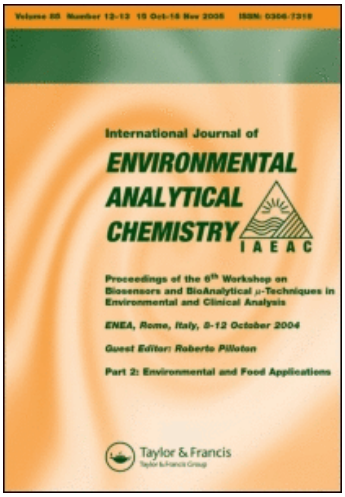

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Acid Volatile Sulphide and Pyrites Using Microdiffusion

R. Bruce Williamson[a]; Lawrence F. Van Dam[ab]; B. E. Wise[a]; Dean J. Lee[a]
[a] NIWA, National Institute of Water and Atmospheric Research, Hamilton, New Zealand [b] Perkin-Elmer (NZ) Ltd., Auckland, New Zealand

To cite this Article Williamson, R. Bruce , Van Dam, Lawrence F. , Wise, B. E. and Lee, Dean J.(2001) 'Analysis of Acid Volatile Sulphide and Pyrites Using Microdiffusion', International Journal of Environmental Analytical Chemistry, 80: 3, 187 — 199
To link to this Article: DOI: 10.1080/03067310108044369
URL: http://dx.doi.org/10.1080/03067310108044369

Intern. J. Environ. Anal. Chem., Vol. 80(3), pp. 187-199
Reprints available directly from the publisher
Photocopying permitted by license only

ANALYSIS OF ACID VOLATILE SULPHIDE AND PYRITES USING MICRODIFFUSION

R. BRUCE WILLIAMSON*, LAWRENCE F. VAN DAM†, B.E. WISE and DEAN J. LEE‡

NIWA, National Institute of Water and Atmospheric Research, PO Box 11–115, Hamilton, New Zealand

(Received 27 July 2000; In final form 28 December 2000)

The microdiffusion method published by Brouwer and Murphy[1] for analysis of acid volatile sulphide (AVS-chiefly FeS) has been extended to both AVS and FeS_2in a two step process. For the first step (AVS analysis), excellent recoveries (~100%) are obtained for Na_2S, FeS, PbS, CdS, and ZnS provided diffusion times are long enough. Recovery from other insoluble metal sulphides (Ag_2S and HgS) were low, while for CuS were variable. In the second step, recoveries were ~100% for ground, crystalline FeS_2. This work re-emphasises the importance of adding a sufficiently strong reducing agent during AVS determination in sediments to prevent oxidation of $S^{2-}$by Fe^{3+} produced in the acid dissolution of ferric phases. The method is amenable to adoption to different apparatus provided recoveries and reaction times are checked with suitable standards.

Keywords: Acid volatile sulphide; pyrites; sediments; analysis

INTRODUCTION

Acid Volatile Sulphide (AVS) and iron pyrites (FeS_2) are important products of early diagenesis as components in the iron and sulphur cycles[2,3]. Both are important in trace metal partitioning in sediments[4,5]. AVS is the major reservoir for trace metals in polluted sediments, and as such, may affect the acute toxicity of these contaminants to some animals in sediments[5,6].

Methods for the analysis of AVS and FeS_2 traditionally utilise the production of H_2S through addition of acid and reducing agents to the sample, sparging with N_2 to a trapping solution and determination of sulphide in the trapping solu-

* Corresponding author. Fax No.: +64–7–8560151. E-mail: b.williamson@niwa.cri.nz
† Present address, Perkin-Elmer (NZ) Ltd., PO Box 107–077, Auckland, New Zealand
‡ Present address, Fletcher Building, 816 Gt South Rd, Penrose, Auckland, New Zealand

tion[7–9]. The methods are somewhat constrained by the apparatus, which would typically consist of 4 reactors and allow 12–16 determinations of either AVS or FeS_2 per day. In our experience with these methods, we found difficulties with precision and maintaining 100% trapping efficiency. The interest in AVS influence on acute toxicity of trace metals has led to the promulgation of a method for AVS and simultaneously extractable metal[10]. This method uses 1M HCl for both H_2S purge-and-trap and metal extraction.

Recently, a microdiffusion method for AVS analysis has been developed which allows simplification and miniaturisation of procedures[1]. The original principles and practicalities of abietic distillation or microdiffusion were reviewed by Conway[11].

We describe a microdiffusion method for AVS and pyrites based on published N_2 purge-and-trap procedures, combined in a simple two-step process. We test its efficiency in sulphide analysis of amorphous and crystalline metal sulphides, and describe interferences inherent in AVS determination. Because the procedure is amenable to adoption with a wide variety of apparatus we also describe results from different apparatus, and the precautions necessary in the design of microdiffusion apparatus.

EXPERIMENTAL

Microdiffusion Apparatus

The basic apparatus consists of a sealable reaction vessel fitted with a plastic tube as receiver. Sulphide is converted to H_2S in the reaction vessel and allowed to diffuse through the air-space to a trapping solution held in the receiver. To prevent any oxidation during method development, all manipulations are carried out in an oxygen-free nitrogen-filled glove bag until such time as each reaction vessel was sealed. This step was subsequently found to be unnecessary for AVS determination, but we retained it for FeS_2 analysis to prevent the oxidation of the Cr^{2+} reagent solution.

The acid solution used to liberate the sulphide from AVS is 10% $SnCl_2$in 6M HCl[9], while from FeS_2 is 1M $CrCl_2$ and conc. HCl. $CrCl_2$ solution is prepared from $CrCl_3$ solution by reduction on a zinc amalgam column as described by Canfield et al.[8]. The trapping solution used is 1 M NaOH (for iodimetric determination) or SAOB II antioxidant buffer (for ion-selective electrode determination[12]).

The *Flask Method* is suitable for relatively small sample numbers and large samples. The apparatus consisted of a pyrex conical flask (250 ml) as a reaction vessel and a polyethylene centrifuge tube (50 ml) as receiver. The centrifuge tube is a snug fit into the neck of the flask, and is held in position by its cap. Eight holes, about 2 mm in diameter, were drilled into the centrifuge tube, so when the apparatus was assembled, they were positioned 1 cm from the flask-tube seal.

The wet sample (typically 1–10 g) is weighed into the flask and dry weight determined separately. The trapping vessels are filled with 10.00 ml of 1 M NaOH. De-aerated 10% $SnCl_2$in 6M HCl (50 ml) is added to the flask, along with a magnetic flea. The centrifuge tube is fitted into the flask and the neck sealed with parafilm. The apparatus is then gently mixed for the desired time, (routinely for 24 hours). After that time, the trapping solution is removed by pipette and the sulphide determined by titration or sulphide ion-selective electrode. After AVS determination, the trapping vessels are refilled with 10.00 ml of 1 M NaOH, and the apparatus replaced in the glove bag under oxygen free N_2. $CrCl_2$ solution (40 ml), followed by conc. HCl (20 ml) are added to the flask. The procedure then follows that described above. We could routinely process up to 8 samples for both AVS and FeS_2, which require about 4 hours of operator time over 3 days.

The *Vial Method* is more suited for relatively large sample numbers and small samples and is routinely used in our laboratory. The simpler apparatus utilised a 30 ml glass vial, similar to that described by Brouwer and Murphy[1]. A 7 ml glass tube is used as receiver. The wet sample is weighed into the vial in the laboratory (typically 0.1–0.5 g); dry weights are determined separately. (During method development, vials and trapping tubes were placed in an oxygen-free atmosphere, but this step was later found to be unnecessary). SAOB II (2 ml) is placed in the trapping tubes, which in turn are placed in the vials. De-aerated 10% $SnCl_2$ in 6M HCl (2 ml) is added carefully down the inside wall of the vial, which is then capped. The apparatus is then placed on a shaking table for 17 hours at 100 rpm. After that time, the apparatus is placed in an oxygen-free atmosphere, the trapping tube is removed from the vial and capped and stored for analysis. Another trapping tube containing fresh SAOB II is placed in the vial. $CrCl_2$ solution (2 ml), followed by conc. HCl (2 ml) is added to the vial. The vial is capped again and shaken for a further 17 hours. The sulphide concentration in both trapping solutions is determined by sulphide ion-selective electrode. We routinely process up to 50 samples, which require about 5 hours of operator time spread over 2 days for AVS analysis, or 9 hours of operator time spread over 3 days for both AVS and FeS_2 analysis.

Sulphide samples

Sodium sulphide solutions are prepared from $Na_2S.9H_2O$ and standardised using the iodimetric method[13]. Standards are made from a saturated Na_2S stock solution. An intermediate standard (1:100 dilution) is first prepared in deaerated water, which gives a concentration of between 22–28 mM. This is diluted as appropriate.

Freshly precipitated metal sulphides were prepared in the reaction vessel as follows. Equimolar (23 mM) solutions of Na_2S, $FeSO_4$, $Pb(NO_3)_2$, $ZnSO_4$, $Cd(NO_3)_2$, $Hg(NO_3)_2$, $AgNO_3$, $Cu(NO_3)_2$ were prepared and degassed with nitrogen. In each experiment, the precipitated metal sulphide was prepared with a 20% mole excess of the metal cation, to ensure all sulphide was precipitated. All sulphide solutions or slurries had a final volume of 1 ml in the reaction vessel.

The source of FeS_2 was a massive crystalline lump of pyrite which was finely ground and sieved through a nylon 69 μm sieve and was analysed for total Fe after HNO_3 digestion and for total S by microanalysis. Commercial FeS (99.9% pure Aldrich Chemical Company), elemental sulphur (BDH Ltd) and CuS (May & Baker Ltd) were used as supplied.

Shallow sediment samples were collected from a number of estuaries around Auckland, New Zealand. All sediments were muddy in texture, strongly bioturbated with many macropores, and showed strong mottling from mixed redox conditions. Upon returning to the laboratory, the samples were mixed gently until they assumed a homogeneous appearance, then immediately frozen until analysis.

Analysis of sulphide

The concentration of sulphide present in the trapping solution is measured iodimetrically or by ion-selective sulphide electrode. Samples for ion-selective electrode analysis were preserved and measured in a disodium ethylenediamine tetra-acetic acid/NaOH/ascorbic acid buffer (SAOB II)[12]. Concentrations are estimated from standard calibration curves and checked by standard addition. The intermediate solution (saturated Na_2S diluted 1:100) is diluted 10, 100 and 1000 times to the same SAOB II concentration as the trapping solutions. Samples outside this range are diluted with SAOB II as required. The iodimetric method used a slight variation of the method given in "Standard Methods"[13]. An amount of iodine solution deemed to be an excess over the amount of sulphide present is transferred to a conical flask. 6M HCl (4 ml) was then added and the volume made up to about 20 ml with water, before adding the trapping solu-

tion under the surface. If the colour disappeared on the first addition of iodine, the analysis is repeated with more iodine. The solution is then back-titrated with $Na_2S_2O_3$ solution, with starch solution as indicator. Blanks are determined using the 1 M NaOH solution.

For quality assurance, four Na_2S standards are run through the microdiffusion apparatus for every 50 sample batch, although $SnCl_2$ addition is omitted in these standards.

Recovery should be 100 ± 5% for standards >1 μmole. Blank determinations are unnecessary. However, if plastic receiving vessels are used, it is important to treat them to remove absorbed H_2S by soaking in 10% HNO_3 or equivalent, otherwise H_2S carry-over may occur between runs, which may give significant blanks.

RESULTS AND DISCUSSION

Flask method

The rate of diffusion measured by the increase in sulphide concentration in the trapping solution was evaluated for Na_2S solutions and FeS (both freshly precipitated and commercial samples). Diffusion was essentially complete in 24 hours (Figure 1), except for the commercial FeS which took 3 days to reach 92% recovery. Stirring increased the rate of diffusion compared to unstirred solutions. Longer reaction times are suitable, e.g., over weekends, and there may be a significant increase in recovery if the sample contains crystalline forms of FeS. Volume loss from the trapping solution was measurable, but less than 0.1 ml per day.

Table I summarises the recovery for a variety of sulphides and elemental sulphur. For 5 or more replicates the method was reasonably precise (Standard Deviation (SD) <5). The method was effective for sulphide in solution and for amorphous iron, zinc and lead sulphides. Iron pyrites and elemental sulphur did not release sulphide under the reaction conditions for AVS determination (Table I). $SnCl_2$is included in the acid solution to reduce Fe(III) and prevent it oxidising sulphide in solution[9]. Recoveries for sediments without $SnCl_2$ added were low, typically <50% of those with $SnCl_2$ (Table I).

After reaction with $CrCl_2$ solutions, FeS_2 produced recoveries of 102% (Table I). This recovery was based on the purity as determined from total sulphur.

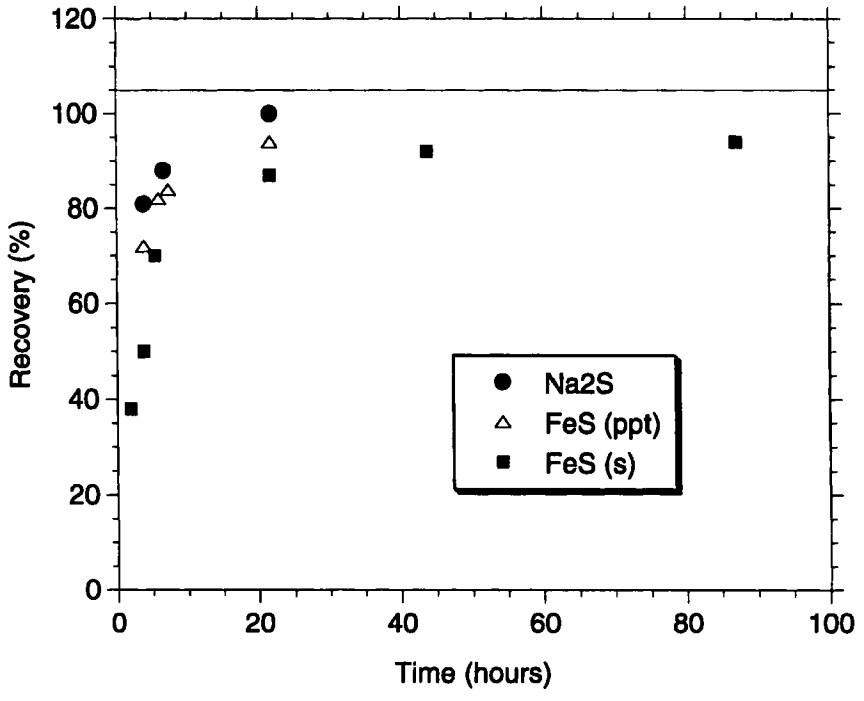

FIGURE 1 Recovery (%) of sulphide from Na_2S and FeS as a function of diffusion time for the flask method

TABLE I Recoveries of sulphide from test phases for the flask method

Sulphur Phase	*S (μmoles)*	*n*	*Recovery ± SD (%)*
Step 1 AVS method			
Na_2S	166	5	102.3 ± 1.3
$Na_2S + Fe^{3+}$ (6.6mmoles)	166	5	47 ± 10
FeS (precipitated)	105	10	94.8 ± 1.9
FeS (precipitated)	16	5	99.2 ± 2.4
ZnS (precipitated)	105	10	88.9 ± 3.2
PbS (precipitated)	105	5	94.6 ± 2.9
FeS_2	1700	5	0.33 ± 0.3
Elemental S	1600	5	2.1 ± 0.3
Commercial FeS	1100	5	80 ± 3
Step 2 FcS_2 method			
FeS_2	840	5	102 ± 0.5
Elemental S	1600	5	1.9 ± 0.3

Vial Method

A variety of different sizes and shapes were tried. Key attributes were a relatively wide bottom to reduce depth of releasing solution, but not too wide that the acid solution splashed into the trapping solution. The results presented here refer to the 30 ml glass vial described in the method section.

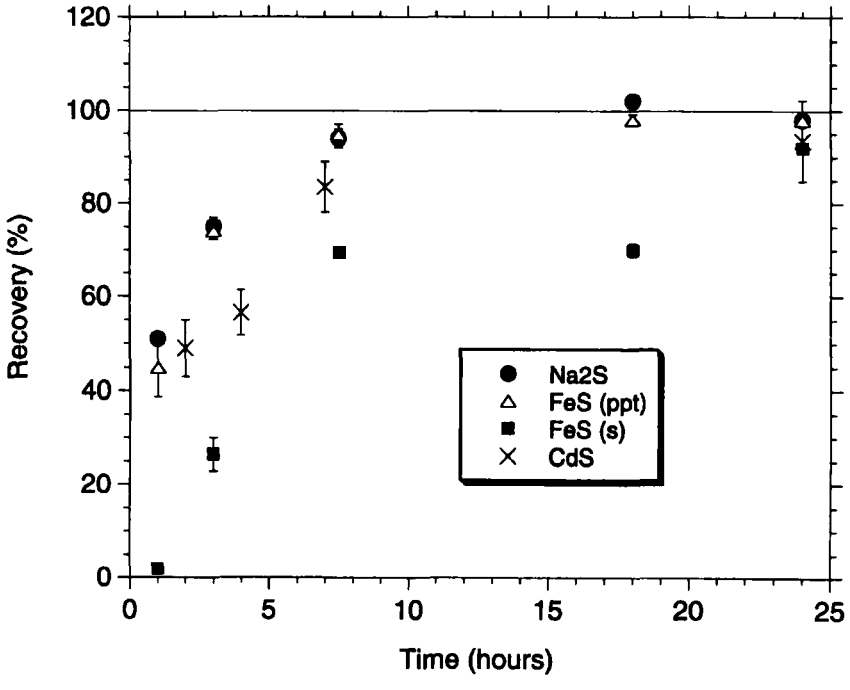

FIGURE 2 Recovery (%) of sulphide from Na_2S, freshly precipitated and crystalline FeS, and CdS as a function of diffusion time for the vial method. Error bars are 1 standard deviation

The time taken for distillation to be 100% complete for Na_2S solutions was initially found to be highly variable, ranging from 2 hours to just over 8 hours. The reason for this variation is no doubt the rates of diffusion in the releasing solution and head space, and it was clear that procedures (addition of acid, shaking speed, configuration of apparatus) must be controlled carefully and that time trials be carried out to characterise procedure and apparatus. As with the flask method, rates of diffusion of freshly precipitated FeS were similar to Na_2S, while rates for crystalline FeS were slower (Figure 2). We finalised on diffusion times of 24 hours because this conveniently fitted into the laboratory schedule and because of the slower reactivity of other metal sulphides (see later). Brouwer and Mur-

phy[1] recommended 1 hour for their smaller microdiffusion apparatus (they used a 20 ml scintillation tube). Their recovery of 93.8 ± 6.7% for Na_2S standards suggests that 1 hour is just sufficient for Na_2S solutions. Our experience suggests longer diffusion times are necessary for 100% recovery of AVS from sediment samples.

Detection limits for the method were better than 0.08 μmoles sulphide (Table II), which is less than the AVS concentrations we encounter in our work in estuarine sediments (> 0.7 μmoles[14]). Higher detection limits quoted in other studies (e.g., Allen et al.[10] may be partly due to oxidation of S^{2-} by Fe (III) as described in the following.

TABLE II Recoveries of sulphide from Na_2S for the vial method (n=3)

S (μmoles)	*Recovery (%)*	*SD*
17.60	96.7	1.6
1.76	99.3	2.8
0.172	105.6	6.1
0.086	98.3	5.9

Our studies showed a strong effect from the presence of an oxidising agent derived from the sediment, because the effect is removed upon addition of sufficient $SnCl_2$. This is illustrated in Figure 3 by the recovery of sulphide from 3 estuarine sediment samples in the presence of variable amounts of $SnCl_2$. Fe (III) has been identified as the likely agent, oxidising H_2S after its formation by the acid[9]. The 3 estuarine sediments contained 10–27 mg Fe/g of amorphous iron hydrous oxides, which would dissolve under the analysis conditions. The longer times for microdiffusion recommended in our method compared with N_2 purge and trap would probably increase the extent of oxidation. The effect of Fe(III) oxidation may explain the <100% (50–90%) recoveries from Na_2S spikes added to sediments in the SEM-AVS method[15]. One down-side of adding $SnCl_2$is its ability to also reduce other forms of sulphur species in solution. These include thiosulphate, but not sulphate or sulphur (Tables I and III). This is not usually a problem with sediment analysis because concentrations of thiosulphate are very low compared with AVS, but it may be a problem when analysts are trying to measure traces of AVS in predominantly aerobic sediments. For example, a thiosulphate concentration of 80 μmoles/l $S_2O_3^{2-}$ (9 mg/l) in interstitial water would give an apparent AVS concentration of about 0.04 μm in 0.5 g of wet sediment. We first noted the problem in the analysis of Na_2S solutions, where greater than 100% recovery was obtained. Oxidation of the Na_2S stock solution no doubt pro-

duced thiosulphate, which was reduced by $SnCl_2$ in the diffusion apparatus to produce H_2S. The apparent >100% recovery was due to the calibration of the electrode with the standards prepared from the same Na_2S solutions directly made up into the SAOB II buffer. The electrode is insensitive to thiosulphate. The effect is further complicated by the fact that the thiosulphate so-formed also reduces iodine in the standardisation procedure, resulting in an over-estimation of the actual sulphide concentration in the Na_2S standards. It is therefore important to prepare fresh Na_2S stock solutions on a weekly basis and standards on a daily basis.

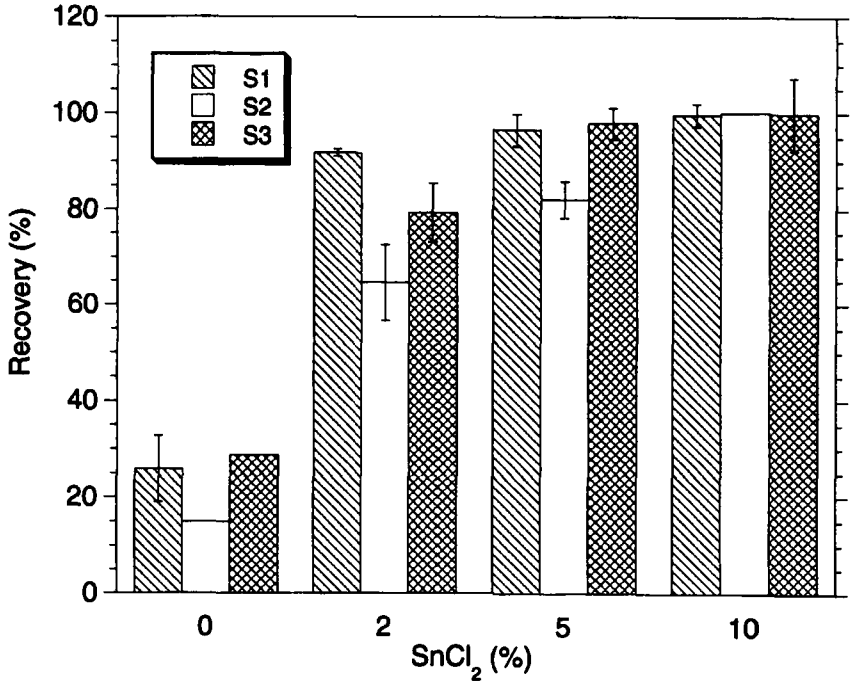

FIGURE 3 Effect of $SnCl_2$ on AVS recovery (%) from 3 estuarine sediments. Error bars are 1 standard deviation

Freshly prepared CdS reacts much more slowly than does Na_2S or FeS, but decomposition and diffusion were essentially complete after 24 hours (Figure 2, Table IV). Similar results were obtained for PbS and ZnS (Tables I and IV). HgS and Ag_2S gave very low recoveries (Table IV), consistent with their low acid solubility[10]. CuS gave mixed results; freshly precipitated copper sulphide gave low recoveries, while commercial CuS gave 88% recovery after 24 hours (Table IV). Allen et al.[10] and Brumbaugh and Arms[15] found good recovery for Ni,

Pb, Zn and Cd, and very low recoveries for CuS. In our method, the addition of $SnCl_2$ was necessary before high recoveries were obtained for the commercial CuS (Table IV). It therefore appears that the longer diffusion times are needed if Zn, Cd, Pb, probably Ni and possibly Cu sulphides are to be included in the AVS analysis by our method and we finalised on 24 hours. The difference between freshly precipitated copper sulphide and crystalline CuS may be the morphology or oxidation state of the freshly precipitated copper sulphide.

TABLE III Recoveries of sulphur from sulphide, thiosulphate and sulphate solutions (2 replicates)

Sample	*$SnCl_2$*	*S (μmoles)*	*Recovery (%) ± SD*
Na_2S	no	26.5	100 ± 1
Na_2S fresh standard	yes	26.5	102.9 ± 1
Na_2S old standards	yes	variable	107–120
$Na_2S_2O_3$	no	14.2	13.2 ± 0.8
$Na_2S_2O_3$	yes	14.2	98 ± 0.5
Na_2SO_4	no	10	0.1
Na_2SO_4	yes	10	0.1

TABLE IV Recoveries from different sulphide phases for the vial method (2 replicates). pt= precipitated

Phase	*S (μmoles)*	*Recovery (%) ± SD*
Commercial FeS	60–240	92 ± 1
CdS (pt)	23.4	93.4 ± 8.7
PbS (pt)	23.4	96 ± 0.6
ZnS (pt)	23.4	100.8 ± 5.6
CuS (pt) + $SnCl_2$	23.4	3.2
CuS (pt) – $SnCl_2$	23.4	0.0
Commercial CuS + $SnCl_2$	150	87.6 ± 3.5
Commercial CuS – $SnCl_2$	150	0.00
Ag_2S (pt)	23.4	0.00
HgS (pt)	23.4	0.9
FeS_2 + $CrCl_2$	28.4	103 ± 9

Sediment sample variability for AVS and FeS_2 on replicated samples is typically 3–14% RSD (Table V). The variability is probably controlled mostly by the ability to prepare a homogeneous sample for replicate analysis. The variation

between replicates analysed on different days is quite good (Table V), despite freezing and thawing the samples between analysis days. Rates of diffusion of AVS were quite rapid, but where sediments had been doped with Cd^{2+}, so that a significant proportion or all of the AVS is CdS, then diffusion was much slower[16] (and see Figure 2).

The effect of variation in sample mass is also shown in Figure 4. There is a strong effect at short diffusion times; with greater mass producing lower recoveries. Longer times reduced the variation in AVS determined from different sample masses. The greater sensitivity to sample mass identified by Brouwer and Murphy[1] is probably due to the short diffusion times (1 hour) of their method. In our method, sample wet weights of 0.5 g or less are recommended.

TABLE V Variability of replicated analysis on 4 estuarine samples. Samples 2–4 were also analysed on different days. Sample size = 0.2 g sediment

Sample	*Analysis*	*Day*	*n*	*S (μmoles/g)*	*RSD (%)*
1	AVS	1	12	11.9	14
	FeS_2	1	4	44.5	4.4
2	AVS	1	4	38.9	2.8
	AVS	2	2	39.6	2.8
3	AVS	1	3	5.4	12.9
	AVS	2	3	6.8	7.3
4	AVS	1	5	28.4	4.6
	AVS	2	2	33.6	0.03

During the method development all experiments were run in an O_2 free atmosphere. We tested the vial method to see if this precaution was necessary, because it adds considerably to the time and complexity of the procedure. Low Na_2S standards were run under an air atmosphere and without taking any special precautions to exclude air, except when preparing standard solutions. The lowest standard (0.073 μmoles) is nearly 10 times lower than the lowest sulphide content we have found in estuarine sediments[14]. The results in Table VI show that O_2-free conditions were not necessary at these sulphide concentrations. We attribute this to a slow oxidation of H_2S in the acid solution, stability of H_2S in the gaseous phase and in the trapping solution.

The effect of shell material on sulphide recoveries in the vial method was examined because evolution of CO_2 upon addition of acid could result in the loss of H_2S from the vial before it is capped. We added sufficient $CaCO_3$ shell to 0.2 g sediment in vials to make 10% shell by weight. The decomposition of the shell material and evolution of CO_2 occurred vigorously over a few seconds after

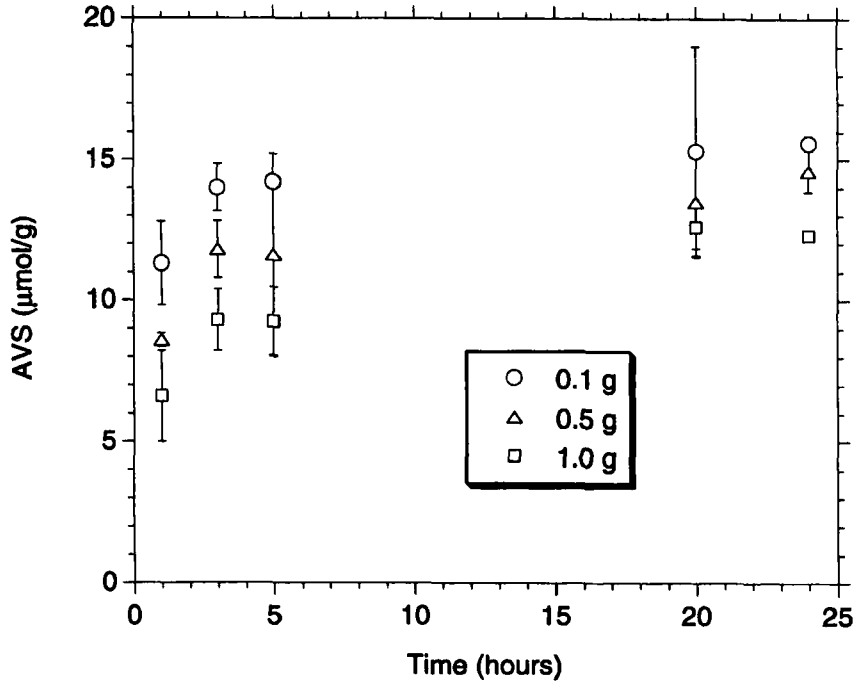

FIGURE 4 Effect of sediment mass on AVS recovery. Error bars are 1 standard deviation

the addition of the acid. The volume of CO_2 released from this amount of shell is 4.5 ml, about one sixth of the volume of the vial. For this sediment sample, AVS was 11.2±0.7 µmoles/g without shell and 10.9±0.6 µmoles/g with shell. The lack of effect of the CO_2 evolution may be due to the relatively rapid release of CO_2 compared with H_2S and/or because the volume of CO_2 released is insufficient to effectively flush the vial headspace. The muddy sediment samples usually analysed in our laboratory do not visibly effervesce upon addition of acid, so we do not anticipate any problem in routine application of the method.

TABLE VI Recovery of sulphide under nitrogen and under air

Sample	*Mean recovery ±SD (%)*	
	Under N_2	*Under air*
0.73 µmoles	97 ± 3.4	95 ± 1.4
0.073 µmoles	98 ± 4.5	98 ± 5.5

CONCLUSIONS

Analysis of sediment AVS and pyrites by two-step microdiffusion is possible with a variety of apparatus. Excellent recoveries (~100%) for Na_2S, FeS, PbS, CdS, ZnS and FeS_2 are obtained provided diffusion times are long enough. A strong reducing agent ($SnCl_2$) must be added to sediment samples to prevent oxidation of released sulphide by Fe (III) as suggested by Morse & Cornwell[9]. Other existing methods e.g., AVS-SEM purge-and-trap, will need to check for interference by Fe (III), because they may be underestimating AVS. We use the method to measure AVS and FeS_2 rather than for determining AVS-SEM ratios, and do not offer it as an alternative to the AVS-SEM method, which is an operationally-defined empirical method with a long history of use and application. The method is reproducible with a low relative standard deviation for AVS and FeS_2 in natural samples (typically 3–14%), provided samples are well mixed. The method is amenable to adoption to different apparatus provided recoveries and reaction times are rigorously checked with suitable standards. For speed and efficiency, especially with large numbers of samples, the vial method is recommended. The flask method is suitable for small batches of samples, and simple apparatus, e.g., where the analyst does not have recourse to a sulphide ISE or spectrophotometer.

References

[1] H. Brouwer and T. P. Murphy, *Environ. Toxicol. Chem.*, **13**, 1273–1275 (1994).
[2] Berner, R. A., *Principles of Sediment Geochemistry.* (McGraw-Hill, New York, 1971), 240pp.
[3] W. Stumm and J. J. Morgan, *Aquatic Chemistry.* (John Wiley & Sons, Brisbane, 1981), 2nd ed., 780pp.
[4] J.W. Morse, *Mar. Chem.*, **46**, 1–6 (1994).
[5] G. T. Ankley, N. A. Thomas, D. M. Di Toro, D. J. Hansen, J. D. Mahony, W. J. Berry, R. C. Swartz, R. A. Hoke, A. W. Garrison, H. E. Allen, C. S. Zarba, *Environ. Manag.*, **18**, 331–337 (1994).
[6] G. T. Ankley, E. N. Leonard and V. R. Mattson, *Water Res.*, **28**, 1071–1076 (1994).
[7] J. P. Chanton and C.S. Martens, *Biogeochem.*, **1**, 375–383 (1985).
[8] D. E. Canfield, R. Raiswell, J. T. Westrich, C. M. Reaves and R. A Berner, *Chem. Geol.*, **54**, 149–155 (1986).
[9] J. W. Morse and J. C. Cornwell, *Mar. Chem.*, **22**, 55–69 (1987).
[10] H. E. Allen, G. M. Fu, and B. L. Deng, *Environ. Toxicol. Chem.*, **12**, 1441–1453 (1993).
[11] E.J. Conway, *Microdiffusion analysis and volumetric error* (Crosby Lookwood London, 1962), 2nd ed., 123p.
[12] Orion Corporation, *Instrument Manual Sulphide Ion Electrode* (Orion Corporation Inc, 1978).
[13] American Public Health Association, *Standard methods for the examination of water and wastewater.* (American Public Health Association; American Water Works Association; Water Pollution Control Federation, Washington, DC, 1989) 17th. ed., 1467p.
[14] R. B. Williamson, R. J. Wilcock, B. E. Wise and S. E. Pickmere, *Environ. Toxicol. Chem.*, **18**, 2078–2086 (1999).
[15] W. G. Brumbaugh and J. W. Arms, *Environ. Toxicol. Chem.*, **15**, 282–285 (1996).
[16] T. H. DeWitt, C. W. Hickey, D. J. Morrisey, D. S. Roper, R. B. Williamson, L. V. Van Dam and E.K. Williams. *Environ. Toxicol. Chem.*, **18**, 1026–1037 (1999).