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DETERMINATION OF SULFIDE IN NATURAL WATERS BY THERMOMETRIC TITRIMETRY

RAHMALAN BIN AHMAD, J.O. HILL and R.J. MAGEE

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083 (Australia)

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ABSTRACT

The thermometric titration of sulfide with permanganate in alkaline solution has been investigated as a potential analytical method for the determination of sulfide in natural waters. The molar enthalpy of the corresponding complex calorimetric reaction has been determined as 1010 ± 36 kJ mol^{-1} and the interference effect of a variety of anionic and heavy metal cationic species has been investigated. The analytical potential of the proposed thermoanalytical method has been further tested by application to sulfide determination in a sewage sample and comparison made with sulfide assay of the same sample by differential pulse polarography.

INTRODUCTION

Sulfur pollution in natural waters originates from a wide variety of natural and anthropogenic sources and exists in diverse forms and species [1]. Many analytical techniques have been used to determine sulfide in water and these include volumetric [2,3] spectrophotometric [4–10], polarographic and related electrochemical techniques [11–18], ion-selective electrode [19–29], gas chromatography [30], ion chromatography [31–34] and atomic absorption spectrometry [35]. Moses et al. [36] have recently reviewed the available analytical methods for sulfoxy anions in aqueous solution.

Of particular relevance to the present study are the applications of thermometric titrimetry to the determination of sulfur species in water. Several enthalpimetric determinations of sulfate in water have been reported [37–39] using the heat of barium sulfate precipitation as the basis of the analytical method. Sensitivity is low and interference by a variety of heavy metals make this method unattractive for the determination of sulfate in natural waters. Weisz et al. [40] have employed the iodine–azide reaction for the enthalpimetric determination of thiosulfate over the range 32.4–324 μg cm^{-3} and Kiba et al. [41] have similarly determined sulfide in water to a sensitivity of 0.02–0.5 mol. Marik-Korda et al. [42] have reported an enthalpimetric method for the simultaneous determination of sulfide and

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thiosulfate in water to a sensitivity of 0.01 mmol, using iodine or bromine as titrant. Bark and Prachuabpaibul [43] have used the heat of precipitation of metal sulfides to assay solutions containing heavy metals such as Cu(II), Cd(II), Hg(II), Bi(III) and Fe(III). The lower detection limit varied over the range 20–70 ppm. Sajo and Sipos [44] have reported an enthalpimetric method for the determination of the sulfur content of alloys such as steel or cast iron based on sulfide/permanganate thermometric titration. A lower detection limit of 0.005% is suggested.

In the context of development of thermometric titrimetry for the determination of sulfur anionic species in aqueous solution, the sulfide/permanganate system has been re-investigated and the effect of interfering ions determined. The procedure has also been applied to the analysis of dissolved sulfide in a sewage effluent sample and the results compared with those obtained by differential pulse polarography.

EXPERIMENTAL

Calorimeter and accessories

The thermometric titrimetry system employed, and the calibration and data analysis procedures have been described in detail elsewhere [45]. The calorimeter vessel was purged with nitrogen prior to the introduction of titrate. All thermodynamic data refer to 298 K and the uncertainty associated with such data is quoted as the standard deviation from the mean.

Titrants and titrates

All solutions were prepared by using deionised water and were purged and stored under nitrogen. Sodium thiosulfate (0.1 M), iodine (0.1 M) and sodium sulfide (1.5×10^{-2} M) stock solutions were prepared by routine procedures [2] and were standardised iodometrically. Sodium hydroxide (1.0 M) and potassium permanganate (1.0 M) stock solutions were prepared by routine procedures and the latter standardised by oxalate titration [2]. Standard solutions were diluted as appropriate. For interference studies, CO_3^{2-}, $C_2O_4^{2-}$, HCO_3^-, IO_3^-, NO_3^-, SO_3^{2-} (as Na^+ or K^+ salts) (1.0 M) and Ag^+, Cu^{2+}, Fe^{3+}, K^+, Pb^{2+} and Zn^{2+} (as NO_3^- salts) (0.1 M) stock solutions were diluted as appropriate.

The titrate volume throughout was 90 cm^3. The burette delivery rate was 1.0355 ± 0.0011 cm^3 min^{-1}.

Analytical procedure

Reaction heats, Q_R (kJ), and molar reaction enthalpies, ΔH_R (kJ mol^{-1}), are calculated on the basis of the determined temperature rise, ΔT (mV), for the relevant quantitative reaction and the mean heat capacity, C_{pM} (kJ mV^{-1}), of the system: C_{pB} and C_{pA} (kJ mV^{-1}) refer to the system heat capacities before and after titration. Sulfide concentration was determined on the basis of the heat generated in the corresponding S^{2-}/MnO_4^- thermometric titration.

Calibration of the thermometric titrimetric system in terms of the alkaline oxidation of sulfide by permanganate was effected using the conventional spiking method. The effect of variation of $[OH^-]$ and $[MnO_4^-]$ on the titrimetric reaction was determined by maintaining the sulfide mass in the calorimeter at 100 μg and varying $[OH^-]$ and $[MnO_4^-]$ over the ranges 0.1–1.0 and 0.02–0.1 M, respectively.

Interference studies were conducted on the basis of a 1:1 sulfide/interferent mole ratio. The interference effect is expressed as the ratio Q'_R/Q_R where Q'_R is the S^{2-}/MnO_4^- reaction heat in the presence of an interfering ion.

Sulfide in environmental samples was separated from the corresponding aqueous matrices as H_2S, which was absorbed in NaOH (0.01 M). Quantitative separation of sulfide was effected using an all-glass apparatus of design similar to that described by Wheatland and Lowden [46]. The trapped sulfide was subsequently transferred to the calorimeter vessel by means of a conventional nitrogen, pressure-gradient system.

Differential pulse polarography (DPP)

A PAR-170 electrochemical system was used with a dropping mercury electrode as the working electrode, a saturated calomel electrode as reference electrode and a coiled platinum wire as counter electrode. The polarographic cell (50 cm^3) was maintained at 25 ± 1°C and was continuously purged with nitrogen. The voltage range of −0.4–1.0 V was scanned at 5 mV s^{-1}; the mercury reservoir height was 80 cm, the drop time 1 s, the modulation amplitude was 25 mV (pp) and the current range 10 μA (fs). Quantitation of sulfide in the sample solution was made using the standard addition method and a sulfide mass range of 5–20 μg.

RESULTS AND DISCUSSION

Sajo and Sipos [44] have reported that in alkaline solution, oxidation of sulfide by permanganate is rapid and quantitative and the corresponding stoichiometric reaction is: $Na_2S + 8KMnO_4 + 8KOH \rightarrow Na_2SO_4 + 8K_2MnO_4 + 4H_2O$. It is difficult to assess the analytical significance of the thermodynamic data of Sajo and Sipos [44] since the molar enthalpy of the S^{2-}/MnO_4^- reaction is not quoted. Results leading to the molar enthalpy of the S^{2-}/MnO_4^- reaction are summarised in Table 1. The relatively large

TABLE 1

Molar enthalpy of the S^{2-}/MnO_4^- reaction [a]

S^{2-} ($\times 10^{-6}$ mol)	C_{pB} (kJ mV^{-1})	C_{pA} (kJ mV^{-1})	ΔT (mV $\times 10^{-2}$)	ΔH_R (kJ mol^{-1})
0.141	0.21193	0.21284	0.07221	1084
0.142	0.21062	0.22058	0.06710	1019
0.424	0.21329	0.21407	0.19256	970
0.448	0.21530	0.22314	0.20217	990
0.566	0.21487	0.21781	0.25075	959
0.597	0.21343	0.22362	0.28589	1047
0.707	0.21391	0.21434	0.33987	1029
0.746	0.21775	0.21911	0.34813	1019
0.849	0.21334	0.21554	0.38770	1029
0.990	0.20994	0.21805	0.47843	1034
0.132	0.21149	0.21351	0.51466	966
1.273	0.21286	0.22115	0.58806	1002
1.414	0.21085	0.22805	0.62647	972
1.492	0.21411	0.21989	0.68319	993
3.465	0.21456	0.21773	1.67760	1046
4.476	0.21579	0.21810	2.15800	1046
				Mean: 1010 ±36

[a] $[OH^-] = 0.1$ M; $[MnO_4^-] = 0.08$ M.

reaction enthalpy suggests that the S^{2-}/MnO_4^- reaction has potential [47] as the basis of a thermoanalytical method for the determination of sulfide in water. The analytical significance of this reaction is further illustrated by the calorimetric data given in Table 2 and Figs. 1 and 2, relating to a series of "spiked" sulfide thermometric titrations. Linear $\Delta T/[S^{2-}]$ and $Q/[S^{2-}]$

TABLE 2

Variation of Q_R with $[S^{2-}]$ [a]

$[S^{2-}]$ (mg l^{-1})	C_{pM} (kJ mV^{-1})	T (mV)	Q_R (kJ $\times 10^{-3}$)
0.053	0.215602	0.000671	0.1447
0.106	0.221080	0.001594	0.3523
0.159	0.219217	0.002022	0.4432
0.213	0.218526	0.002859	0.6247
0.266	0.218429	0.003481	0.7604
0.531	0.217000	0.006832	1.4825
1.595	0.216947	0.021580	4.6817
3.721	0.216436	0.049730	10.7630
4.784	0.218719	0.064922	14.1997
5.847	0.216265	0.079138	17.1148

[a] $[OH^-] = 0.1$ M; $[MnO_4^-] = 0.08$ M.

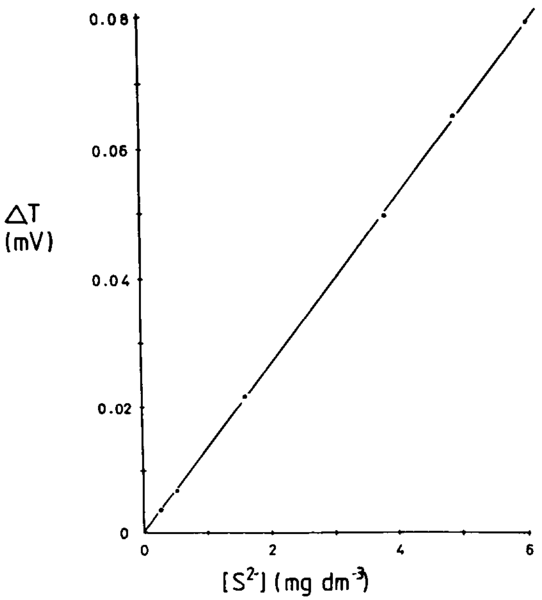

Fig. 1. ΔT vs. $[S^{2-}]$.

plots were obtained. It is apparent from the calorimetric data given in Tables 3 and 4 that variation of $[OH^-]$ and $[MnO_4^-]$ over the ranges 0.01–1.00 and 0.02–0.10 M, respectively, has little effect on the overall thermochemistry of the system and hence the analytical potential of the S^{2-}/MnO_4^- reaction.

Detailed analysis of the calorimetric data for a selection of S^{2-}/MnO_4^- thermometric titrations over a 1–5 ppm S^{2-} concentration range indicates

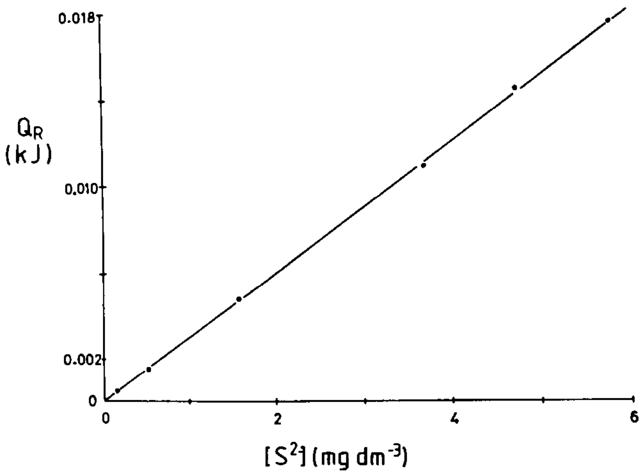

Fig. 2. Q_R vs. $[S^{2-}]$.

TABLE 3

Variation of Q_R with $[OH^-]$ [a]

$[OH^-]$ (mol l^{-1})	C_{pB} (kJ mV^{-1})	C_{pA} (kJ mV^{-1})	ΔT (mV)	Q_R (kJ $\times 10^{-3}$)	% Deviation from mean Q_R
0.01	0.2136	0.2171	0.0143	3.1001	−1.59
0.05	0.2138	0.2157	0.0140	3.0137	−4.34
0.10	0.2128	0.2157	0.0150	3.2183	+2.16
0.20	0.2111	0.2164	0.0156	3.3469	+6.24
0.40	0.2134	0.2156	0.0144	3.0980	−1.66
0.60	0.2117	0.2149	0.0145	3.0975	−1.68
1.00	0.2116	0.2138	0.0149	3.1781	+0.88
				Mean: 3.1504	

[a] $[MnO_4^-] = 0.02$ M.

that the calorimetric reaction is more complex than that proposed by Sajo and Sipos [44]. The reaction period segments of the thermograms (Fig. 3) indicate that two sequential reactions are involved, which are proposed as:

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

$$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$$

Reduction of permanganate to MnO_2 progressively predominates as the S^{2-} concentration increases. Stewart [48] has confirmed that oxidation of sulfide by permanganate in concentrated basic media is associated with precipitation of MnO_2 according to the reaction

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

TABLE 4

Variation of Q_R with $[MnO_4^-]$ [a]

$[MnO_4^-]$ (mol l^{-1})	C_{pB} (kJ mV^{-1})	C_{pA} (kJ mV^{-1})	ΔT (mV)	Q_R (kJ $\times 10^{-3}$)	% Deviation from mean Q_R
0.02	0.2233	0.2164	0.0133	2.9240	−5.52
0.02	0.2128	0.2128	0.0140	2.9792	−3.74
0.04	0.2150	0.2173	0.0146	3.1558	+1.97
0.04	0.2147	0.2139	0.0149	3.1931	+3.17
0.06	0.2135	0.2163	0.0138	2.9656	−4.17
0.06	0.2135	0.2167	0.0145	3.1197	+0.80
0.08	0.2138	0.2156	0.0149	3.1990	+3.36
0.08	0.2134	0.2156	0.0145	3.1103	+0.50
0.10	0.2136	0.2171	0.0147	3.1656	+2.29
0.10	0.2134	0.2171	0.0146	3.1361	+1.33
			Mean Q_R =	3.0948	

[a] $[OH^-] = 0.1$ M.

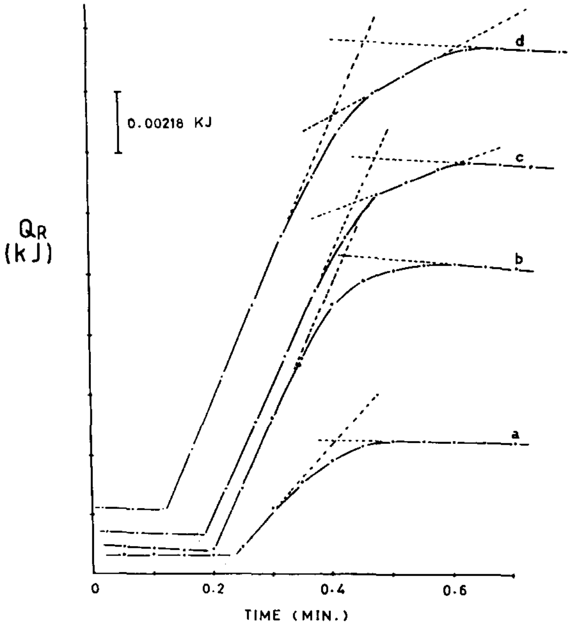

Fig. 3. Q_R vs. t enthalpograms: $[S^{2-}]$ (mg l^{-1}) = (a) 1.59; (b) 3.72; (c) 4.78; (d) 5.85.

This means essentially that the S^{2-}/MnO_4^- reaction is suitable as a basis for the thermoanalytical determination of sulfide at environmentally significant concentration levels, if the sulfide content is assayed on the basis of reaction heat and not on the basis of permanganate titre.

The direct analysis of sulfide in natural waters is difficult due to the presence of a wide variety of interfering ions. Anions, such as F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, CO_3^{2-}, CN^-, $CH_3CO_2^-$, $C_2O_4^{2-}$, HCO_3^-, HSO_3^-, HSO_4^-, IO_3^-, SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$, may coexist with sulfide in the aquatic environment [1]. The interference effect of a selection of these anions on the analytical determination of sulfide by thermometric titration with permanganate is apparent from the calorimetric data given in Table 5. IO_3^- decreases the net reaction heat due to reduction of sulfide concentration according to the reaction:

$$4IO_3^- + 3S^{2-} \rightarrow 4I^- + 3SO_4^{2-}$$

Conversely, $S_2O_3^{2-}$ increases the net reaction heat due to reaction with permanganate according to the reaction:

$$2MnO_4^- + 4H_2O + 6S_2O_3^{2-} \rightarrow MnO_2 + 8OH^- + 3S_4O_6^{2-}$$

I^-, NO_3^-, $C_2O_4^{2-}$, CO_3^{2-}, HCO_3^- exhibit no interference.

A variety of heavy metals exist in natural waters [49] and sulfur anionic species contribute to the control of concentration and distribution of heavy metals in the environment [1]. The interference effect of cations such as Ag^+,

TABLE 5

Anion interference effect [a]

Anion	C_{pM} (kJ mV^{-1})	Q_R or Q'_R (kJ)	Interference effect (Q'_R/Q_R)
–	0.2154	0.00321	–
	0.2141	0.00320	
	0.2144	0.00316	
I^-	0.2141	0.00311	0.972
	0.2115	0.00310	
	0.2145	0.00310	
IO_3^-	0.2151	0.00156	0.480
	0.2145	0.00149	
	0.2145	0.00154	
SO_3^{2-}	0.2151	0.00350	1.088
	0.2145	0.00341	
	0.2149	0.00350	
$S_2O_3^{2-}$	0.2151	0.00615	1.962
	0.2148	0.00639	
	0.2150	0.00624	
NO_3^-	0.2150	0.00318	1.003
	0.2155	0.00321	
	0.2145	0.00320	
$C_2O_4^{2-}$	0.2133	0.00323	1.019
	0.2149	0.00320	
	0.2143	0.00332	
CO_3^{2-}	0.2151	0.00264	0.809
	0.2144	0.00259	
	0.2144	0.00251	
HSO_3^-	0.2133	0.00314	0.994
	0.2145	0.00328	
	0.2140	0.00308	
HCO_3^-	0.2146	0.00270	0.834
	0.2148	0.00260	
	0.2138	0.00267	

[a] $[MnO_4^-] = 0.02$ M; $[OH^-] = 0.1$ M.

Cu^{2+}, Fe^{3+}, Pb^{2+} and Zn^{2+} on the determination of sulfide by thermometric titration with permanganate is apparent from the calorimetric data recorded in Table 6. Figure 4 indicates that for metal ions such as Ag^+, Cu^{2+}, Pb^{2+} and Fe^{3+}, which precipitate as sulfides in alkaline solution, a linear correlation exists between the extent of interference and the solubility product of the corresponding metal sulfide. The non-conformity of Zn^{2+} is rationalised in terms of the partial solubility of ZnS in alkaline solution. K^+ exhibits no detectable interference effect. To test the applicability of the proposed analytical method for sulfide determination in natural waters, a sewage effluent sample was investigated. A preliminary thermometric titration of

TABLE 6

Cation interference effect [a]

Cation	C_{pM} (kJ mV^{-1})	Q_R or Q'_R (kJ)	Interference effect (Q'_R/Q_R)
–	0.2154	0.00321	–
	0.2141	0.00320	
	0.2144	0.00316	
K^+	0.2150	0.00318	1.003
	0.2155	0.00321	
	0.2145	0.00320	
Ag^+	0.2142	0.00154	0.492
	0.2109	0.00160	
	0.2110	0.00156	
Pb^{2+}	0.2149	0.00062	0.229
	0.2146	0.00066	
	0.2131	0.00092	
Zn^{2+}	0.2147	0.00248	0.768
	0.2143	0.00248	
	0.2152	0.00238	
Cu^{2+}	0.2140	0.00090	0.270
	0.2144	0.00073	
	0.2146	0.00096	
Fe^{3+}	0.2135	0.00198	0.762
	0.2145	0.00270	
	0.2145	0.00262	

[a] $[MnO_4^-] = 0.02$ M; $[OH^-] = 0.1$ M.

this untreated sample with permanganate indicated no detectable sulfide. The sample was subsequently spiked with sulfide to environmentally significant concentration levels and a sulfide assay was obtained by thermometric

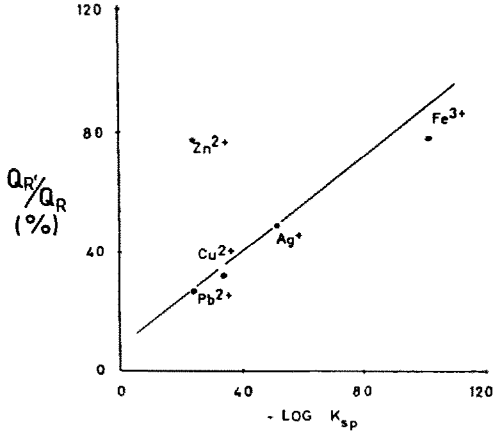

Fig. 4. Cation interference effect: Q'_R/Q_R vs. log K_{SP}.

TABLE 7

[S^{2-}] in a sewage sample

Original sample volume (cm^3)	C_{pB} (kJ mV^{-1})	C_{pA} (kJ mV^{-1})	ΔT (mV)	Q_R (kJ)	[S^{2-}] (mg l^{-1})	
					Enthalpimetry	DPP
167.5	0.2123	0.2155	0.005075	0.001086	0.402	0.401
168.0	0.2113	0.2168	0.003968	0.008495	0.318	0.362
71.0	0.2119	0.2154	0.004162	0.000889	0.388	0.327
96.0	0.2115	0.2143	0.004945	0.001053	0.340	0.337

titrimetry and differential pulse polarography. The results are given in Table 7. In the absence of total analysis data for the sewage sample in terms of heavy metal, non-metal and organic matter content, it may be premature to propose the S^{2-}/MnO_4^- thermometric titration as an analytical method for the determination of sulfide in environmental waters, but the close agreement of calorimetric and electrochemical data obtained (Table 7) for an artificial sample suggests considerable progress in this direction.

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