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An evaluation of wet chemical methods for quantifying sulfur fractions in freshwater wetland peat¹

Abstract—The specificity and efficiency of procedures for fractionating total S into inorganic and organic constituents were evaluated by analyzing a series of known standards. Acid volatilization was specific for FeS. Chromium reduction recovered over 90% of the S from FeS, S⁰, and FeS₂. Acetone extraction followed by chromium reduction of the filtrate was specific for S⁰. Hydriodic acid reduction recovered >90% of the S from FeS, SO₄²⁻, and *p*-nitrophenyl sulfate, an organic aryl ester sulfate analog. The Zn-HCl reduction procedure is of questionable value, only partially recovering S from SO₄²⁻, S⁰, and FeS₂. None of these procedures affected L-methionine. Analyses were performed on both moist and oven-dried peat from Big Run Bog, West Virginia. Oven-drying of peat samples increased estimates of ester sulfate S and SO₄²⁻-S and decreased estimates of carbon-bonded S, which was calculated by difference.

Biogeochemical transformations involving sulfur are of interest from a variety of perspectives. In both salt marshes and coastal marine sediments, the cycling of sulfur and carbon is linked by the process of bacterial sulfate reduction, which may account for a considerable proportion of organic matter mineralization (Howarth and Teal 1979; Skyring et al. 1978; Jørgensen 1982). Sulfur diagenesis in both freshwater and marine peats bears on the origin of sulfur in coal (Casagrande et al. 1977; Altschuler et al. 1983). In addition, the phenomenon of acid precipitation has led to the investigation of sulfur cycling in freshwater wetland (Gorham et al. 1984), freshwater lake (Schindler et al. 1982; Kelly et al. 1982;

Mitchell et al. 1984), terrestrial (Johnson et al. 1982; Fitzgerald et al. 1982; McFee 1983), and agronomic (Olson 1983; Mortvedt 1983) ecosystems.

Many wet chemical procedures have been developed to fractionate the total sulfur pool in sediments, soils, and peat into its inorganic and organic constituent compounds. We here evaluate procedures for the determination of acid-volatile sulfur, Zn-HCl-reducible sulfur, acetone-soluble sulfur, chromium-reducible sulfur, and hydriodic-acid-reducible sulfur and report quantitative measurements of the specificity and efficiency of each procedure for various inorganic and organic sulfur compounds. The effects of oven-drying peat before analysis vs. analyzing moist samples are also evaluated using *Sphagnum*- and *Polytrichum*-derived peat from Big Run Bog, West Virginia. The distribution of sulfur compounds in Big Run Bog peat is compared to data for Okefenokee Swamp and Florida Everglades peats.

Each of the wet chemical procedures involved the reduction of S to H₂S in a Johnson-Nishita apparatus and trapping the evolved H₂S in Zn-acetate solutions. Trapped sulfide was quantified by iodometric titration (Am. Public Health Assoc. 1981) with a 0.025 N iodine solution and 0.0125 N Na₂S₂O₃ titrant. Iodometric titration produced consistently lower coefficients of variation than colorimetric determination of sulfide with methylene blue (Gilboa-Garber 1971).

Our distillation apparatus incorporated slight modifications of that used by Johnson

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and Nishita (1952). Oxygen, water, and organic compounds were removed from the incoming N_2 gas stream by an in-line, disposable gas purifier (Oxyclear, VWR Scientific 32574). The reaction flask was a 250-ml, round-bottom, three-neck flask, with an N_2 inlet via a bleed tube inserted in one neck and the central neck connected to a condenser. The third neck was fitted with a stopcock to allow introduction of liquid solutions to the flask with a minimum of O_2 . No gas washing column was used between the condenser and the two sequential Zn-acetate traps (50 ml of 5% Zn acetate plus 1 drop of antifoaming agent). We consistently recovered >95% of the H_2S in the first of the two sequential traps.

The material to be analyzed was added to the reaction flask along with 5 ml of either ethanol or distilled, deionized, deoxygenated water (for HI reduction), and the system was purged with N_2 at a bubbling rate in the Zn-acetate traps of 1–2 bubbles per second for at least 10 min before the introduction of additional reagents. For each analysis, the duration of the distillation step was determined by running time-courses with peat samples, changing the Zn-acetate traps at 15-min intervals.

Acid-volatile sulfur (AVS) was determined by introducing 8 ml of 12 N HCl (concd) into the reaction flask. Heat was applied after 10 min, the material was brought to boiling, and after 45 min the traps were removed and the sulfide titrated.

The procedure for determining Zn-HCl-reducible sulfur (Zn-HCl S) was similar to that for AVS except that after adding 8 ml of 12 N HCl, we added 3 g of Zn metal through the side neck of the reaction flask (Aspiras et al. 1972). We were cautious during the addition of the Zn metal since a vigorous effervescence sometimes resulted. Heat was applied after 10 min and the material boiled for 1 h before removal of the traps and titration.

Chromium-reducible sulfur (Cr^{2+} -reducible S) was determined by passing a 1 M solution of $CrCl_3 \cdot 6H_2O$ in 0.5 M HCl through a Jones reductor column containing Zn amalgamated with Hg, thereby reducing Cr^{3+} to Cr^{2+} (Zhabina and Volkov 1978; Howarth and Jørgensen 1984). Sixteen

milliliters of the reduced chromium solution was introduced into the reaction flask, heat was applied after 10 min, and the material treated as above.

Acetone-soluble sulfur (acetone-soluble S) was determined by an overnight (12–16 h) extraction of the material to be analyzed (0.5 g if peat) in 20 ml of histological grade acetone. The extraction flask was covered with Parafilm and placed on a rotary shaker. The mixture was filtered and rinsed with additional acetone to produce a final filtrate volume of 25 ml. The entire filtrate volume was subjected to Cr^{2+} reduction as described above (Zhabina and Volkov 1978).

Hydriodic-acid-reducible sulfur (HI-reducible S) required the preparation of a reducing solution containing 50% hypophosphorous acid, 90% formic acid, and hydriodic acid in a 4 : 2 : 1 proportion (Freney 1961). Eight milliliters of this solution, which was prepared fresh daily, was introduced into the reaction flask. After 10 min, heat was applied and the material was boiled for 90 min before removing the traps and titrating.

Each of the above procedures was carried out on the following sulfur standards: Na_2SO_4 , ACS Certified, Fisher Scientific, S-421; $Na_2S_2O_3 \cdot 5H_2O$, ACS Certified, Fisher Scientific S-445; $Na_2S_2O_4$, Fisher Scientific S-310; elemental S, USP sublimed flowers of sulfur, J. T. Baker, 4088; FeS_2 , iron pyrites, granular, 85% minimum through 50 mesh, MCB Reagents, IX0260-1; FeS, granular, Fisher Scientific, I-150; *para*-nitrophenyl sulfate (PNPS), potassium salt, crystalline, Sigma Chemicals, N-3877; and L-methionine, Sigma grade, Sigma Chemicals, M-9625. PNPS was used as an inorganic analog of an organic aryl ester sulfate (King and Klug 1980).

For each analysis, extraction/distillation efficiencies were determined by adding about 50 μ mol S as one of the above standard compounds to each of triplicate reaction flasks and following the procedures above. In addition, a surface (0–20 cm) *Sphagnum* peat sample collected from Big Run Bog, West Virginia (Wieder 1985), was oven-dried, ground to pass a 2-mm mesh, and analyzed in triplicate by each of the five procedures. Either 50 mg (for HI reduction)

or 500 mg (for all other analyses) of peat was added to a reaction flask.

To verify extraction efficiencies, we combined between 20 and 150 μmol of S in each of the six inorganic S compounds with 500-mg peat samples (50 mg for HI reduction) and analyzed three replicate mixtures by each of the five extraction/distillation procedures. Expected recoveries of S calculated from the recoveries obtained by analysis of the individual S compounds and of peat were compared to actual recoveries.

To evaluate the effects of oven-drying peat before analysis as opposed to analyzing moist peat samples, we applied the five analytical procedures to nine surface (0–20 cm) peat samples from Big Run Bog that had been oven-dried at 50°C. The only slight modification of the above protocols was that the analyses for AVS and Cr^{2+} -reducible S were done sequentially on the same peat subsample in the same flask. In addition, water-soluble SO_4^{2-} -S was determined by mixing 0.5 g of peat with 20 ml of distilled deionized water for 1 h and filtering. This same peat sample was then extracted with a 5.3 mM PO_4^{3-} solution (Johnson and Henderson 1979). Sulfate in both the water-soluble and phosphate-extractable filtrates was analyzed by ion chromatography. These two sulfate fractions were summed and are reported here simply as SO_4^{2-} -S.

A second set of 12 surface peat samples from Big Run Bog was not oven-dried but was dewatered in a Reeburgh (1967) press with the filtrate volume measured and retained for SO_4^{2-} analysis. Sulfate in this filtrate was considered as contributing to the SO_4^{2-} -S fraction. Four subsamples of the moist peat were analyzed: one was oven-dried at 50°C to obtain a moist mass to dry mass conversion factor, ground, and retained for total S determination; one was subjected to the procedure for AVS; one was subjected to Cr^{2+} reduction; and one was sequentially extracted for water-soluble SO_4^{2-} -S, PO_4^{3-} -extractable SO_4^{2-} -S, elemental S, and HI-reducible S, as described above.

For all of these peat samples, total S was determined on a Leco IR 32 total S determinator by personnel of the West Virginia Geological and Economic Survey. All data

were converted to a per gram dry mass basis.

Analysis for AVS recovered an average $\geq 90\%$ of the S present as either $\text{S}_2\text{O}_4^{2-}$ or FeS (Table 1). An average of 38 and 5% of the S present as $\text{S}_2\text{O}_3^{2-}$ and FeS_2 was recovered as AVS. Recoveries were $< 1.5\%$ for SO_4^{2-} , S^0 , PNPS, and methionine. Our results differ somewhat from those of Aspiras et al. (1972) who recovered 100, 26, and 0% of the S from known standards of Na_2S , $\text{Na}_2\text{S}_2\text{O}_3$, and $\text{Na}_2\text{S}_2\text{O}_4$. Although we recovered only 92% of the S from FeS, our FeS standard had a lot analysis of 95.4% FeS, 2.4% FeS_3O_4 , 1.2% Fe, and 0.3% FeS_2 (Fisher Scientific pers. comm.). Thus, the recovery values reported in Table 1 are probably slight underestimates. The 5% of the FeS_2 recovered as AVS may well have reflected FeS contamination of our pyrite standard, which had a guaranteed purity of only 85%. The determination of S present as FeS by HCl volatilization is reasonable, if we assume that intermediate oxidation forms of S, like $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_2\text{O}_4^{2-}$, are negligible. In salt marsh systems, soluble sulfides comprise 50–80% of the total soluble reduced sulfur, with $\text{S}_2\text{O}_3^{2-}$ -S as the only other major contributor (Howarth et al. 1983). If this is also true for freshwater wetland systems, then within the top 40 cm of Big Run Bog peat, where H_2S concentration averages 30 $\mu\text{mol liter}^{-1}$, volumetric water content of the peat averages 91% and bulk density of the peat averages 0.07 g dry mass cm^{-3} (Wieder 1982, 1985), $\text{S}_2\text{O}_3^{2-}$ -S concentration should be $< 0.4 \mu\text{mol g}^{-1}$ dry mass. With a mean recovery of 38.2% by HCl volatilization, $\text{S}_2\text{O}_3^{2-}$ would contribute $< 0.15 \mu\text{mol S g}^{-1}$ dry mass.

The addition of Zn metal to the reaction flask (Zn-HCl S) slightly increased the efficiencies of $\text{S}_2\text{O}_4^{2-}$ and FeS determinations and also resulted in $> 90\%$ recovery of S from $\text{S}_2\text{O}_3^{2-}$ (Table 1). However, the liberation of S from SO_4^{2-} , S^0 , and FeS_2 was incomplete. Neither PNPS nor methionine was significantly affected by the Zn-HCl procedure. Our results contrast with those of Aspiras et al. (1972) who obtained 100% recovery of S from Na_2S , S^0 , and $\text{Na}_2\text{S}_2\text{O}_3$, and only 33% recovery of S from $\text{Na}_2\text{S}_2\text{O}_4$. David et al. (1982) assumed that the Zn-

Table 1. Percent recoveries of known amounts of inorganic and organic S compounds by five extraction/distillation procedures.

Procedure	Recovery	Percent recovery of S added as							
		Na ₂ SO ₄	Na ₂ S ₂ O ₃	Na ₂ S ₂ O ₄	S ⁰	FeS ₂	FeS	PNPS	Methionine
AVS	Max	1.3	38.7	95.0	1.6	6.4	94.3	0	0.2
	Min	0.6	38.0	82.3	1.0	4.8	89.1	0	0.2
	Mean	1.1	38.2	90.0	1.4	5.4	92.2	0	0.2
Zn-HCl S	Max	24.0	99.2	98.2	13.1	55.0	99.2	0	0.2
	Min	15.5	95.9	94.4	11.2	28.0	87.3	0	0.2
	Mean	21.1	97.8	96.1	11.9	46.1	93.0	0	0.2
Cr ²⁺ -reducible S	Max	3.5	113.0	100.7	101.3	93.7	96.9	0	4.3
	Min	3.1	87.3	84.9	87.1	91.3	94.1	0	1.5
	Mean	3.3	99.6	93.4	94.4	92.8	95.4	0	2.5
Acetone-soluble S	Max	4.4	3.0	2.4	104.7	3.0	5.4	0	0
	Min	1.1	1.8	1.0	93.6	1.7	1.3	0	0
	Mean	3.0	2.5	1.6	97.6	2.4	3.4	0	0
HI-reducible S	Max	100.0	99.0	98.4	70.0	2.9	101.0	96.0	0
	Min	82.4	85.0	97.6	65.8	1.6	98.0	94.5	0
	Mean	94.1	90.7	98.1	67.9	2.3	100.0	95.4	0

HCl fraction included all inorganic nonsulfate S. Casagrande et al. (1977) called the S liberated by Zn-HCl distillation pyritic S. Given the considerable disagreement about the nature of the Zn-HCl fraction, its utility as an analytical procedure is suspect.

Analysis by Cr²⁺ reduction resulted in recoveries $\geq 93\%$ of the S in all of the inorganic compounds examined except for SO₄²⁻ (Table 1). Neither PNPS nor methionine was affected by the analysis. Cr²⁺ reduction was developed by Zhabina and Volkov (1978) as a method of quantifying pyritic S; we recovered 93% of the S from an FeS₂ standard whose minimum guaranteed purity was 85%. When Cr²⁺ reduction is used to quantify pyritic S, FeS and S⁰ must either be removed first or determined separately and subtracted from the Cr²⁺-reducible S value. Also, thiosulfates, dithionates, and other intermediate oxidation state S compounds must either be assumed to be negligible relative to pyrite or must be removed by rinsing the sample before Cr²⁺ reduction (cf. Howarth and Jørgensen 1984).

Acetone extraction followed by Cr²⁺ reduction of the acetone-soluble fraction was specific for S⁰ and yielded an average of 98% recovery (Table 1). Less than 4% of the S in all other inorganic fractions was recovered by this procedure, and the sulfur

from PNPS and methionine was not detectable. Acetone is both specific and efficient for the removal of S⁰. Other workers have used CHCl₃ (Casagrande et al. 1977) or CS₂ (Howarth and Jørgensen 1984) to extract elemental S.

HI reduction resulted in $>90\%$ recoveries

Table 2. Recoveries of S from *Sphagnum* peat samples to which known amounts of inorganic S compounds had been added. Expected recoveries were calculated from the mean percent recovery values for peat and for each inorganic S compound (Table 1).

Procedure	Replicate	Total added	Expected	Actual	Mean % deviation
			recovery	recovery	
		(μmol S)			
AVS	1	224	96	95	-6.3
	2	247	76	73	
	3	222	57	49	
Zn-HCl S	1	264	136	131	-2.8
	2	273	126	124	
	3	365	159	154	
Cr ²⁺ -reducible S	1	328	291	292	+3.4
	2	283	208	216	
	3	311	270	286	
Acetone-soluble S	1	404	59	64	+3.9
	2	358	174	176	
	3	282	53	60	
HI-reducible S	1	426	313	328	+3.4
	2	350	217	230	
	3	446	279	277	

Table 3. Sulfur fractions (concn in $\mu\text{mol g}^{-1}$ dry mass) in surface peat from Big Run Bog as determined on both oven-dried ($n = 9$) and moist ($n = 12$) samples. Values are means \pm SE. For comparison, data are also shown for freshwater peat from the Okefenokee Swamp (Casagrande et al. 1977; values are the means of the Minnie's Lake and Chesser Prairie sites) and from the Florida Everglades (Altschuler et al. 1983; values are the means of core 2, 20–25 cm, and core 8, 14–19 cm).

	Big Run Bog		Okefenokee	Everglades
	Oven-dried	Moist		
Total S	135.7 \pm 8.4	136.6 \pm 10.2	57.1	261.1
Organic S	116.2 \pm 8.0	116.3 \pm 9.0	54.1	198.4
Carbon-bonded S	56.0 \pm 7.6	85.5 \pm 5.3	39.7	135.9
Ester sulfate S	60.2 \pm 11.9	30.8 \pm 5.3	14.4	62.5
Inorganic S	19.5 \pm 1.4	20.3 \pm 1.6	3.0	62.7
FeS ₂ -S	10.5 \pm 1.1	14.2 \pm 1.4	0.8	—
FeS-S	2.4 \pm 0.6	3.4 \pm 0.4	—	0.2
S ⁰ -S	1.9 \pm 0.4	1.8 \pm 0.3	1.1	—
SO ₄ ²⁻ -S	4.7 \pm 0.4	0.9 \pm 0.1	1.1	54.7

of S from all of the inorganic S compounds except S⁰ (68% recovery) and FeS₂ (2% recovery). An average of 95% of the S was recovered from PNPS, while methionine was unaffected by HI reduction. HI reduction is commonly used to measure organic ester sulfate S, with the attendant assumption that the procedure liberates S from all inorganic S compounds as well (Kowalenko 1978). Our results indicate that this assumption should be modified since HI reduction only partially liberated S from S⁰ and left FeS₂ largely unaffected.

A bulk *Sphagnum* peat sample from Big Run Bog had S concentrations of 1.5 $\mu\text{mol g}^{-1}$ dry mass for AVS, 12.0 $\mu\text{mol g}^{-1}$ for Zn-HCl S, 22.0 for Cr²⁺-reducible S, 2.7 for acetone-soluble S, and 79.0 for HI-reducible S. When known amounts of all of the inorganic S compounds were added to subsamples of this *Sphagnum* peat and the mixtures subjected to the different extraction/distillation procedures, actual S recoveries differed from predicted recoveries on average <7% (Table 2).

Total S in oven-dried and moist peat samples from Big Run Bog was fractionated into its organic and inorganic constituents (Table 3). In both oven-dried and moist peat, ~85% of the total S was present in an organic form. In the oven-dried samples carbon-bonded S and ester sulfate S were about equal in abundance, but in the moist peat samples carbon-bonded S comprised 74% of the organic S. David et al. (1982) obtained similar results for dried vs. moist

mineral soils, attributing the observed effect to the possible conversion of carbon-bonded S to either ester sulfate S or to SO₄²⁻-S during drying.

Sulfate concentration in the oven-dried peat was five times that in the moist peat (Table 3) and corresponding differences in the concentrations of FeS₂-S and FeS-S suggest that reduced S compounds may have been oxidized during oven-drying. Increased SO₄²⁻ concentrations as a result of oven-drying have also been reported for mineral soils (e.g. Freney 1958; Williams 1967; David et al. 1982).

Data from the Okefenokee Swamp (Casagrande et al. 1977) and the Florida Everglades (Altschuler et al. 1983) in Table 3 were obtained from the analysis of dried peat samples. Although the three sites differ considerably in total S concentration, in all sites most of the S (between 76 and 94%) is present in an organic form. For the Okefenokee Swamp and the Everglades, carbon-bonded S was the dominant form of organic S; this was also the case for the moist peat samples for Big Run Bog. Sulfate was the dominant inorganic S form in the Everglades peat, comprising 87% of the inorganic S (Table 3). Sulfate, elemental S, and pyritic S were of about equal abundance in the Okefenokee Swamp peat. In contrast, reduced sulfur forms dominated the inorganic S pool in Big Run Bog peat, especially when moist samples were analyzed.

Although the analytical methods used by Altschuler et al. (1983) were substantially

different from ours, many of the methods used by Casagrande et al. (1977) were similar. Casagrande et al. removed SO_4^{2-} -S (using 0.1 M LiCl) and S^0 -S (using CHCl_3) before dividing their samples and subjecting one subsample to HI reduction and another subsample to the Zn-HCl procedure. Zn-HCl S was called pyrite and was subtracted from HI-reducible S to estimate ester sulfate S. Since AVS was not analyzed, we cannot determine definitively whether the $0.8 \mu\text{mol S g}^{-1}$ dry mass liberated by the Zn-HCl procedure (Table 3) actually represents FeS, pyrite, or both. In any case, it does appear that the concentration of iron sulfides in Big Run Bog peat is greater than in Okefenokee Swamp peat. This difference may be attributable to relatively greater iron availability at Big Run Bog. Relatively high iron concentrations in Big Run Bog peat (avg $176 \mu\text{mol g}^{-1}$ dry mass) reflect the fact that the wetland is really a minerotrophic fen, receiving runoff from the surrounding upland mineral soils (Wieder 1982, 1985).

In the Okefenokee Swamp peat, if in fact the S liberated by the Zn-HCl procedure was mostly or entirely pyrite, not only is the pyrite value an underestimate (cf. Table 1), but also the S should not have been subtracted from the HI-reducible S value to estimate ester sulfate S, since HI reduction does not affect pyrite (Table 1). Thus, the ester sulfate S value in Table 3 should be increased by $0.8 \mu\text{mol g}^{-1}$ dry mass and the carbon-bonded S value decreased by the same amount. For the Okefenokee Swamp data this potential error would be of a relatively small magnitude, resulting in a $<5\%$ change in ester sulfate S and carbon-bonded S concentration estimates. But in other types of peat, such an error could have major implications. For example, Casagrande et al. (1977) also reported data for mangrove peat with values for ester sulfate S, pyrite S, and carbon-bonded S of 381, 231, and $762 \mu\text{mol g}^{-1}$ dry mass. If we follow the above reasoning, then if all of the Zn-HCl S were indeed pyrite, it should not have been subtracted from HI-reducible S. Upon recalculation, instead of carbon-bonded S being twice as abundant as ester sulfate S, ester sulfate S would be more abundant than carbon-bonded S (612 and $531 \mu\text{mol g}^{-1}$ dry mass).

Our results and the examples given above illustrate some of the potential problems of interpretation associated with different analytical methods used to fractionate total sulfur in peat. Our finding that the HI reduction procedure only partially liberates S from S^0 and leaves pyrite largely unaffected has particular bearing on the estimation of ester sulfate S. Moreover, since carbon-bonded S is most frequently determined by difference, inherent in its estimation are all of the potential errors involved in the estimation of the inorganic forms of sulfur and of ester sulfate S. In order to assess the role of biogeochemical sulfur cycling in systems with organic peat deposits, the specificity and efficiency of the analytical methods used must be quantitatively evaluated.

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