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DETERMINATION OF DISSOLVED TOTAL SULFUR IN AQUEOUS EXTRACTS AND SEEPAGE WATER OF FOREST SOILS

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Four methods for determining the concentration of dissolved total sulfur (DTS) in aqueous extracts and seepage water of forest soils characterized by elevated amounts of dissolved organic matter are compared using various standards and aqueous extracts: (i) oxidation with NaBrO followed by HI reduction and methylene blue reaction, (ii) direct determination by ICP-OES, analysis by (iii) ICP-OES or (iv) ion chromatography (IC) after H₂O₂/UV oxidation.

The NaBrO oxidation method showed the best recovery for analysis of DTS in standard samples. In most cases, results of the ICP-OES procedures were not significantly different from those of the NaBrO oxidation method, but more precise. The H₂O₂/UV-IC procedure severely underestimated DTS in some standards. For aqueous soil extracts, the NaBrO method and direct determination by ICP-OES showed equal results, irrespective of sample type and S concentration. Due to its excellent analytical and economical features, we recommend the ICP-OES method for routine determination of dissolved total sulfur in seepage water and aqueous soil extracts containing more than 1 mg S/L.

KEY WORDS: Sulfur determination, soil extracts, dissolved total sulfur, dissolved organic sulfur, seepage water.

INTRODUCTION

As a consequence of elevated S deposition to forested areas of Europe and North America during the last decades and its possible effects on nutrient cycling and ecosystem stability, the study of S cycling in forest soils has become a major issue of soil scientific research. Since physico-chemical reactions (SO₄ adsorption/desorption on soil sesquioxides or clay minerals, perhaps also precipitation/dissolution of Al hydroxy sulfate minerals) are of great importance for the retention and remobilization of deposited S in many acidic forest soils, they have been studied intensively, whereas less attention has been paid to biotic processes as microbial synthesis and mineralization of organic S compounds. However, results of recent research¹⁻⁵ suggest that biotic processes seem to dominate S cycling and S retention in soils characterized by low contents of SO₄-adsorbing pedogenic minerals or effective prevention of SO₄ adsorption^{6,7} due to high concentrations of dissolved organic matter (DOM) in subsoil horizons. In these soil ecosystems, the turnover of organic S is of crucial relevance for S retention and

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remobilization^{3,4}. High DOM concentrations are typical for the seepage water of O and A horizons of podzols and other acidic forest soils, particularly after dolomite applications⁸; appreciable concentrations of DOM have also been reported for subsoil horizons of podzols and planosols⁹. It is suggested^{1,2,10} that under these circumstances a significant part of the S flux through the soil is comprised by dissolved organic S (DOS), so that the S flux through soil compartments is underestimated by calculations solely based on SO_4^{2-} concentrations in the seepage water. This problem can be overcome if in addition to SO_4^{2-} concentrations those of DOS in the soil solution are determined. Furthermore, DOS measurements will help to answer to the question, if high S_{org} (particularly ester sulfate) contents in subsoil horizons reported by various researchers^{1,3,5} have to be interpreted as exclusive result of *in situ* biosynthesis¹¹ or if they, at least to some extent, can be explained as the effect of downward transport and subsequent adsorption of water-soluble S_{org} produced in the forest floor and humic topsoil horizons^{2,10,12}.

In scientific literature, there are only few papers referring to DOS concentrations in soil seepage water or aqueous soil extracts^{10,13,14}. In none of them, DOS was measured directly. The only methods of direct DOS analysis would be combining a chromatography, dialysis or electrophoresis procedure with a subsequent DTS determination. The procedures are tedious and expensive; therefore they currently cannot be used as routine analyses for large sample numbers. Thus, in current forest ecosystem research, DOS in soil solution or aqueous soil extracts is calculated as difference between dissolved total S (DTS) and inorganic SO_4 -S, assuming that other inorganic S compounds (*e.g.* HSO_3^- , SO_3^{2-} , HS^- , $\text{S}_2\text{O}_3^{2-}$, S^{2-}) do not comprise significantly to dissolved inorganic S (DIS) in soil solutions. Schoenau and Bettany¹⁰ analyzed DTS using the oxidation technique of Tabatabai and Bremner¹⁵; Vorhoff¹³ used ion chromatography (IC) after oxidizing the sample with H_2O_2 and simultaneous UV irradiation. SO_4 -S was analyzed by ion chromatography¹⁶ in all studies. However, up to now, no well-documented method for DTS determination, which has been tested for efficiency, accuracy, and precision, is available. Hence, the results of all the studies cited above remain somewhat unclear. The main objective of this paper is to compare different methods for DTS determination with regard to the factors (i) analytical precision and accuracy, (ii) determination range, (iii) necessary equipment and (iv) time and cost of the analysis.

MATERIAL AND METHODS

Methods for determination of dissolved total sulfur (DTS)

Oxidation-reduction method of Tabatabai and Bremner The oxidation-reduction method of Tabatabai and Bremner¹⁵ has been developed for determination of total S in plant¹⁷ and soil samples. In a first step, the entire S pool of a sample is completely oxidized to SO_4^{2-} . This step is followed by complete reduction of SO_4^{2-} to H_2S and quantification of the product using a methylene blue reaction¹⁷. The method can be used for liquid samples as well. In our study, dependent on the expected S concentration, 1 mL ($\text{DTS}_{\text{expected}} = 5$ to 10 mg/L), 5 mL ($\text{DTS}_{\text{expected}} = 1$ to 5 mg/L) or 10 mL ($\text{DTS}_{\text{expected}} < 1$ mg/L) of the solution of interest were pipeted in a glass vessel suitable for subsequent combination to a Johnson-Nishita distillation apparatus. After reducing the 5 mL- or 10 mL- samples to a final volume of 1–2 mL by evaporation at 40°C, the samples were

oxidized with a freshly prepared NaBrO solution in a sand bath at 240–260°C and the amount of HI-reducible S analyzed in accordance with Tabatabai and Bremner¹⁵. The method is suitable for reliable determination of S amounts between 10 and 60 µg; using sample volumes between 1 and 10 mL as described above, this corresponds to DTS concentrations in aqueous extracts between 1 and 60 mg/L. However, the range of determinable S concentrations can be extended by either preconcentrating the samples by rotation-evaporation (lower limit) or using smaller sample volumes (upper limit).

Direct DTS determination by ICP-OES The basic principle of the ICP-OES (Inductively Coupled Plasma—Optical Emission Spectrometry) method is the excitation of S atoms in an Ar plasma and the quantification of the resulting emission spectrum at a characteristic wavelength. The intensity of the S emission spectrum is a direct function of S concentration in solution, irrespective of the type of S-containing compound and the oxidation status of the analyzed S atom. The ICP-OES method has been used successfully for S analysis in plant tissue after sample digestion and oxidation with various mixtures of acids and oxidants^{19–21}. It should be suitable for the determination of organic S compounds as well, if matrix and interference effects are excluded. In our study, all samples were analyzed without pretreatment using an Perkin Elmer Optima 3000 apparatus at the S emission line $\lambda = 180.669$ nm in two replicate determinations. Nebulization, viewing height as well as integration time (in a range between 2 and 20 seconds) were optimized automatically by Optima 3000 software. Background correction was carried out at a distance of 0.028 nm on each side of the emission line maximum. The entire optical system of the instrument was purged with N₂ to avoid the effect of O₂ absorption bands in the 170–200 nm region. The limit of S determination with ICP-OES expressed as [blank value + 6 * standard deviation of the blank value] was about 0.4 mg/L; the calibration graph is linear in the range between 1 and 20 mg/L. Thus, samples containing between 1 and 20 mg S/L can be analyzed directly by ICP-OES; the determination range can be extended by preconcentration or dilution.

UV/H₂O₂ oxidation followed by ion chromatography (IC) The presented UV/H₂O₂ oxidation/ion chromatography procedure is a modification of an unpublished method developed at the Institute of Soil Science and Forest Nutrition, University of Freiburg/Germany. It is based on the complete oxidation of DOM (and thus all organic S compounds in solution, as well) by the attack of hydroxyl radicals which are produced when H₂O₂ is irradiated with UV.

25 mL of the sample were pipeted into a 100-mL quartz beaker. After addition of 1 mL of 30% H₂O₂ (reagent-grade) the sample was UV-irradiated ($\lambda = 254$ nm) using a N 90 apparatus (Konrad Benda Comp., Wiesloch, Germany) until it was completely evaporated, at least for 24 h. The remaining salt efflorescence was transferred to a 25-mL glass flask by repeated washings with deionized water (two times 5 mL), 0.5 M HCl (100 µL), and again deionized water (two times 5 mL). Finally the flask was filled up to 25 mL volume with deionized water. One aliquot of each sample was analyzed for SO₄ by ion chromatography¹⁶ using a DIONEX 2020i ion chromatograph and a AS4A column. The analytical range of S determination with IC is the same as given for the ICP-OES method.

UV/H₂O₂ oxidation followed by ICP-OES analysis Another aliquot of each UV/H₂O₂-oxidized sample was analyzed by ICP-OES using the method described before for direct DTS determination.

Determination of DTS in standard substances

In a first study, the described methods were tested for their efficiency, accuracy, and precision using various organic standard substances with different stabilities and type of S bonds (Table 1). For calibration, one inorganic standard (Na_2SO_4) was used. All standards were prepared from reagent-grade substances in two concentrations (2 and 20 mg S/L), reflecting typical concentrations in aqueous extracts and seepage water of mineral soils and forest floor layers. With each method, five replicates of each standard were analyzed.

Determination of DTS in aqueous soil extracts

In a second study, the methods were compared using water extracts of soils characterized by different levels of DOM. Water extracts are supposed to represent the chemical composition and structure of DOM in soil seepage water quite well. Because it would have been very difficult to achieve the large amount of seepage water needed in our study by sampling with suction cups, water extracts were preferred to soil-seepage water. In order to test the general applicability of the methods, our investigation was carried out with samples from three forest soil types derived from different parent material (Table 2). For all soils, samples of the forest floor (Oh layer) and humic A horizons (0–5 cm or 0–10 cm depth) were analyzed. Additionally, the Bh horizon (40–60 cm depth) of the Haplic Podzol Schluchsee, which is characterized by high contents of organic matter as documented by the C_{org} values in Table 2 and by high DOC concentrations in the seepage water⁹ was included in our investigation. Hence, the methods could be tested for different DOS levels. With each method, five replicates of each water extract were analyzed.

The water extracts were achieved by shaking air-dried, sieved (< 2 mm) mineral soil or forest floor material for 18 h with deionized water in weight proportions of 1:10 (forest floor) and 1:5 (mineral soil) with an end-over-end shaker, subsequent centrifugation and membrane filtration (0.45 μm cellulose acetate filters; Schleicher and Schuell Comp.).

Statistical analysis

The results of five replicate DTS analyses performed with each method for the various standard samples and soil extracts were tested for significant differences by one-factorial analysis of variance combined with a Tukey HSD test (statistical software package SPSS for Windows; Vers. 6.1; procedure one-way ANOVA).

Table 1 Standard substances used for comparison of the methods.

<i>Substance</i>	<i>Formula</i>	<i>Type of S bond</i>
L-methionine	$\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$	C-bonded S (aliphatic)
L-cysteine	$\text{C}_3\text{H}_7\text{NO}_2\text{S}$	C-bonded S (aliphatic)
Sulfo salicylic acid	$\text{C}_7\text{H}_6\text{O}_5\text{S} \cdot 2 \text{H}_2\text{O}$	C-bonded S (aliphatic)
Thiophene-2-carboxylic acid	$\text{C}_5\text{H}_4\text{O}_2\text{S}$	C-bonded S (aromatic)
Sodium dodecyl sulfate	$\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$	ester sulfate
Sodium sulfate	Na_2SO_4	inorganic sulfate

Table 2 Chemical parameters of the soil samples used for method comparison.

Sample	Soil type/ parent material	Depth/Horizon	C_{org} [$mg\ g^{-1}$]	S_{org-1} [$\mu g\ g^{-1}$]	BS^a [%]	pH ($CaCl_2$)
Höglwald	Orthic Luvisol/ tertiary sediments covered with loess	Oh	318.5	1824	28.4	2.9
		0–5 cm/Aeh	28.7	266	7.5	3.3
Villingen	Dystric Cambisol/ triassic sediments (sandstone with clay layers)	Oh	457.5	1849	16.8	2.9
		0–10 cm/Ah	57.2	340	6.6	2.9
Schluchsee	Haplic Podzol granite	Oh	339.5	1791	24.4	3.0
		0–10 cm/Aeh-Ahe 40–60 cm/Bhs	66.1 27.3	481 180	5.5 4.5	3.0 4.3

BS: Base saturation: $\sum (Ca^{2+} + Mg^{2+} + Na^+ + K^+) / CEC * 100$

RESULTS AND DISCUSSION

DTS determination in standard samples

With the Tabatabai and Bremner method, for all standard samples, between 94 and 104% of the given S concentration were determined; no significant effect of the S concentration level or the type of organic compound was noticeable (Table 3). The precision, referred as coefficient of variation c_v , always was about 2% (exception: thiophene-2-carboxylic acid: 4 to 5%). The results indicate that not only aliphatic C-S bonds, but also those in aromatic ring structures seem to get quantitatively disrupted during the oxidation procedure. However, the somewhat lower precision of the method for thiophene-2-carboxylic acid compared to the other compounds may reflect the greater stability of the aromatic C-S bond to an oxidative breakdown.

A direct measurement of the standard samples with ICP-OES without pretreatment gave good recoveries (95 to 101%) at the 20 mg S/L level for all substances, except thiophene-2-carboxylic acid; in most cases the precision was excellent ($c_v \ll 1\%$). For S concentrations of 2 mg/L, recoveries were good as well; however, with a c_v between 1.2 and 4.4%, the precision was lower. This holds as well for the inorganic standard Na_2SO_4 used for calibration ($c_v \approx 3\%$) and thus can be explained as a consequence of the fact that the determination limit of this method is not far below 2 mg/L²⁰. The results achieved with the ICP-OES method were not significantly different from those achieved by the Tabatabai and Bremner procedure except for sulfo salicylic acid at the 2 ppm level and for thiophene-2-carboxylic acid. The inefficiency of the ICP-OES procedure for the determination of S bound in thiophene-2-carboxylic acid (only 70% recovery) cannot be due to the stability of the aromatic C-S bonds, because at temperatures of 4000 to 6000° K in the Ar plasma even very stable organic bonds should be cleaved and hence S atoms should completely exist in the atomic state. We suggest changes in aspiration or nebulization as consequence of the rather hydrophobic type of compound (thiophene-2-carboxylic acid is one of the very few water-soluble compounds containing S as part of an aromatic ring) to be the reason of the low S recovery observed. This explanation is supported by the fact that the recovery increased, when the thiophene-2-carboxylic acid concentration was lowered to 2 mg S/L.

If the standard samples were subjected to a photochemical oxidation procedure (H_2O_2 /UV treatment) prior to the ICP-OES determination, the S recovery was slightly

Table 3 Efficiency and precision of different methods for determination of total dissolved sulfur in standard samples. Significantly different ($p < 0.05$) arithmetic mean values of five replicate analyses of each sample performed with each method are indicated by different letters behind the values.

Substance	Tabatabai & Bremner method			ICP-OES without oxidation			ICP-OES after H_2O_2/UV oxidation			IC after H_2O_2/UV oxidation			
	real DTS concentration [mg/L]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]
L-methionine	2.00	2.01 ^a	100	2.2	2.01 ^a	100	1.2	1.91 ^a	96	2.9	0.15 ^b	7	48.3
L-cysteine	2.00	1.92 ^a	96	2.4	2.02 ^a	101	2.4	1.92 ^a	96	5.4	1.60 ^b	80	14.0
sulfo salicylic acid	2.00	1.96 ^a	98	2.3	2.17 ^b	108	2.7	1.95 ^a	98	3.3	1.84 ^c	94	5.7
thioph.-2-carb. acid	2.00	1.96 ^a	98	4.1	1.42 ^b	71	4.4	1.88 ^a	94	7.0	1.81 ^a	91	5.4
Na dodecyl sulfate	2.00	1.89 ^a	94	2.4	2.08 ^a	104	3.6	1.97 ^a	99	3.0	2.12 ^a	106	12.6
Na ₂ SO ₄	2.00	2.00 [*]	100 [*]	1.4	2.00 [*]	100 [*]	3.0	2.00 [*]	100 [*]	1.5	2.00 [*]	100 [*]	0.7
L-methionine	20.00	20.82 ^a	104	2.3	20.18 ^{ab}	101	0.2	19.71 ^b	99	1.1	2.68 ^c	13	24.5
L-cysteine	20.00	19.55 ^a	98	2.6	19.42 ^a	97	0.5	19.40 ^a	97	1.7	4.73 ^b	24	1.6
sulfo salicylic acid	20.00	19.89 ^a	99	2.4	19.76 ^a	99	0.3	18.75 ^a	94	1.8	12.84 ^b	64	8.7
thioph.-2-carb. acid	20.00	19.08 ^a	95	4.9	13.30 ^b	67	0.4	17.59 ^c	88	2.8	15.38 ^d	77	1.7
Na dodecyl sulfate	20.00	19.18 ^a	96	2.4	18.95 ^a	95	2.1	19.18 ^a	96	0.6	13.92 ^b	70	1.5
Na ₂ SO ₄	20.00	20.00 [*]	100 [*]	2.2	20.00 [*]	100 [*]	0.6	20.00 [*]	100 [*]	2.2	20.00 [*]	100 [*]	1.8

(*): Na₂SO₄ samples were used for calibration.

decreased to values between 94 and 99% for all substances except thiophene-2-carboxylic acid (Table 3). This might be due to the fact that even repeated washings with water and HCl did not achieve a complete transfer of S from the quartz beakers used for the photochemical oxidation to the ICP-OES autosampler containers, probably because of adsorption of S-bearing compounds at glass or quartz surfaces. As well, a small part of organic S might be lost during the UV/H₂O₂ oxidation procedure as volatile S compound which could have been formed as intermediary product. However, the arithmetic mean values achieved using the H₂O₂/UV-ICP-OES method were not significantly different from those achieved by the Tabatabai & Bremner method, except two samples (thiophene-2-carboxylic acid and methionine, 20 ppm).

For most samples, H₂O₂/UV pretreatment decreased the overall precision of the ICP-OES method. This holds true especially for the 20 mg S/L level, where the c_v increased by a factor of 3 to 6 compared to the direct determination procedure for all samples except Na dodecyl sulfate. The observed deterioration in precision is thought to be a consequence of the addition of two analytical steps (oxidation, transfer). In contrast to the other standard substances, the recovery of thiophene-2-carboxylic acid was greatly enhanced by the oxidation procedure to values of 94% and 88% for the 2 and 20 ppm level, respectively. However, the data show that the photochemical oxidation of that compound was not quantitative. Additionally, the lower precision (c_v : 3 to 7%) indicates a remarkable variation of oxidation efficiency between the single thiophene-2-carboxylic acid sample replicates.

Compared to the other procedures, the combination H₂O₂/UV pretreatment with ion chromatography gave much lower, in most cases significantly different results for almost all standard samples in study (Table 3). The almost complete S recovery with the ICP-OES method after UV/H₂O₂ oxidation excludes a considerable S loss during sample oxidation or transfer. Thus, it is suggested that, especially at the higher concentration level, a significant part of the S bound in organic compounds in a oxidation state lower than +VI was not converted to SO₄²⁻. This finding holds especially true for the amino acids, most distinct for methionine, where only 10% of the S was recovered as SO₄²⁻ after oxidation. Much more, chromatograms of these samples indicated the formation of an unidentified oxidation product.

DTS determination in aqueous soil extracts

The range of DTS concentrations in the aqueous extracts was between 0.9 and 11 mg/L (Table 4). The relative efficiency of the studied methods is presented in Figure 1. For extracts of forest floor horizons, the Tabatabai and Bremner procedure and the ICP-OES method show excellent agreement, whereas slightly lower results were yielded with the UV/H₂O₂ oxidation/ICP-OES method. The UV/H₂O₂ oxidation/IC method consistently gave higher, significantly different results compared to the other methods. For extracts of mineral soil samples, in most cases fairly equal recoveries were achieved with all methods (Figure 1). However, an increasing underestimation of DTS with the UV/H₂O₂ oxidation/ICP-OES procedure compared to the other methods can be noticed, as the S concentration in the sample decreases. For the sample Schluchsee 0–10 cm, higher S contents were measured with the ICP-OES and the UV/H₂O₂ oxidation/IC methods than with the Tabatabai and Bremner procedure. As indicated by the high coefficient of variation of the latter method (Table 4), this result is probably due to an underestimation of DTS by the Tabatabai and Bremner method in some of the five sample replicates. As shown by the c_v values (Table 4), which always are lower than 6% irrespective of the

Table 4 Efficiency and precision of different methods for determination of total dissolved sulfur in aqueous soil extracts. Significantly different ($p < 0.05$) arithmetic mean values of five replicate analyses of each sample performed with each method are indicated by different letters behind the values.

Sample	Tabatabai & Bremner method			ICP-OES without oxidation			ICP-OES after H_2O_2 /UV oxidation			IC after H_2O_2 /UV oxidation			
	DIS (dissolved SO_4^{2-} S) (IC analysis) [mg/L]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]	measured DTS concentration [mg/L]	recovery [%]	c_v [%]
Höglwald Oh	5.74	9.32 ^{ab}	100*	4.0	9.53 ^a	102	2.1	8.94 ^b	96	2.5	11.36 ^c	122	2.8
Schluchsee Oh	5.12	7.80 ^a	100*	2.1	7.78 ^a	100	2.5	7.00 ^b	90	1.8	9.03 ^c	116	3.0
Villingen Oh	9.22	10.76 ^{ab}	100*	4.5	11.23 ^a	104	0.5	10.43 ^b	97	1.0	13.18 ^c	122	3.0
Höglwald 0–5 cm	2.88	4.65 ^c	100*	2.5	4.91 ^b	105	2.3	4.16 ^c	89	2.8	4.83 ^{ab}	104	2.1
Schluchsee 0–10 cm	3.92	5.22 ^{ab}	100*	13.9	5.89 ^a	113	5.7	4.79 ^b	92	4.1	5.69 ^a	109	5.5
Villingen 0–10 cm	3.24	4.91 ^{ab}	100*	2.4	5.37 ^a	109	1.8	4.17 ^c	85	7.7	4.62 ^{bc}	94	13.5
Schluchsee 40–60 cm	0.80	0.93 ^c	100*	3.6	0.91 ^c	99	4.2	0.58 ^b	63	6.9	0.97 ^a	104	4.2

(*Results obtained using the Tabatabai and Bremner method set as 100% recovery for comparison reasons.)

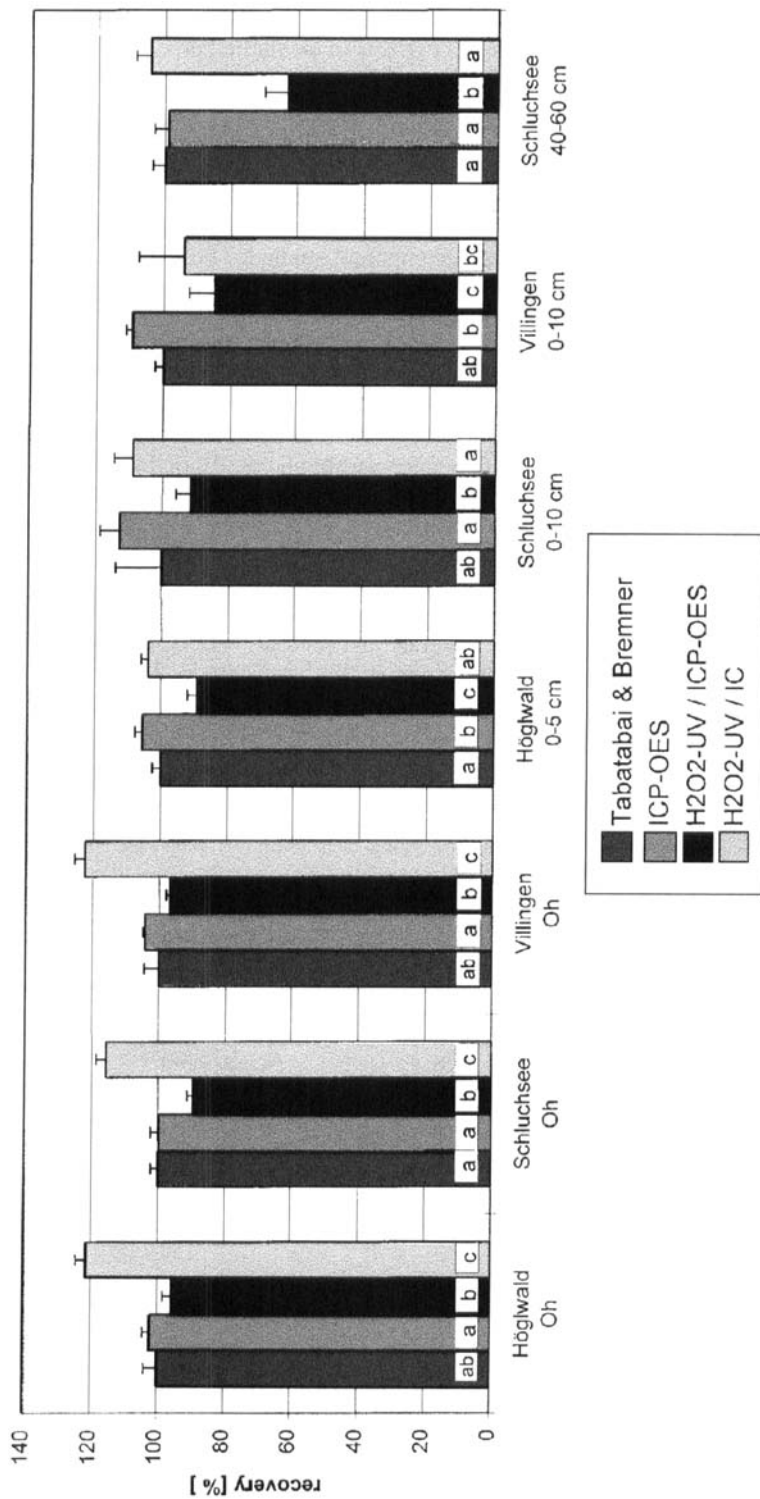


Figure 1 Recovery of dissolved total sulfur in aqueous soil extracts with the different methods in study (Tabatabai and Bremner method = 100%). Significantly different ($p < 0.05$) arithmetic mean values of five replicate analyses of each sample performed with each method are indicated by different letters in the bars.

level of S concentration, the ICP-OES method has the best precision regarding the determination of DTS in aqueous soil extracts of all studied procedures.

CONCLUSIONS

Our recovery experiments with standard substances (Table 3) demonstrate that the Tabatabai and Bremner method is most accurate in determining dissolved total sulfur (DTS) originating from any organic compound studied. The ICP-OES method seems to underestimate DTS, if it consists of compounds containing S in aromatic ring structures; the H_2O_2/UV oxidation/IC procedure obviously fails to determine amino acid S quantitatively. However, DTS in aqueous soil extracts was analyzed with satisfactory results by all methods in study, regardless of the contribution of organical S compounds to DTS, which varied for the aqueous extracts of the studied soils between 15 and 40% (Table 4). This finding implies that neither water-soluble compounds containing S in aromatic ring structures like thiophene-2-carboxylic acid nor free S-containing amino acids seem to contribute significantly to dissolved S in soil extracts, at least for the investigated samples taken from a variety of acidic forest soil types and different soil horizons. Rather, DOS in aqueous soil extracts as well as in humic¹⁰ or fulvic acid of mineral forest soil horizons¹² seem to consist primarily of ester sulfates. Direct DTS determination in standard samples of water-soluble organic compounds and in aqueous soil extracts by ICP-OES is very accurate and precise; with respect to the required time and cost it beats all other procedures in study by far (Table 5). Therefore we recommend the ICP-OES method for routine determination of DTS in aqueous soil extracts and soil solution samples containing more than 1 mg DTS/L. The Tabatabai and Bremner

Table 5 Comprehensive comparison of the investigated methods for determination of total S in standard samples and aqueous soil extracts

	<i>Tabatabai & Bremner method</i>	<i>ICP-OES without oxidation</i>	<i>ICP-OES after H_2O_2/UV oxidation</i>	<i>IC after H_2O_2/UV oxidation</i>
Recovery [%]	Standards: 94–104	Standards: 95–108 (Thioph.carb. acid: 67) Extracts: 99–113*	Standards: 94–99 (Thioph.carb.acid: 88) Extracts: 63–97*	Standards: 7–106 Extracts: 94–122*
Precision (c) [%]	Standards: 2.2–4.9 Extracts: 2.1–13.9	Standard: 0.2–3.6 (Thioph.carb.acid: 4.4) Extracts: 0.5–5.7	Standards: 0.6–5.4 (Thioph.carb.acid: 7.0) Extracts: 1.0–7.7	Standards: 1.5–48.3 Extracts: 2.1–13.5
Time required for analysis of 50 samples	several days	2 hours	several days	several days
Equipment required	-Johnson/Nishita apparatus -spectrophotometer -sand bath	-ICP-OES	-ICP-OES -UV digester	-IC -UV digester
Cost/sample (without equipment)	20 US\$	2 US\$	10 US\$	15 US\$

(*: compared to values achieved using the Tabatabai and Bremner method set as 100%).

procedure is the ideal method for special investigations on few samples, especially if aromatic S compounds are likely to comprise significantly to DTS or if a further fractionation of DTS into the fractions carbon-bonded S and ester sulfate S is required. In contrast to the other methods presented, the Tabatabai and Bremner method can be used for S determination in non-aqueous soil extracts as well²².

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