the iodometric methods (4) are rather cumbersome, requiring elaborate sample handling and preparation and lengthy calibration. In situ measurement of sulfide activity has been made possible through the introduction of ion-selective membrane electrodes (4). However, since these electrodes are sensitive to sulfide activity, determination of total sulfide can be accomplished only after the samples are buffered to high pH by a high ionic strength buffer such as SAOB II (5). Total sulfide can be calculated from a simultaneous measurement by sulfide and pH electrodes. A suitable microcomputer interface for implementing such an instrumentation system has been recently described by Ben-Yaakov et al. (6). Frevert and Galster (7) proposed an analog method for direct determination of total sulfide by using a sulfide ion selective electrode coupled to a pH glass electrode. This method is limited to solutions with pHs <6.0.

This is a rather severe limitation as the pH of most natural waters as well as treated and untreated wastewaters are above this range (1-3).

The purpose of this study was to develop a direct method, based on analog instrumentation, for determination of total sulfide concentration in the pH range above pH 7 applicable for in situ measurements. The present approach differs from the one proposed by Brand and Rechnitz (8) who considered direct differential measurement between two ion selective electrodes such as a pH glass electrode and a sodium ion selective electrode. Their approach, which is similar to the one also suggested by Wilde and Rogers (9), does not allow for total concentration determination when the valencies of the pertinent ions are not identical.

THEORETICAL CONSIDERATIONS

Total concentration of sulfide (S_T) in solution can be expressed as (7)

$$S_T = [S^{2-}] \left(1 + \frac{a_{H^+}{}^2}{K_1'K_2'} + \frac{a_{H^+}}{K_2'} \right) \quad (1)$$

where

$$S_T = [S^{2-}] + [HS^-] + [H_2S]$$

$$K_1' = \frac{a_{H^+}[HS^-]}{[H_2S]}$$

$$K_2' = \frac{a_{H^+}[S^{2-}]}{[HS^-]}$$

and brackets denote concentrations. The K 's are apparent constants (7) which are defined in terms of both activity (a_{H^+}) and concentrations.

This expression clearly indicates that there are three zones, for a given value of the apparent constants K_1' and K_2' , in

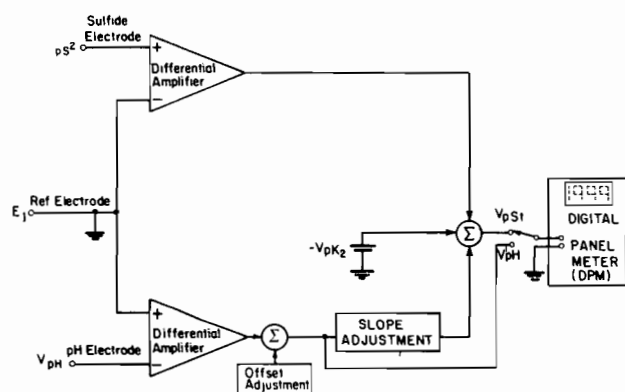


Figure 1. Schematic diagram of proposed total sulfide meter.

which S_T can be approximated by logarithmic expressions of the form

$$pS_T \approx 2pH + pS^{2-} - p(K_1'K_2') \quad \text{for } pH < pK_1' \quad (2)$$

$$pS_T \approx pS^{2-} + pH - pK_2' \quad \text{for } pK_2' > pH > pK_1' \quad (3)$$

$$pS_T \approx pS^{2-} \quad \text{for } pH > pK_2' \quad (4)$$

where

$$pH = -\log a_{H^+}$$

$$pX = -\log [X]$$

Equation 3 which is valid for the range pH 7 to pH 13 can be implemented by ion selective electrodes in conjunction with an analog electronic circuit of the form given in Figure 1.

Taking into account the liquid junction potentials of the reference electrode (E_j), the electrodes output voltages will be (8, 9)

$$V_{pH} = E^{\circ}pH + S_{pH} \cdot pH + E_j \quad (5)$$

$$V_{pS^{2-}} = E^{\circ}pS^{2-} + S_{pS^{2-}} \cdot pS^{2-} + E_j \quad (6)$$

where $E^{\circ}pH$ and $E^{\circ}pS^{2-}$ are constants, and S_{pH} and $S_{pS^{2-}}$ are the slopes of the glass and sulfide electrodes, respectively.

For ideal electrodes the slope should follow the Nernst expression

$$S = \frac{RT}{nF}$$

where R , T , F , and n are as usual.

The deviation of the practical ion selective electrode from ideal behavior can be expressed as

$$S_{pH} = qpH \cdot \frac{RT}{F} \quad (7)$$

$$S_{pS^{2-}} = -qpS^{2-} \cdot \frac{RT}{2F} \quad (8)$$

where qpH and qpS^{2-} are constants whose numerical value is normally smaller than one.

The output voltage of the proposed electronic circuit given in Figure 1 will thus be

$$V_{pS_T} = V_{pS^{2-}} - z(V_{pH} + m) - V_{pK_2'} \quad (9)$$

where z and m represent the slope and offset adjustments of the electronic processor (Figure 1). By combining eq 5-9 one obtains

$$\begin{aligned} V_{pS_T} &= E^{\circ}pS^{2-} + S_{pS^{2-}} \cdot pS^{2-} + E_j - \\ &\quad z(E^{\circ}pH + S_{pH} \cdot pH + E_j + m) - V_{pK_2'} \\ &= \frac{-RT}{F} \cdot \frac{qpS^{2-}}{2} \left(\frac{z \cdot qpH}{qpS^{2-}} \cdot 2pH + pS^{2-} \right) + \\ &\quad M - V_{pK_2'} \quad (10) \end{aligned}$$

where

$$M = E^{\circ}pS^{2-} - z(E^{\circ}pH + m) + E_j(1 - z)$$

If z is adjusted so that

$$z = \frac{1}{2} \cdot \frac{qpS^{2-}}{qpH}$$

Equation 10 reduces to the form

$$V_{pS_T} = K \left(pH + pS^{2-} - \frac{V_{pK_2'}}{K} \right) \quad (11)$$

where

$$K = -\frac{RT}{F} \cdot \frac{qpS^{2-}}{2}$$

Since the expression of V_{pS_T} (eq 12) is similar in form to eq 3, the output voltage of the proposed circuits will be linearly proportional to pS_T in the range of $pK_1' < pH < pK_2'$.

The proposed adjustment method for z applies two standard solutions having the same S_T (whose value may be unknown) at different pHs (pH_1 and pH_2). The output voltage of the instrument in the two standard solutions will be

$$V_{pS_{T1}} = V_{pS_1^{2-}} - (V_{pH_1} + m)z - V_{pK_2'} \quad (12)$$

$$V_{pS_{T2}} = V_{pS_2^{2-}} - (V_{pH_2} + m)z - V_{pK_2'} \quad (13)$$

If m ("offset adjustment" of Figure 1) is initially adjusted, so that $m = -V_{pH_1}$, i.e., $V_{pH_1} = 0$ (Figure 1) the output voltages will be

$$V_{pS_{T1}} = V_{pS_1^{2-}} - V_{pK_2'} \quad (14)$$

$$V_{pS_{T2}} = V_{pS_2^{2-}} - (V_{pH_2} - V_{pH_1})z - V_{pK_2'} \quad (15)$$

Final adjustment is made in the standard pH_2 ("slope adjustment" of Figure 1) so that the output voltage is identical with the one registered for the standard of pH_1 , i.e., $V_{pS_{T2}} = V_{pS_{T1}}$.

The required z value will be

$$z = \frac{V_{pS_2^{2-}} - V_{pS_1^{2-}}}{V_{pH_2} - V_{pH_1}}$$

Note that the adjustment of z does not change V_{pH_1} which was earlier made equal to zero. The adjustment procedure thus requires only two steps: adjustment of m to obtain $V_{pH_1} = 0$ when the electrodes are inserted in the standard solution of pH_1 , and adjustment of z to obtain $V_{pS_{T2}} = V_{pS_{T1}}$ when the electrode assembly is inserted in the standard solution of pH_2 . Once these adjustments are made the output voltage V_{pS_T} should be linear with pS^{2-} even if the specific ion electrodes exhibit a nonideal slope. Following m and z adjustment the assembly can be calibrated by conventional techniques such as the standard addition method.

EXPERIMENTAL SECTION

Electrodes. The pH electrode was a combination double junction type 9092 (Broadly James Inc.). The pS^{2-} electrode was a sulfide ion activity electrode, type F1212S (Radiometer, Denmark).

Reagents and Solutions. All reagents except for sodium sulfide ($Na_2S \cdot 9H_2O$) were analytical grade. Initial adjustments were made with two Na_2S (10^{-4} M) solutions prepared in a pH 7 buffer (NBS Standard Buffer) (10) which was then adjusted to about pH 9 by NaOH. Electrode calibration was performed on pH 7 buffer solution to which concentrated (2 M) Na_2S solution was added incrementally by buret and the pH was adjusted by NaOH (2 M) addition.

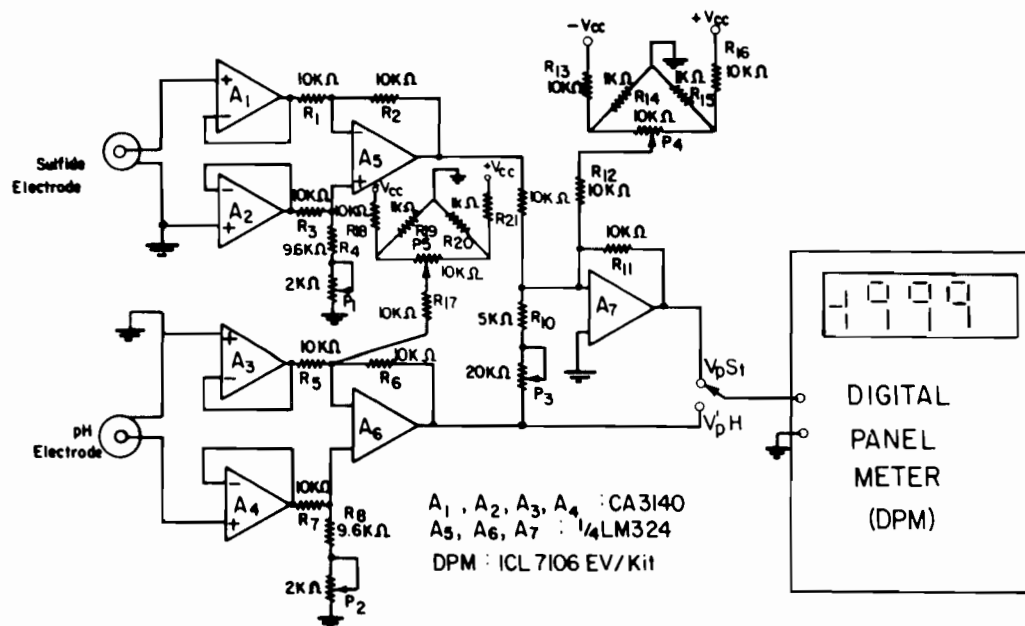


Figure 2. Electronic circuit diagram of the instrument used in the present study.

Apparatus. The basic configurations of Figure 1 needed to implement the relationship of eq 11 were tested by an analog instrument (Figure 2). The electronic design applies two high input impedance, low input current operational amplifiers (RCA CA3140) and a general purpose operational amplifier (National LM324) to realize the required differential and summing operations (8, 9, 11). It should be noted that the sulfide and pH electrodes are connected in opposite polarities to the corresponding differential amplifiers to compensate for the opposite sign of the slopes (SpH and SpS^{2-}). The functions of the trimmers and potentiometers (P_1 – P_5) are as follows: P_1 and P_2 are used for optimizing the common mode rejection ratio of the two differential amplifiers. P_5 is the offset adjustment (m) and P_3 is used for slope adjustment, i.e., the z adjustment discussed above. P_4 is used to control the magnitude of the voltage which simulate pK_2' (eq 11). This potentiometer is used in effect as a general output voltage offset to ensure compatibility between signal voltage range and the dynamic range of the digital panel meter (DPM) used. The latter was a $3\frac{1}{2}$ digit printed circuit module (INTERSIL ICL7106EV).

Instrument Adjustments and Calibration. The initial adjustments and calibration consisted of the following steps: (1) A buffer solution with pH in the range $pK_1' + 1 < pH < pK_2' - 2$ and known Na_2S concentration was prepared (in this work pH 8 and 1 M, respectively). (2) By use of P_2 , V_{pH1} was adjusted to zero. (3) $V_{pS_{T1}}$ was registered. (4) The pH of the standard solution was increased by about one pH unit using 2 M NaOH solution. (5) $V_{pS_{T2}}$ was made equal to $V_{pS_{T1}}$ by setting P_3 . (6) The output signal level was adjusted by P_4 to bring it to within the midscale of the DPM. (7) The calibration curve of $pS_T = f(V_{pS_T})$ was determined by incremental addition of concentrated (2 M) Na_2S solution.

RESULTS AND DISCUSSION

The theoretically expected error of S_T determination by the proposed method, as a function of pH, was evaluated by comparing the S_T values calculated by eq 1 to those obtained from the approximation of eq 3. The simulation was carried out for the range of pH 3 to pH 13 assuming that the values of pK_1' and pK_2' are 6 and 14, respectively (7, 12, 13). The theoretical error of this approximation (Figure 3) was calculated to be less than 5% in the pH range 7.5–12.5 and should be less than 1% in the range pH 9 and pH 11.

The pH range for which the approximation of eq 3 holds depends on the numerical values of pK_1' and pK_2' . The expected variation of pK_1' and pK_2' with ionic strength can be estimated by relating the apparent constants to the thermodynamic dissociation constants K_1, K_2 through the application

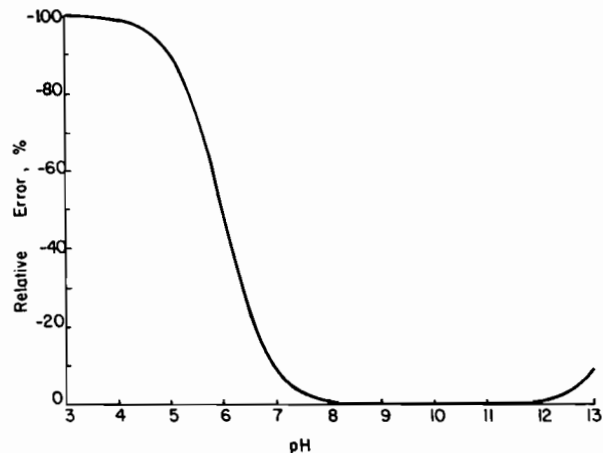


Figure 3. Expected error of S_T determination by the proposed method as a function of pH, assuming $pK_1' = 6$ and $pK_2' = 14$.

of the extended Debye–Hückel equation (EDHE) (14). The apparent constants can be expressed in the form (15)

$$pK_1' = pK_1 + \log(\gamma_T H_2S) - \log(\gamma_T HS^-) \quad (16)$$

$$pK_2' = pK_2 + \log(\gamma_T HS^-) - \log(\gamma_T S^{2-}) \quad (17)$$

where γ_T is the total activity coefficient, i.e., the ratio between single ion activity and its total concentration (both free and complexed) (16). Neglecting ion pair formation (i.e., assuming $\gamma_{T_1} = \gamma_i$) the last two terms in each of the above expressions can now be approximated by EDHE (14)

$$pK_1' = pK_1 - \frac{0.5\sqrt{\mu}}{1 + \sqrt{\mu}} \quad (18)$$

$$pK_2' = pK_2 - \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad (19)$$

Although the EDHE is valid only for low ionic strength ($\mu < 0.1$) the upper limits for apparent constants variations can be derived by assuming that $\mu \rightarrow \infty$.

$$\Delta pK_{1'_{max}} = (pK_{1'} - pK_1)_{max} \cong -0.5 \quad (20)$$

$$\Delta pK_{2'_{max}} = (pK_{2'} - pK_2)_{max} \cong -1 \quad (21)$$

Table I. Results of an Evaluation Test of the Proposed Total Sulfide Meter^a

$S_T = 6.66 \times 10^{-5}$ mol/L			$S_T = 1.66 \times 10^{-4}$ mol/L			$S_T = 3.33 \times 10^{-4}$ mol/L			$S_T = 1.113 \times 10^{-3}$ mol/L		
pH	$10^{-5}S_{TM}$, mol/L	rel error, %	pH	$10^{-4}S_{TM}$, mol/L	rel error, %	pH	$10^{-4}S_{TM}$, mol/L	rel error, %	pH	$10^{-3}S_{TM}$, mol/L	rel error, %
3.88	0.44	-93.29	4.06	0.11	-92.85	4.69	0.445	-86.63	5.46	0.395	-64.45
4.83	1.33	-80.0	5.69	0.79	-52.34	5.42	1.11	-66.46	5.82	0.527	-52.62
5.55	2.97	-55.29	6.19	1.11	-32.71	6.19	2.22	-33.14	6.05	0.702	-36.85
6.14	5.60	-15.86	7.09	1.98	19.54	8.00	3.52	5.88	6.41	0.884	-20.52
8.00	6.65	-0.034	8.58	1.57	-5.0	8.85	3.32	-0.028	6.82	1.113	0.017
9.49	6.65	-0.034	10.39	1.57	-5.0	9.85	3.52	5.88	7.81	1.113	0.017
10.53	6.65	-0.034	10.89	1.48	-10.31	10.71	3.14	-5.61	9.67	1.113	0.017
10.80	6.65	-0.034	10.94	1.57	-5.0	10.89	3.32	-0.028	10.39	1.113	0.017
10.94	6.65	-0.034	11.12	1.67	0.610	10.98	3.32	-0.028	10.71	1.113	0.017
11.12	6.65	-0.034	11.39	1.67	0.610	11.25	3.32	-0.028	10.98	1.113	0.017
11.30	6.65	-0.034	11.43	1.67	0.610	11.53	3.32	-0.028	11.16	1.113	0.017
11.39	6.65	-0.034	11.52	1.67	0.610				11.43	1.05	-5.57
11.52	6.65	-0.034							11.57	1.05	-5.57

^a S_T = actual concentration. S_{TM} = measured concentration.

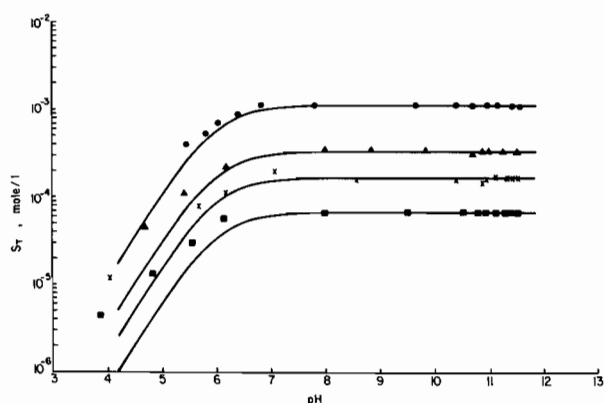


Figure 4. Response of experimental instrument to pH variation for different total sulfide concentrations (S_T): (circles) $S_T = 10^{-3}$ mol/L; (triangles) $S_T = 2 \times 10^{-4}$ mol/L; (crosses) $S_T = 1.66 \times 10^{-4}$ mol/L; (squares) $S_T = 6 \times 10^{-5}$ mol/L; (solid lines) model calculations assuming $pK_1' = 6$; $pK_2' = 14$.

As already discussed, the usable pH range of the instrument for a 5% error limit is

$$pK_1' + 1.5 < \text{pH} < pK_2' - 1.5 \quad (22)$$

Hence, the safe range is from about pH 7.5 to about pH 12. At higher ionic strength the lower pH limit may reach the value of pH 7.

Another possible error source is the variation of the liquid junction potential between the calibration and test solution. This error is lower than in the usual case, due to the partial cancellation of the liquid junction potential by the analog computation scheme. The effect of the liquid junction potential is reduced by the factor $(1-z)$ (eq 10), which assumes the numerical value of $1/2$, if the slope of the sulfide ion selective electrode is half the slope of the glass electrode. Both the pK_2' and E_j errors could be circumvented by calibrating the instrument in the test solution using the standard additive method.

Under constant composition and ionic strength, the instrument exhibits an excellent linearity as long as the pH is held between pH 8 and pH 10. It should be noted that sulfide ion activity at the lower end of this calibration curve is about 10^{-9} M which is apparently within the "mud" level of the sulfide electrode used (12, 17).

The proposed adjustment procedure of the instrument (see above) was found to be effective in balancing out slope non-ideality of the electrodes. The adjusted instrument was in-

sensitive to pH within the expected range (Table I and Figure 4). Tests were not carried out in solutions with pH values higher than 11.5 to avoid marked variation of total ionic strength.

The discrepancy between the experimental data points and the theoretical response (Figure 4) below pH 7 should be attributed to the uncertainty in the value of pK_2' used in the evaluation of the theoretical curve. Since the numerical values of apparent constants are a function of ionic strength and ionic composition (15) it is unlikely that the values which were originally cited for seawater (7, 12, 13) are directly applicable here. Fortunately, the proposed method does not require a knowledge of these constants as long as calibration and measurements are made in the "safe" pH range: pH 7.5 to pH 11.5.

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Registry No. Sulfide, 18496-25-8; water, 7732-18-5.

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