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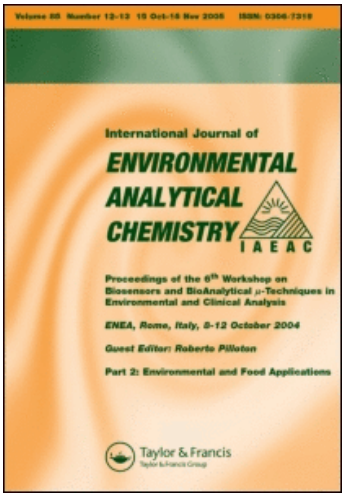

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Electrochemical Analysis of Sulphur Compounds of Environmental Interest†

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The introduction relates to previous uses of sulphide ion-selective electrodes (ISEs) in applications of environmental relevance, such as, control of the treatment of obnoxious sulphur compounds to avoid their release to the environment. This preamble is followed by details of the work at UWIST on assessing applications of sulphide ISEs for monitoring sewage and industrial effluents, growth studies of sulphate-reducing bacteria and brief details of microcomputerised controlled systems.

Flow-injection analysis (FIA) requires a carrier stream of 5×10^{-6} M sodium sulphide in SAOB for satisfactory results. A "high strength" SAOB (40 g dm^{-3} L-ascorbic acid in 2 M sodium hydroxide), containing 5×10^{-6} M sodium sulphide background is a suitable FIA carrier stream for overcoming any detrimental effect of hydrogen peroxide on sulphide ISEs. Such a carrier stream has been used for the illustrated monitoring of untreated sewage effluent samples as well as for samples treated with hydrogen peroxide.

Sulphide ISEs may be used for monitoring the growth of *Desulfovibrio* sulphate-reducing bacteria, illustrated here for *D.desulfuricans*, *D.gigas* and *D.vulgaris*. The electrode can be used in the indirect mode (sulphide trapping solution in separate container from culture) or in the direct mode (electrodes placed in the culture). Sulphide recoveries match sulphate-consumption by the bacteria as well as consumption of metabolic intermediates, such as, sulphite, thiosulphate, etc. and organic sulphur sources. The various phases of bacterial growth may be followed by monitoring the generation of sulphide.

KEY WORDS: *Desulfovibrio* bacteria, hydrogen peroxide interferences on SAOB, sewage analysis for sulphide, sulphate-reducing bacteria, Sulphide anti-oxidant buffer SAOB.

†Presented at the 14th annual symposium on the analytical chemistry of pollutants, Barcelona, November 21–23, 1984.

INTRODUCTION

Various sulphur compounds are of environmental concern because of their obnoxious odours and toxicity. This applies especially to sulphides and, to some extent, thiols, all of which can be present in sewage and general effluents. Also, sulphide can arise from more general microbial action, such as, by that of sulphate-reducing bacteria to cause corrosion of underground pipes, oil storage tanks, sulphate-containing rocks, etc. There is, therefore, a need for monitoring methods for determining sulphides and thiols in the environment context, and uses of sulphide ion-selective electrodes (ISEs) for this purpose have been described from time to time.

The classical example of the use of the sulphide ISE for monitoring control of the release of volatile odours from an industrial process is that of the oxidation stage (oxygen or air sparging) for the highly alkaline (pH 12) "black liquor" of the pulp and paper trades.[1] The Orion 94-16 sulphide ISE provided useful information on the oxidation stages. Thus, within the first 30 min of oxygen sparging, the initial sulphide content ($\approx 5 \times 10^{-2}$ M) drops by three decades and by more than 12 decades in the next 30 min. Thereafter, sulphide concentration actually increases by about three decades, albeit temporarily, but in the final 90 min it falls greatly to about 10^{-20} M as indicated by the final potential of about -270 mV.

Swartz and Light[1] concluded from the e.m.f. change patterns that two forms of sulphur exist in black liquor: simple inorganic sulphide, which is essentially uncomplexed and readily oxidized in the first 30 min of oxygenation, and highly undissociated organosulphur compounds like mercaptans and alkyl sulphides, which oxidize more slowly.

Other instances of the use of sulphide ISEs include the analysis of lime liquors in leather processing,[2,3] industrial waste waters,[4] coke oven gas,[5] flotation pulps[6] and natural water.[7] Of particular relevance to this lecture is the use of sulphide ISEs for monitoring hydrogen sulphide in effluents[8] and the measurement of sulphide in sewage waters with an iodide ISE.[9] In this last respect, various studies have been carried out at UWIST on the scope of sulphide ISEs for flow injection analysis (FIA) monitoring sulphide levels in sewage effluents, both before and after treatment with hydrogen peroxide.[10,11]

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FIA OF SULPHIDE IN SEWAGE EFFLUENTS

FIA principles

In FIA with ISEs, calibration standards and samples are allowed to flow over or through the membrane of the sensing electrode coupled to a suitable reference electrode.[12-15] Practical difficulties in the application of ISEs to sulphide and thiol measurements relate to oxidation and frequently to volatility of the sample components.[16-18] Nevertheless, FIA systems can be used with the sulphide ISE as has previously been shown for the monitoring of a process stream and for ethane thiol.[18,19] Measurements with the sulphide ISE are best carried out on samples and standards in a background of Sulphide Anti-Oxidant Buffer (SAOB).[20] It is important that the SAOB, normally added in volume equal to that of the sample, is either freshly prepared or preserved by storage under nitrogen.[21] Normally, SAOB consists of sodium hydroxide (2 M) with ascorbic acid ($20\,g\,dm^{-3}$), but there are other compositions, e.g., a "double-strength" SAOB is made up of sodium hydroxide (4 M) and ascorbic acid ($40\,g\,dm^{-3}$)[11]

Carrier stream parameter studies for FIA with sulphide ISEs have been made[11] for a carrier flow rate of $2.23\,cm^3\,min^{-1}$ and injected samples of $40\,mm^3$. Poor calibrations resulted from having either SAOB or 10^{-6} M sodium sulphide in SAOB as carrier streams for an Orion 94-16A sulphide ISE used in the "cascade" flow mode. On the other hand, a carrier stream of 5×10^{-6} M sodium sulphide for the "cascade" flow Orion electrode gave good calibrations for sulphide standards with a linear calibration ranging between 10^{-2} M and 5×10^{-5} M sulphide. Similar calibrations for an EDT Research EES flow-through sulphide ISE as indicator showed the carrier stream of 5×10^{-6} M sodium sulphide in normal SAOB to be very effective and the linear calibration range extended to $<10^{-5}$ M sulphide.

Hydrogen peroxide interference studies

The data in Table I summarize the effects of varying SAOB and of the presence of hydrogen peroxide in SAOB antioxidant on the Orion 94-16A sulphide ISE with respect to sulphide response.[11] Lowering of the sodium hydroxide level of SAOB from 2 M to 1 M

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TABLE I

Effect of varying the SAOB quality including effect of added hydrogen peroxide on the Orion 94-16A electrode for calibration between 10^{-2} M and 10^{-6} M sodium sulphide at 20°C. (Data from Ref. 11)

Expt. no.	Background solution	Lower limit of linear range/M	Slope /mV decade^{-1}	E^0 versus Corning reference electrode/mV
1	Normal SAOB, [NaOH] = 2 M	10^{-6}	−29.0	−901
2	SAOB, [NaOH] = 1 M	1.2×10^{-5}	−26.8	−803
3	SAOB, [ascorbic acid] = 40 g dm^{-3}	10^{-6}	−29.2	−891
4	Normal SAOB, H_2O_2 (0.1 M) in sulphide increments only	3×10^{-5}	−29.0	−892
5	Normal SAOB with $[H_2O_2] = 0.1$ M	3×10^{-5} 10^{-4}	−27.5[a] −24.0[a]	−890 −874
6	Normal SAOB, for electrode reconditioned after H_2O_2 (0.01 M) contact	10^{-6}	−29.0	−904
7	SAOB, [ascorbic acid] = 40 g dm^{-3} and $[H_2O_2] = 0.1$ M	5×10^{-6}	−28.7	−900

[a]Calibrations not linear after two runs.

(items 1 and 2 in Table I) is not recommended because of the poorer detection limit and a fall in the electrode slope. On the other hand, increasing the amount of L-ascorbic acid (to 40 g dm^{-3}, item 3 in Table I) has virtually no effect on calibrations, except for a small change in E^0.

Only two calibrations of the Orion 94-16A sulphide ISE were possible in normal SAOB containing 0.1 M hydrogen peroxide (item 5 in Table I) after which the electrode did not yield a satisfactory calibration for e.m.f. *versus* log[sulphide]. However, restoration of electrode quality was possible by soaking in sodium sulphide (0.1 M) for two days followed by polishing of the membrane surface. The electrode could be used with high strength SAOB (with 40 g dm^{-3} ascorbic acid) in the presence of 0.1 M hydrogen peroxide (item 7 in

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Table I). The maximum tolerable level of hydrogen peroxide must be regarded as 0.1 M; in any case, economic reasons dictate that such an excess should rarely be met for sewage and effluent samples treated with peroxide.

The high strength SAOB (item 7 in Table I) provides an extra "buffer" for preventing the detrimental effect of hydrogen peroxide on the Orion 94-16A sulphide ISE. Lower levels of ascorbic acid do not give this "buffer", not even for 0.01 M hydrogen peroxide (item 5 in Table I), but fortunately the electrode can be rejuvenated (item 6 in Table I). Hydrogen peroxide present in samples only (item 4 in Table I) reduces the electrode range, but the slope remains near-Nernstian.

The above shows that the use of "high strength" SAOB containing $40\,g\,dm^{-3}$ L-ascorbic acid in 2 M sodium hydroxide provides an additional "buffer" against the derimental effect of hydrogen peroxide on sulphide ISEs. The data indicate that sulphide ISEs can be tested for monitoring sulphide levels in effluents treated with hydrogen peroxide.

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Sewage effluent analysis for sulphide

The ability to use sulphide ISEs to monitor sulphide levels in sewage effluents before and after treatment with hydrogen peroxide is important in view of the increasing use of hydrogen peroxide for treating and controlling the deleterious sulphide types in effluents, including sewage effluents.[22] Preliminary assessment[11] of sulphide in sewage effluents by direct potentiometry with the Orion 94-16A sulphide ISE indicated that a stronger SAOB with $40\,g\,dm^{-3}$ L-ascorbic acid in 2 M sodium hydroxide gave sulphide data nearer to colorimetric reference values than for normal SAOB with $20\,g\,dm^{-3}$ L-ascorbic acid in 2 M sodium hydroxide. Thus, a group of four sewage samples containing 10.3, 1.9, 3.0 and 18.6 ppm sulphide determined by colorimetry yielded just 67, 15, 43 and 79 percent of these values, respectively, by direct potentiometry on samples in normal SAOB. On the other hand, a group of three samples showing 4.5, 9.9 and 4.8 ppm sulphide by colorimetry yielded direct potentiometric data in the higher strength SAOB which were up to 93 percent of the colorimetric values.

An assessment of the merit of high strength SAOB (with

TABLE II

Sulphide content of sewage effluents after storage for 3 days in sealed containers determined by colorimetry, direct potentiometry and FIA.[a] (Data from ref. 11). (S.d. in parentheses for $n=4$)

	Sulphide content/ppm			
			FIA	
Sample no.	Colorimetry	Direct potentiometry	EDT EES flow-through electrode	Orion 94-16A "cascade flow" ISE
Samples 1 to 4				
1	2.1 (0.2)	1.5 (0.2)	2.1 (0.3)	—
2	15.2 (0.8)	11.1 (0.2)	15.0 (2.0)	—
3	11.6 (0.3)	14.8 (2.0)	12.8 (0.1)	—
4[a]	0.20 (0.1)	0.20 (0.0)	0.22 (0.55)	—
Mean	7.28	6.90	7.52	
Samples 5–8				
5	17.8 (0.5)	14.5 (1.2)	—	17.9 (0.1)
6	16.5 (1.1)	13.2 (0.1)	—	16.7 (0.9)
7[b]	0.10 (0.05)	0.12 (0.05)	—	0.45 (0.07)
8[b]	2.4 (1.1)	1.3 (0.8)	—	2.0 (1.0)
Mean	9.0	7.28		9.26

[a]For FIA the carrier stream was 5×10^{-6} M sodium sulphide in normal SAOB and samples were diluting (1+1) with SAOB containing ascorbic acid (80 g dm^{-3}) in 4 M sodium hydroxide.
[b]Sewage effluent treated with hydrogen peroxide.

40 g dm^{-3} L-ascorbic acid in 2 M sodium hydroxide) is shown in Table II for sewage effluent samples.[12] Having regard to the fact that the colorimetric sulphide levels of samples 4 and 7 are nearer to the background level (5×10^{-6} M = 0.16 ppm) of sulphide in the FIA carrier stream, and which really excludes these from the discussion, the FIA data by both "Cascade" and "flow-through" ISEs for the remaining samples are close to the colorimetric data. This shows that FIA in either mode, following sample treatment with the high-strength SAOB (sample diluted 1+1 with SAOB containing 80 g dm^{-3} ascorbic acid in 4 M sodium hydroxide), is suitable for control monitoring of sulphide in sewage effluents. Such monitoring

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can also be made of hydrogen peroxide treated sample (4, 7 and 8) when the objective is to ensure that sulphide is kept below a threshold value.

SULPHIDE PRODUCED BY SULPHATE-REDUCING BACTERIA

Anaerobic sulphate-reducing bacteria of the *Desulfovibrio* species are widely distributed and, as stated above, they cause many corrosion and other problems[23–26] to the extent that techniques for monitoring their growth and other parameters are relevant to environmental chemistry. The organisms not only cause anaerobic corrosion of buried iron or steel materials but spoil stored petrol and cutting oil emulsions, corrode oil-well casings and oil-storage tanks, blacken paper pulp and produce hydrogen sulphide in natural and manufactured gases. Underground corrosion of iron pipes by these bacteria was estimated in 1960 to cost the U.S.A. between $M500 and $M2000 per year and to account for an annual loss of £M50 in the U.K.

Orion 94-16A sulphide ISEs have been used successfully for monitoring the growth and nutrient parameters of *Desulfovibrio* species of sulphate-reducing bacteria.[27,28] The monitoring has been made by indirect and direct modes for *D.desulfuricans*, *D.gigas* and *D.vulgaris*. The sulphide determined matched amounts expected from the nutrient present in the culture media (Tables III and IV), thus demonstrating that the ISE approach is a suitable monitoring approach. From the e.m.f. *versus* time data, it was possible to determine pauses in growth (Fig. 1, plot B) corresponding to the lag phase and which were more pronounced for older starter cultures.[27] Features corresponding to nutrient starvation (Fig. 1, plot C) correspond to low sulphide.[27]

All three species of bacteria thrived on the metabolic intermediates of sulphite, thiosulphate, metabisulphite and dithionite.[27,28] The species, represented by *D.vulgaris*, also grow in certain organic sulphur species, e.g., cysteine, cystine and glutathione as alternative sulphur sources to sulphate.[28] However, they will not grow with methionine as sulphur source, and this is attributed to the relative stability of C–S–C bonds that are not adjacent to the amino group.

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TABLE III

Sulphide production by *desulfovibrio* species from sodium sulphate (indirect monitoring mode). (Data from ref. 27)

Desulfovibrio species	Na_2SO_4/g	S_i in medium/g	S^{2-} in monitoring flask: Sulphide electrode/g	S^{2-} in monitoring flask: Gravimetric/g	Age of inoculum/d
D.desulfuricans	0.500	0.113	0.108	0.105	43
	0.564	0.127	0.128	0.131	11
	none	—	4×10^{-5}	none	22
D.gigas	0.500	0.113	0.106	0.108	24
	0.564	0.127	0.136	0.131	28
	none	—	3×10^{-5}	none	161
D.vulgaris	0.500	0.113	0.112	—	10
	0.564	0.127	0.128	0.118	4
	none	—	0.006	none	49

TABLE IV

Sulphide production by *desulfovibrio* species from various inorganic sulphur (S_i) sources (direct monitoring mode). (Data from ref. 27)

Sulphur source	S_i in medium/g	S^{2-} by sulphide ISE/g	*Desulfovibrio* species	Age of inoculum/d
0.564 g Na_2SO_4	0.127	0.123	*D.vulgaris*	93
No inorganic sulphur	—	0.0001	*D.vulgaris*	49
0.564 g Na_2SO_4	0.127	0.134	*D.desulfuricans*	11
No inorganic sulphur	—	0.002	*D.desulfuricans*	32
0.564 g Na_2SO_4	0.127	0.136	*D.gigas*	28
0.500 g $Na_2S_2O_3.5H_2O$	0.129	0.122	*D.desulfuricans*	121
0.500 g Na_2SO_3	0.127	0.123	*D.vulgaris*	254
0.377 g $Na_2S_2O_5$	0.127	0.122	*D.vulgaris*	265

The various growth phases, namely, lag, growth, stationary and death, can be discerned by daily renewal of the highly alkaline sulphide trapping medium in the monitoring flask of the indirect monitoring method (Fig. 2). The stationary and death phases are not resolved in the direct monitoring mode but the three stages of lag, growth and stationary/death can be clearly seen (K, L, M in Fig. 3).

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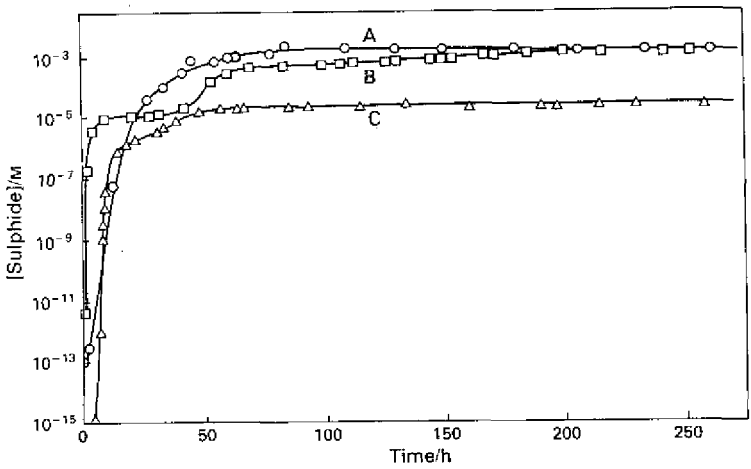

FIGURE 1 Sulphide produced by *D.vulgaris* (indirect monitoring). A: 0.564 g of Na_2SO_4 or sulphur nutrient and starter culture aged 10 d; B: 0.564 g of Na_2SO_4 and starter culture aged 73 d; and C: no inorganic sulphur nutrient for starter culture aged 49 d. (Reference 27)

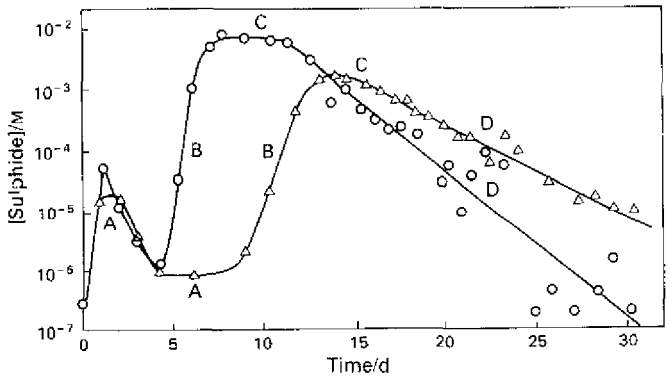

FIGURE 2 Growth phases of *D.gigas* monitored by the indirect method (daily renewal of alkaline trap for sulphide in monitoring flask). Bacterium inocula ages: circles 87 d; triangles 153 d. A: lag (pause) phase; B: logarithmic growth phase; C: stationary phase; and D: death phase. (Reference 27)

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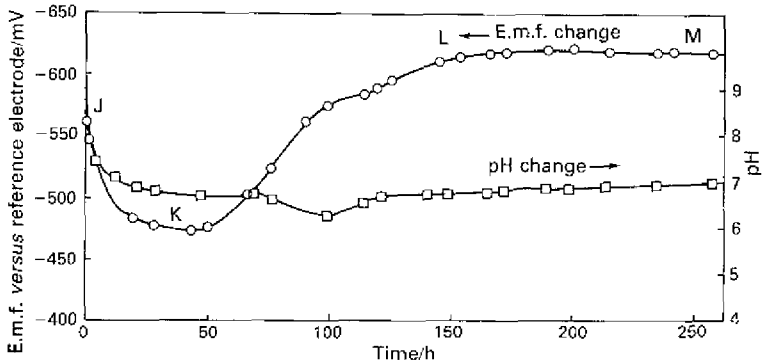

FIGURE 3 Sulphide production (e.m.f. change) and pH curves of *D.vulgaris* monitored directly by having electrodes in the air-tight growth flask. J: starter culture injected; K: lag phase; K to L: logarithmic growth phase; L to M: stationary and death phases. (Reference 27)

The ISE method is superior to turbidimetric methods of determining growth for it avoids the errors due to clumping of bacterial colonies.

Sodium tetraborate(III) (2% m/v) and 2,4-dinitrophenol (2% m/v) are confirmed as effective bactericides for *D.vulgaris* which is the most robust of the three species (*D.sulfuricans*, *D.gigas* and *D.vulgaris*) studied.[27,28]

CONCLUSION

Sulphide ISEs in various configurations are effective monitors for a range of applications of environmental relevance. Flow injection analysis can deal with discrete samples, while the applications with sulphate-reducing bacteria indicate the scope for continuous monitoring for prolonged periods. The further development of these kinds of applications, and especially that for the surveillance of hydrogen peroxide treated and untreated sewage effluents can be geared to microcomputer control. The interfacing of microcomputers to monitoring systems involving ISEs is very feasible. Such interfaced systems are readily adaptable to a variety of functions as already described for a titration system involving the ZX 81 microcomputer and for which a calibration sequence for ISEs have been described.[29] This has been extended to titrations of sulphides and thiols in effluents controlled by the more adaptable ZX spectrum microcomputer.[30]

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