

# Determination of Selected Sulphur Speciation Forms in Fresh Water Lakes and Bottom Sediments

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*Received: March 3, 2001*

*Accepted: April 9, 2001*

## Abstract

Analytical procedures for the determination of selected speciation forms of sulphur have been proposed. The method for conversion of sulphur sols into homogeneous solutions allowing simultaneous determination of sulphur either in model solutions or in environmental samples has been described. The methods for determination of sulphur sols, elemental sulphur, soluble and insoluble sulphides, sulphates and total sulphur have been optimized. Selected speciation forms of sulphur were determined in the same samples of water and bottom sediments from the eutrophic lakes Lipno and Kiekrz, lying close to Poznan. The speciation analysis proposed is based on the catalytic, chromatographic, ion-selective methods and absorption spectrometry. The concentrations of the speciation forms of sulphur determined ranged from micrograms to milligrams per litre.

**Keywords:** speciation, sulphur forms, freshwater lakes, bottom sediments

## Introduction

In the waters of lakes and their bottom sediments, there are very many different sulphur compounds. These compounds have a considerable impact on the natural environment, and the sulphur cycle in the ecosystem of naturally occurring water bodies has been described in the literature. Acid rain, caused by large SO<sub>2</sub> emissions and over-used chemical fertilizers, are the main causes of exceeding safe limits of inorganic sulphur compound concentrations in the natural environment of waters and bottom sediments of lakes, rivers and freshwater reservoirs [1]. A reduction of organic compounds of sulphur and sulphates by some bacterial strains to sulphur salts, elemental sulphur and hydrogen sulphide is also a source of bottom sediment pollution by inorganic sulphur compounds. The solubility of sulphur in organic solvents is

often very close to the solubility of alkanes. Consequently, during ecological disasters involving hydrocarbons, considerable amounts of various, often-toxic sulphur compounds enter the soils, waters and bottom sediments. Among factors, the presence of the following compounds was noted and determined: SO<sub>4</sub><sup>2-</sup>, S<sub>elemental</sub>, S<sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, CS<sub>2</sub>, COS, CH<sub>3</sub>-S-CH<sub>3</sub>, CH<sub>3</sub>-S-S-CH<sub>3</sub>, CH<sub>3</sub>-S-C<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SH, including trisulphides, mercaptans and thiophenes in the bottom sediments of freshwater reservoirs [2] as well as sediments of arctic lakes of considerable salinity [3]. Due to a marked toxicity of the majority of the above compounds and their influence on the sulphur cycle of the ecosystem of naturally occurring waters, there should be a continuous monitoring of compounds found in environmental samples. A monitoring of all types of waters and sediments has been attempted, which allows for an optimal evaluation of the state of pollution of the natural environment by sulphur compounds.

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Determination of sulphur compounds is usually preceded by mineralization. In order to mineralize organic sulphur compounds, an oxidation method employing wet mineralization (mixing with concentrated acids) or dry mineralization (oxidation in air, in oxygen or by means of solid oxidants). Mineralization of organic sulphur compounds may also be accomplished by means of wet reduction methods (Raney's nickel, metals, acids, electrolytic reduction), as well as dry ones (in a hydrogen atmosphere, metals, pyrolysis in an argon, CO<sub>2</sub> etc. atmosphere). The oxidation product is SO<sub>2</sub> or SO<sub>4</sub><sup>2-</sup>. Most often, in order to determine SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>, the following analytical techniques are employed: microspherometry, X-ray spectrometry, fluorescent spectrometry, ionic chromatography, atomic absorption, emission spectrometry, ICP and MIP. Reduction methods are usually based on H<sub>2</sub>S emission. In order to determine H<sub>2</sub>S, the most often used methods include chromatography, spectrometry as well as titration and ionically selective ones.

The literature is dominated by papers concerned with the determination of most often one type of sulphur compound in bottom sediments. Ripl and Michel determine sulphates and total sulphur content [3], Hordijk et al. - total sulphur content [4] Heim, et al. - elementary sulphur [5], Dunette et al. - H<sub>2</sub>S [6], and Davison et al. - sulphites [7].

There is no reference in the available literature to complete analyses of sulphur compounds and analyses of sulphur speciation forms in the bottom sediments of lakes and rivers [8]. Regarding samples of sediments and waters, the literature does not describe determinations of sulphur concentrations in the form of sols - only qualitative analyses confirming the presence of colloidal sulphur in waters and bottom sediments.

The purpose of this research is to develop a method for transforming a sulphur sol into a homogenous solution, developing a method of determining sulphur sols in model solutions and environmental samples of waters and bottom sediments as well as developing methods of determining sulphur sols, elementary sulphur, soluble and insoluble sulphides, sulphates and total sulphur content in bottom sediments and in waters. Samples of bottom sediments were taken in November 1995 and April 1996 from two lakes in the vicinity of Poznan (Lakes: Lipno and Kiekrz). Determinations employing catalytic, chromatographic, ionically selective and AAS methods were used. These techniques were most often preceded by mineralization of samples in a microwave oven or furnace.

## Experimental Procedure

### Apparatus and Instruments

Elektronika 3C microwave oven (Russia) power rating: 550/450/290 W;

Sharp 85 W 1 microwave oven, power rating: 85/295/425/595/850 W;

Milestone MLS 1200 microwave oven (Italy) adjustable power rated to 1200 W;

Specol 10 spectrometer and nephelometric module (Carl Zeiss Jena, Germany);

Varian Spectra A 20 Plus atomic absorption spectrophotometer (AAS);

Specord UV VIS spectrophotometer (Carl Zeiss Jena, Germany);

Specord M 40 spectrophotometer (Carl Zeiss Jena, Germany);

DU 7500 spectrophotometer (Carl Zeiss Jena, Germany);

OK.-102/1 conductivity meter (Radelkis, Hungary) and HACH pH - meter;

Milestone HPS 100/110 100 cm<sup>3</sup> Teflon bombs with rotor (Italy).

### Reagents and Solutions

The following "reagent grade" solvents were employed: methanol, ethanol, propanol, benzene, hexane, heptane, N,N - dimetyloformamide (Gliwice Poland) as well as the following solid "reagent grade" chemicals: NaOH, KOH, NaN<sub>3</sub>, NaNO<sub>2</sub>, crystalline sulphur (Gliwice Poland).

Working standard solutions of the analyte were prepared: sulphur in benzene, in hexane, in heptane - 1 mg/dm<sup>3</sup>, sulphur in methanol, in ethanol, in propanol - 0.1 mg/cm<sup>3</sup>, sulphur in dimetyloformamide 1 mg/dm<sup>3</sup>.

Bases: NaOH and KOH in methanol, ethanol and propanol - 0.01 mol/dm<sup>3</sup>, in formamide and dimetyloformamide, in water 0.1 mol/dm<sup>3</sup>.

Nucleophilic reagents: NaN<sub>3</sub> in dimetyloformamide - 4 i 10 mg/cm<sup>3</sup>, in methanol, ethanol and propanol - 0.4 mg/cm<sup>3</sup>, in water 0.1 mol/dm<sup>3</sup>, NaNO<sub>2</sub> in formamide dimetyloformamide - 4 mg/cm<sup>3</sup>, in methanol, ethanol and propanol - 0.4 mg/cm<sup>3</sup>, in water 8.0 mg/cm<sup>3</sup>.

Other solutions: aqueous solution with a Ba<sup>2+</sup> concentration of 0.5 mg/cm<sup>3</sup>.

All solutions were prepared with deionized water (Millipore).

### Recommended Analytical Procedure

1. *Introducing a sulphur sol into homogenous solution* - method based on its reaction with sodium borohydride:

A 4% solution of NaBH<sub>4</sub> was added to a sulphur sol in a pseudo solution of organic solvent and water. The reduction of sulphur bonds lasted from 1 to 10 min., dependent on the concentration of sulphur the end of the reduction was signaled by the disappearance of the blue hue of the pseudo solution, which gradually became colorless and clear. The reduction products were boron-sulphur compounds, which could then be quantitatively oxidized (25% H<sub>2</sub>O<sub>2</sub>) to sulphates. The excess of undecomposed NaBH<sub>4</sub> was removed by adding 3 mol/dm<sup>3</sup> HCl and heating the sample for several minutes.

- microwave method:

Reduction of sulphur bonds in sols in an aqueous-organic solvent pseudo solution was conducted in 100 cm<sup>3</sup>

Teflon pressure bombs. Apart from the soil, the bomb also contained a nucleophile ( $\text{NaN}_3$ ,  $\text{NaNO}_2$ ) or a basic solution of ( $\text{KOH}$ ,  $\text{NaOH}$ ). The total volume of the sample in the bomb was always  $4 \text{ cm}^3$ . After the bomb was sealed, it was placed in the microwave. Exposure was experimentally determined following a series of experiments for each system. An initial value of 550 W power and a time of 5 min were chosen. Following exposure of the bomb to microwaves, it was cooled with water for 20 minutes.

### 2. Taking samples of bottom sediments

Lake bottom sediment samples were gathered by means of the "Nurek-1" sampling apparatus, capable of gathering  $500 \text{ cm}^3$  of sediment and able to work at a depth of up to 50 meters. In order to avoid changes in the chemical content and properties of sediment samples, the container and samples was filled so that there was no air bubble beneath the stopper, and further to later analytical tests, the sample was cooled or frozen. Samples destined for analysis of dissolved components were filtered immediately after sampling, and preservatives were added ( $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$  etc.) to some samples.

### 3. Determination of elementary sulphur in bottom sediments

A sediment sample was placed in a  $100 \text{ cm}^3$  polyethylene container sealed with a perforated cover and frozen for 2 hours. The frozen sample was then dried for approximately 30 hours. After reaching room temperature, the dry sample was placed in a desiccator. The solidified sample block was, within several minutes, pulverized manually in an agate mortar. From this dry sediment, elemental sulphur was extracted with three subsequent portions of hexane or cyclohexane ( $50 \text{ cm}^3$  deaerated with solvent nitrogen), in a mechanical shaker. Three hexane or cyclohexane samples were poured together and the solvents were evaporated under reduced pressure to a volume of several  $\text{cm}^3$ . To this remaining sample was added a  $1 \text{ cm}^3$  solution of  $\text{NaNO}_2$  in DMF ( $4 \text{ mg/cm}^3$ ) and  $19 \text{ cm}^3$  DMF. This was heated until any hexane or cyclohexane was completely removed, thanks to the large difference between the boiling temperature of DMF ( $153^\circ\text{C}$ ). This included, as well, removal of the solvents used for extracting elemental sulphur (hexane -  $68.7^\circ\text{C}$ ; cyclohexane -  $80.7^\circ\text{C}$ ). After cooling, the sample was transferred to four Teflon containers (dividing it into four equal parts) and subjecting them to microwave heating to reduce S-S bonding in the  $\text{S}_8$  ring. To cleave sulphur bonds, the sample was subjected to 5 minutes of a microwave field of 550 W, following which the Teflon bombs were cooled for 20 minutes. The contents of the Teflon containers were poured into a  $25 \text{ cm}^3$  flask and filled up to the mark with DMF. A  $5 \text{ cm}^3$  portion of the solution was removed from the flask, diluted with methanol at a ratio of 1:6 (sample:methanol) and a UV spectrum obtained to confirm complete sulphur bond cleavage. Determination of the sulphur within the sample was performed by the iodo-azidic method in a non-aqueous environment [1].

### 4. Determination of soluble sulphides in bottom sediments [11]

To  $100 \text{ cm}^3$  of a fresh sediment sample was added  $10 \text{ cm}^3$   $0.1 \text{ mol/dm}^3$   $\text{NaOH}$  and shaken for several minutes in a  $250 \text{ cm}^3$  separation flask. The contents were filtered through a medium grade filter and the clear solution transferred (in a "transfer container" without air bubbles) to the laboratory. The sample was transferred to a volumetric flask and filled to the  $50 \text{ cm}^3$  line. To  $5 \text{ cm}^3$  of this mix poured into a conical flask was added as much hydrochloric acid ( $0.3 \text{ M}$ ) as needed to obtain a  $\text{pH}=6.8$ . Sulphides were then determined by Kurzawa's titration method, employing the reaction of azide and iodine [2].

### 5. Determination of volatile sulphides in bottom sediments [11]

To  $10 \text{ cm}^3$  of fresh bottom sediment was added  $2 \text{ cm}^3$  of  $0.1 \text{ mol/dm}^3$   $\text{NaOH}$  and transported without air bubbles to the laboratory. The sample was placed in a glass flask and  $\text{H}_2\text{S}$  was generated by adding  $5\text{-}10 \text{ cm}^3$  of sulphuric acid ( $14.2 \text{ mol/dm}^3$ ). This process was conducted according to a previously developed procedure [3]. The  $\text{H}_2\text{S}$ , thus generated was "transported" by nitrogen flowing into an absorption chamber containing a  $\text{NaOH}$  solution, where  $\text{H}_2\text{S}$  reacted quantitatively with  $\text{NaOH}$ . The sample was then transported to a flask, to which was added an appropriate amount of  $0.3 \text{ mol/dm}^3$   $\text{HCl}$  to obtain a  $\text{pH}=6.8$ ; sulphides were determined by a catalytic method [1].

### 6. Determination of pyritic sulphur in bottom sediments [12]

From the pulverized sediment, according to the procedure from point No.7, a  $100 \text{ mg}$  portion was weighed out and the pyritic sulphur was determined according to an indirect method based on an analysis of iron by means of atomic absorption spectrometry. A selective separation of iron bonded in  $\text{FeS}_2$  was obtained using Begeijn's [4] procedure. Into the sediment sample ( $100 \text{ mg}$ ),  $1 \text{ cm}^3$   $\text{H}_2\text{SO}_4$  (96%) and  $3 \text{ cm}^3$   $\text{HF}$  (48%) was poured. After 1 minute, this was followed by a still hot  $\text{HCl}$  ( $4 \text{ mol/dm}^3$ ) solution to dissolve, within 10-30 minutes, the nonpyritic forms of iron. Following this, the sediment was centrifuged, rinsed three times with  $\text{HCl}$  ( $1 \text{ mol/dm}^3$ ) and the pyritic remains dissolved in nitric acid (68%). In the sample thus prepared, iron was determined by the AAS method and the amount of sulphur was calculated.

### 7. Determination of soluble sulphates in bottom sediments [12]

A  $50 \text{ cm}^3$  sample of fresh sediment was filtered through a hard filter and rinsed with two portions of water ( $25 \text{ cm}^3$ ). The solution was filled to a volume of  $100 \text{ cm}^3$  and the sulphates were precipitated by means of  $\text{BaCl}_2$ . The excess barium was then determined by means of spectrometric emission [5] and the amount of sulphates in the sediment calculated.

### 8. Determination of total sulphur content in bottom sediments [9,10]

The  $1 \text{ cm}^3$  sample of sediment was placed in a Teflon bomb together with  $4 \text{ cm}^3$  of concentrated  $\text{HNO}_3$  and

1 cm<sup>3</sup> 30% H<sub>2</sub>O<sub>2</sub>. The sample was mineralized in a microwave field of 850 W for 10 minutes. Following mineralization, the mixture was cooled and transferred to a conical flask and 1 cm<sup>3</sup> of concentrated HCl was added and heated to remove any unreacted nitric acid. The mixture was then placed in a volumetric flask and filled with water to a volume of 100 cm<sup>3</sup>. Sulphur, as sulphates were determined as in No. 7, above.

#### 9. Determination of conductivity and pH of the filtrates of bottom sediments

Samples of sediments as in No.2, and the electrical conductivity and pH of the filtrate were measured.

#### 10. Sampling the waters of Lakes : Lipno and Kiekrz

Samples were taken with the "Toń-2" apparatus, allowing for 1-5 dm<sup>3</sup> sampling at any depth. Samples were taken up to a depth of 7 m every 1 m - the last sample taken 20 cm above the bottom. Visual analysis did not confirm the presence of a sol in the first four "upper" samples (samples from a depth of 1, 2, 3 and 4 m from the lake surface). Whereas in the samples from depths of 5, 6 and 7 m, a clouding typical of sulphur sols was noted.

#### 11. Determination of sulphur sols in the waters of Lakes: Lipno and Kiekrz [9, 10]

In the samples of waters taken at various depths according to No.2, the presence of a sol was initially confirmed by the nephelometric method at depths of 5, 6 and 7 meters. These same samples were then subjected to the microwave procedure according to No.3 and then, following oxidation of the sulphur to sulphates, the latter being determined indirectly by the AAS [6] method.

#### 12. Determination of sulphur sols in the bottom sediments of Lakes: Lipno and Kiekrz [9, 10]

Determinations were conducted according to procedure A as well as procedure B

##### Procedure A:

The fresh sediment (100 cm<sup>3</sup>) was rinsed with water on an average grade filter allowing soluble sulphides and sulphates as well as sulphur sols to pass through with the filtrate. Elemental sulphur, among others, remains on the filter. BaCl<sub>2</sub> and zinc granules (previously activated by hydrochloric acid) were added to the filtrate. After three hours this filtrate was again filtered through a medium grade filter, leaving only the sulphur sol to pass on to the filtrate. This filtrate was analyzed for sulphur content by the S-S bond cleavage and sulphide determination procedure described in No.5

##### Procedure B:

Following sulphide determination (by the iodo-azide method) and sulphates (by the indirect AAS method) the sum of dissolved sulphides and sulphates and sulphur sols were then determined. These functions were performed in the following order:

- reduction of sulphur sols to sulphides,
- oxidation of sulphides to sulphates,
- determination of sulphate totals.

From the results obtained, the content of colloidal sulphur in the sample was calculated.

## Results and Discussion

In many of the above-described procedures, microwave heating was employed in order to reduce sulphur bonds. Elemental sulphur and sulphur sols were first of all subjected to microwave treatment, since this has been shown to be the most effective and shortest means for a quantitative reduction of S-S bonds. Elemental sulphur is most soluble in non-polar solvents - in carbon disulphide, toluene or benzene, whereas non-polar solvents are completely useless in microwave techniques. Because they are only minimally able to absorb microwaves, there is practically no temperature increase in non-polar solutions during exposure to microwaves. In choosing solvents for tests, the following parameters were of primary importance:

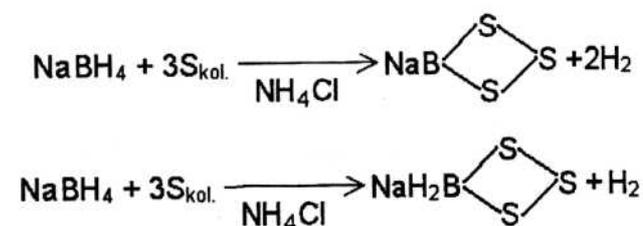
- the solubility of sulphur,
- the coefficient of microwave absorption
- miscibility with water
- solubility of nucleophiles and bases employed in the analysis.

From the point of the view of the above parameters, the best medium would be a solvent characterized by a great solubility of sulphur, allowing for the conduct of analyses over a broad range of concentrations. This should have a high coefficient for absorbing microwave radiation, allowing for a shorter microwave exposure time. It ought to have a high solubility for the nucleophiles and bases employed, critical in cases of large sulphur concentrations. Unlimited miscibility with water would allow the use of techniques for determining sulphur that is characteristic of aqueous systems.

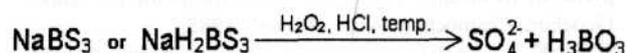
The following solvents were chosen in the analyses:

- alcohols: methanol, ethanol, propanol, iso-propanol, butanol - inexpensive and readily available, good nucleophilic solvents employed in research;
- amides: formamide, N-metyloformamide, N,N-dimetyloformamide - solvents with a large permanent electrical permeability and resultant large coefficients of microwave absorption;
- acetone: an excellent solvent for sulphur;
- toluene, benzene: non-polar aromatic solvents with a high sulphur solubility, used in microwave techniques, always as a pseudo solution with a given polar solvent.

Quantitative oxidation of colloidal sulphur in aqueous-organic pseudo solutions is impossible to achieve without a previous splitting of the S-S bond in the sulphur particle. An initial splitting of the sulphur bond is first necessary. Using borohydride as the reducing agent, the cleavage occurs according to the following reaction:



The reduction products in the above reactions are sodium borohydride sulphides that can be quantitatively oxidized to sulphates:



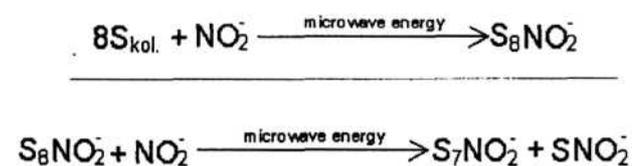
An X-ray analysis of the sodium borohydride sulphide oxidation confirmed that under experimental conditions, sulphates are formed from the sulphide and sulphur. The presence of H<sub>3</sub>BO<sub>3</sub>, apart from the sulphates, as product of the oxidation reaction was confirmed by spectrophotometric analysis with carminic acid. Determination of sulphate concentrations, and consequently, an intermediate determination of sol sulphur content, is based on the precipitation of BaSO<sub>4</sub> and a subsequent determination of excess uncombined barium by emission ASA techniques [13]. Chosen results of sol sulfur concentrations determined by ASA techniques following the transfer of sol sulfur in aqueous-methanol (1:4, v/v) and aqueous-acetone ones (1:3, v/v) and transformation into sulfates in reaction with sodium borohydride are shown in Table 1.

Table 1. Results of sulfur sol determinations following reduction with borohydride and oxidation to sulfates.

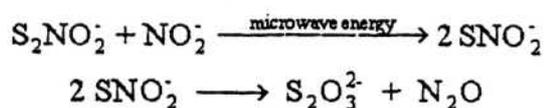
Solvent:	S <sub>colloidal</sub> (µg)	SO <sub>4</sub> <sup>2-</sup> calculated (µg)	SO <sub>4</sub> <sup>2-</sup> determined (µg)
methanol	80	240	233
	150	450	461
acetone	100	300	308
	180	540	544

Reduction of sulfur bonds by means of microwave energy is effective and quantitatively in the presence of a nucleophilic factor, i.e. azide, arsenic, sulfite, nitrite, cyanide or in the presence of bases.

Reduction of S-S bonds by the action of sodium nitrite and microwave energy is shown in the following reaction:



in stages up to



The process of reducing sulfur bonds in sols proceeds like the reduction reaction in elemental sulfur. Reduction of sulfur bonds in the presence of sodium azide and microwave energy is completed with the creation of the SN<sub>3</sub><sup>-</sup> group. Both S<sub>2</sub>O<sub>3</sub><sup>2-</sup> as well as SN<sub>3</sub><sup>-</sup> catalyze the iodazide reaction and have been determined by this technique in an anhydrous environment [14, 15, 16 and 17]. The sulfur in both of these groups may be oxidized to SO<sub>4</sub><sup>2-</sup>, and determined by indirect means through AAS techniques, as well the case in the method based on a reaction with sodium borohydride [13]. The results are presented in Table 2. The sols of sulfurs in aqueous-methanol, ethanol and acetone pseudo solutions were extracted with hexane, heptane and cyclohexane.

Table 2. Results of sulfur sol determinations following microwave heating with NaNO<sub>2</sub> and oxidation to sulfates.

Solvent:	S <sub>colloidal</sub> (µg)	SO <sub>4</sub> <sup>2-</sup> calculated (µg)	SO <sub>4</sub> <sup>2-</sup> determined (µg)
methanol	100	300	311
ethanol	100	300	309
acetone	100	300	305

The results of experiments, however, show that a method based on the extraction of sulfur sols by means of a water immiscible solvent cannot be employed in transferring sulfur into homogenous solutions, since the efficiency of this operation does not exceed 36% and the results are not repeatable. Although a method of transferring sulfur sols into homogenous solutions based on the reaction of sulfur with sodium borohydride and microwave energy give quantitative results, a more useful method is that of microwave reduction due to its simplicity and operation time.

Table 3 shows the result of elemental, colloidal, pyritic and volatile sulfide sulfur analysis, following acidification (mainly FeS) in bottom sediments. The sediment sample was averaged, but it is evident from further analyses that the upper layers of sediments in the lake contain different concentrations of sulfur compounds than do the lower ones. For instance, there is more pyrite in the deepest sediment layer; on the other hand, there is more elemental sulfur on the bottom layer of the lake. This conclusion was confirmed by an intermediate analysis of iron speciation forms in the bottom sediments of Lake Lipno [18]. Table 4 shows the concentrations of colloidal sulfur, soluble sulfides and sulfates. It is evident that sulfides and sulfates are present in all analyzed samples, whereas sulfur sol appears only from a depth of 5 m. and its concentration increases together with depth.

Table 3. Concentration of sulfur compounds determined in the bottom sediments of Lake Lipno measured in November 1995 (mg/dm<sup>3</sup> of wet sediment).

S <sup>0</sup> elemental	S <sub>colloidal</sub>	pyrites	volatile sulfides
0.90 – 1.10	0.40 – 0.50	40.0 – 52.0	320.0 – 370.0

Table 4. Concentration of determined sulfur compounds in the waters of Lake Kiekrz measured in April of 1996 (mg/dm<sup>3</sup>).

Depth [m]	S <sub>colloidal</sub>	Soluble sulfides	Soluble sulfates
1	–	12.5	29.8
3	–	14.0	41.0
5	0.80	15.2	67.5
7	1.10	17.1	92.1

The results obtained according to this procedure are similar to those cited in the literature [19] and obtained by other methods, which is a recommendation of the above analytical procedure. This paper demonstrates advancements in the analysis of speciation forms of sulfur compounds in samples of waters and bottom sediments.

### Acknowledgements

Research financed by the Committee for Scientific Research (KBN 3 T09A 061 10).

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