

Determination of the Reduced Sulfur Species in the Water of Anoxic Basins

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Introduction. Development of anoxia in marine basins leads to formation of hydrogen sulfide and the intermediate reduced sulfur species – thiosulfate, sulfite, zero-valent sulfur and sulfur of polysulfides. Except for thiosulfate, the data on the other reduced species of sulfur in the Black Sea water are scarce. The thiosulfate concentration in the papers of different authors varies from 20 to 40 μM ; and it can be a consequence of hydrogen sulfide oxidation during sampling and analyzing.

Data and methods. The previously proposed (by I. I. Volkov and N. N. Zhabina) method for determining the sulfur reduced species (sulfite + thiosulfate, zero-valent sulfur + sulfur of polysulfides) in the anaerobic basins' water has been re-evaluated and developed. Addition of suspension $\text{Zn}_2(\text{OH})_2\text{CO}_3$ to a seawater sample destructs polysulfides and transfers the elemental sulfur to precipitation. The elemental sulfur, sulfur polysulfides and sulfides are separated from the sum of thiosulfate and sulfite by filtration. To analyze the reduced species of sulfur, we applied their reduction to hydrogen sulfide which is determined spectrophotometrically after its distillation in the argon stream and precipitation as ZnS .

Results. The results of determining the sulfur species were tested by analyzing 2% solutions of NaCl with the introduced contents of thiosulfate (0.5–1.5 μmol), sulfite ($< 1 \mu\text{mol}$), elemental sulfur ($< 1 \mu\text{mol}$) against the background of much higher concentrations of hydrogen sulfide (60 μmol). Such ratios of concentrations of the sulfur reduced species and hydrogen sulfide are found in the Black Sea water.

Discussion and conclusion. It is shown that the proposed method correctly reflects presence of the reduced species of sulfur in the solutions. To analyze the sulfur species, the Niskin bottles are necessarily filled with the inert gas and the samples are filtered in the inert atmosphere. The method for determining the sulfur reduced species is highly sensitive. The detection limit for ($\text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-}$) is 0.03 μM , for ($\text{S}^0 + \text{S}^0$ polysulfide) is 0.02 μM and for sulfide sulfur – 0.01 μM .

Keywords: thiosulfate, sulfite, zero-valent sulfur, polysulfides, hydrogen sulfide, method of determination, detection limit, the Black Sea.

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Introduction

Microbial reduction of sulfates due to the organic matter oxidation leads to the appearance of hydrogen sulfide in anaerobic basins. Apart hydrogen sulfide, other reduced forms of sulfur (the intermediate ones), mainly represented by sulfite

(SO_3^{2-}), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), zero-valent sulfur (S^0) and polysulfides (S_n^{2-}) [1–9] were found in water. The available data for the anaerobic waters of the Black Sea and the Cariaco Basin show that the content of intermediate reduced forms of sulfur can be 2–3 orders of magnitude lower than the content of hydrogen sulfide. Sulfite in the hydrogen sulfide presence in water is reactive with it and turns into thiosulfate [10]. High contents of zero-valent sulfur (S^0) were found in the near Bosphorus area in the Black Sea, where the oxygen-containing waters of the lower Bosphorus current penetrate into the hydrogen sulfide waters of the anaerobic zone of the Black Sea [11]. The accumulation of zero-valent sulfur was also found below the horizon of the hydrogen sulfide disappearance in the upper part of the anaerobic zone [3, 4]. In the presence of hydrogen sulfide and the products of its dissociation in the anaerobic zone, zero-valent sulfur is reactive with them forming polysulfides (S_n^{2-}) [1, 2 and 9].

Content of thiosulfate combined with sulfite was previously determined by titration of excess iodine in the filtrate after precipitation of hydrogen sulfide [12, 13]. Dissolved inorganic forms of sulfur in the Black Sea water were measured applying method of voltammetry [3], and spectrophotometric method after filtration and cyanolysis was used for elemental sulfur [4]. High performance liquid chromatography allowed determining the concentrations of thiosulfate and sulfite separately in the entire water column of the Black Sea for the first time [5]. This method, in one modification or another, is widely used today to study these compounds in anaerobic waters [6–9].

In 1990, a method for determining hydrogen sulfide, the sum of zero-valent sulfur and polysulfides, as well as the sum of thiosulfate and sulfite from a single water sample in the shipboard laboratory was proposed [14, 15]. It can be applied to determine the content of the listed forms of sulfur with a detection limit of about $1 \mu\text{g S}$. The main problem of this method is the inability to determine the sulfite and thiosulfate separately and to divide sulfur of polysulfides from zero-valent sulfur. Despite these shortcomings, the method has a number of undoubted advantages. It has a high sensitivity, can be used in the ship's conditions and obtain data already during a cruise and be used to study the isotopic composition of sulfur of reduced forms [16].

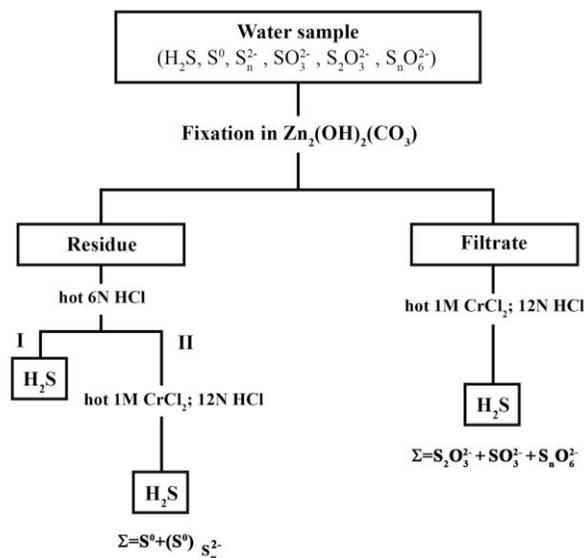


Fig. 1. Scheme of analyzing. Modified version of Fig. 2 from [16, p. 62]

The method provides for the separation of the sulfur forms after precipitation of hydrogen sulfide, polysulfides and zero-valent sulfur with $Zn_2(OH)_2CO_3$ suspension (Fig. 1). Thiosulfate and sulfite remain in the filtrate. In [14, 15], the authors do not present data on the stability of thiosulfate and sulfite in solutions with $Zn_2(OH)_2CO_3$ suspension, the achievement of completeness of the analysis, the limits of detection of sulfur forms in seawater solutions and the reproducibility of the method. There is also no data on the way how the Niskin bottle filled with the air or inert gas when sampling water, as well as the filtration of samples in the air (according to the recommendations of the authors), affect the experiment results. In addition, the degree of complete removal of sulfide from the sample and its effect on the determination of thiosulfate and zero-valent sulfur remained unclear.

The present paper gives the results of the study of reduced forms of sulfur, carried out using our corrected methods for their determination. Changes in the methodology were made based on experimental data. The influence on the results of the analysis of the sulfur forms for sampling water from the Niskin bottle after its filling with the air or argon is considered. Filtration to separate $Zn_2(OH)_2CO_3$ suspension from seawater was carried out in the air and argon atmosphere. The stability of thiosulfate and sulfite in the filtrate of 2% NaCl solutions was studied. It is important for estimating the storage time of samples before analysis. The time required for quantitative analysis and the limits of detection of sulfur forms are specified. Taking into account the experimental data, new results were obtained for the upper part of the anaerobic zone of the Black Sea.

Methods of determination

Data on the reduced species of sulfur in the Black Sea water were obtained at Ashamba-7 and Ashamba-9 stations (July 9 and 13, 2016) with coordinates 44.489°N and 37.869°E to the 320 m depth (potential density was 16.78 kg/m³). Hydrophysical measurements were carried out by *Sea-Bird SBE 19plus* CTD.

Sampling was carried out by *Rosette* complex, equipped with six 4-liter Niskin bottles. The hydrogen sulfide content was determined by the spectrophotometric method [17].

Flow chart of the method for determining the sum of sulfite and thiosulfate, the sum of zero-valent sulfur and sulfur polysulfides, and sulfide is shown in Fig. 1. The method of preparation of reagents and the sequence of operations are described in [14, 15] and have not practically been changed. The seawater volume for the analysis of thiosulfate and sulfite was 200 ml, except for experiments with 2% NaCl solution (60 or 100 ml). The seawater volume for the analysis of zero-valent sulfur was usually about 500 ml. The $Zn_2(OH)_2CO_3$ suspension in the sample was always coagulated during 1 hour. All filtration operations were carried out on the *Millipore* filtration system (the *Durapore* membrane filter, pore size $0.45\ \mu m$ HV and diameter 47 mm). Filtration was carried out either in the air or in a high purity argon atmosphere (99.998%). The filtrate or filter (depending on the type of sulfur form detection) is introduced into a 350 or 500 ml reaction flask filled with argon. After the sample introduction, it is continued to be flushed with argon for 5 minutes. In the case of determining the sum of sulfite and thiosulfate, 15 ml of 12N HCl and 30 ml of 1M $CrCl_2$ are added to the filtrate. The solution is heated to boiling, achieving a constant argon flow (80–90 bubbles in the absorber, which is filled with Zn acetate (20 ml)) (Fig. 2).

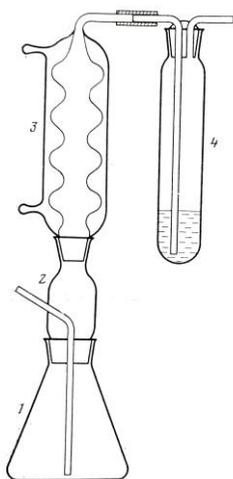


Fig. 2. Device for determining the reduced sulfur species: 1 – reaction flask (300 or 500 ml); 2 – adaptor with a gas-streaming pipe filled with Ar; 3 – backflow condenser; 4 – test-tube absorbing H_2S . Modified version of the figure from [14, p. 583]

The distillation time after the start of boiling is always 30 minutes. This reaction time was found empirically, so the H_2S absorbers are changed every 30 minutes. The first absorber is used to determine the sum of thiosulfate and sulfite (the analysis results are recalculated for thiosulfate only). In the second one, the complete distillation and the magnitude of the blank experiment are determined. Completeness of the analysis (distillation) was estimated by the value of ratio (in %) between introduced and obtained analyte amount in the analysis. In quantitative analysis, it should be close to 100%. The yield depends on the distillation time; it turned out to be close to 100% at a distillation time of 30 minutes. This parameter is checked by varying the distillation time with a change of the absorber after a certain time.

The determination of sulfide and zero-valent sulfur is carried out from a precipitation on a filter, which is placed in a reaction flask flushed with argon (Fig. 2). After placing the sample, 30 ml of 6N HCl is added, the solution with the precipitation is heated to boiling in a stream of argon. Distillation after the heating termination lasts 30 minutes.

. After the change of the first absorber, in which the sulfide is determined, in the second absorber the complete removal of hydrogen sulfide is controlled. Then 30 ml of 1M CrCl₂ are added to the same flask.

After the start of boiling the distillation takes 30 minutes without heating. In the third absorber, the zero-valent sulfur content is obtained, and in the next one, after the change, in the fourth – the complete distillation and the experimental blank. Thus, hydrogen sulfide is absorbed by two absorbers with zinc acetate for 1 hour (30 + 30 min) during the distillation of filtrate. Four absorbers with zinc acetate are necessary for determination of sulfur species in precipitation, the duration is 2 hours. The detection limit is calculated as three standard deviations from the mean value for the blank experiment.

Results and their discussion

Determination of the stability of thiosulfate and sulfite in the filtrate after removal of zinc hydroxocarbonate suspension

To separate the sulfur forms, the Zn₂(OH)₂CO₃ suspension mixed with glycerol is used [13]. Glycerol in the suspension contributes to the sulfite stability in solution. In the method [14, 15], it is assumed that the analysis should be carried out immediately after sampling water from the Niskin bottles, which is not always possible. To determine the stability limits of thiosulfate and sulfite in solution, a series of experiments were carried using 2% NaCl solutions prepared in oxygen-free water. The amount of salt in 2% NaCl solution approximately corresponds to the salt (electrolyte) content in the Black Sea water. A similar concentration of electrolyte in the 2% NaCl solution and in Black Sea water leads to the same conditions for coagulation of zinc hydroxocarbonate. This factor determines the sample filtration time and the amount of colloidal particles entering the filtrate. The use of NaCl solutions instead of seawater is associated with the possible presence of thiosulfate and sulfite in seawater.

After filtration under an argon atmosphere, a series of 100 ml samples (from 5 to 9) were taken from the filtrate. One of the samples was used to determine oxygen by the Winkler Method [18], the rest were analyzed to determine the forms of sulfur at certain time intervals. When storing a thiosulfate solution (concentration from 2.20 to 2.45 μM) in a closed polyethylene bottle at + 4 °C in the dark place for 67 days, the thiosulfate content was not less than 98% of the introduced (Fig. 3). The experiments on the stability of sulfite were similarly carried out. In the first series, the output of sulfite with the initial content of 4.10–4.65 μM ranged from 86% on the first day to 76% after 30 days of the experiment. In the second series with a higher oxygen content, the yield of sulfite was from 82% at the beginning of the experiment to 27% on the 62nd day (Fig. 3). Experiments have shown high stability of thiosulfate in solutions and preservation up to 90% of sulfite for at least three days of storage of solutions.

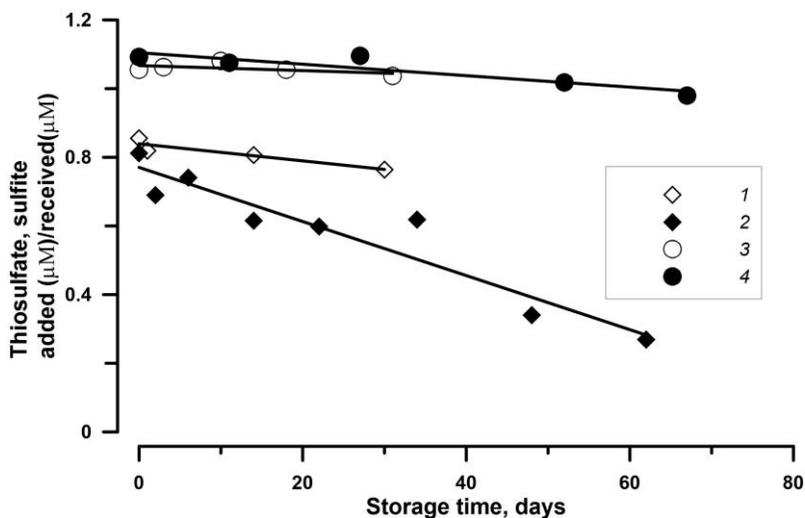


Fig. 3. Change of concentration of Na_2SO_3 ($\sim 5 \mu\text{M}$) (1, 2) and $\text{Na}_2\text{S}_2\text{O}_3$ ($\sim 2.5 \mu\text{M}$) (3, 4) in the filtrate of the 2%-solution of NaCl after filtering the $\text{Zn}_2(\text{OH})_2\text{CO}_3$ suspension at different initial concentrations of the dissolved oxygen: 1 – 58 μM ; 2 – 87 μM ; 3 – 51 μM ; 4 – 135 μM

Determination of thiosulfate in the presence of large amount of hydrogen sulfide

The previously recommended time for analyzing one form of sulfur was 20–25 minutes [14, 15]. We increased the analysis time to 30 minutes based on the experimentally established duration of achieving its completeness. The assessment of the completeness of the determination of sulfur forms, the accuracy and detection limit was carried out in the 2% NaCl solution, adding 10 ml of $\text{Zn}_2(\text{OH})_2\text{CO}_3$ suspension and solutions of zero-valent sulfur, thiosulfate, sulfite and sodium sulfide of known concentrations.

Table 1

Variation of the sulfur species content in the process of the hydrogen sulfide oxidation, $\mu\text{g S}$

Time of the samples preparation (analysis), day	In filtrate				In sediment on the filter				Total content (sulfur yield) with the subtracted blanks
	Absorbers								
	1	2	3	4	1	2	3	4	
	H_2S	blank	S_2O_3	blank	H_2S	blank	S^0	blank	
0(1)	1.3	0.1	9.4	0.4	1869	6.3	2.5	0.3	1875 (1.03)
0(3)	1.0	0.1	9.5	0.7	1868	2.9	2.5	0.2	1877 (1.03)
0(6)	1.6	0.1	11.0	0.7	1894	5.9	1.8	0.2	1901 (1.05)
3(3)	10.9	0.7	120.0	3.4	1602	6.9	9.4	0.3	1731 (0.95)
7(7)	27.9	1.4	305.0	4.4	1083	0.8	12.2	0.4	1420 (0.78)
21(21)	33.3	2.7	451.0	7.0	775	0.3	12.7	0.2	1261 (0.69)
35(35)	26.3	1.9	433.0	4.1	574	0.3	28.9	0.2	1056 (0.58)

Note. The hydrogen sulfide initial content in the 2%-solution of NaCl equals 1818 $\mu\text{g S}$ (56.8 $\mu\text{mol H}_2\text{S}$). Total content is obtained after subtracting the blank experiments.

Separation of sulfur forms by the filtration method can cause a noticeable penetration of sulfides into the filtrate with insufficient coagulation of the $Zn_2(OH)_2CO_3$ suspension. According to the method (Fig. 1), these sulfides are defined as thiosulfate and sulfite. To find out the degree of interfering influence of sulfides, the method of analyzing of sulfur species was applied to the sodium sulfide solution. Samples were taken from the Na_2S solution during its storage in a glass flask at $t = 22\text{ }^\circ C$ for 35 days (Tab. 1). An aliquot (1 ml) with H_2S concentration of about 60 μmol was introduced into 2% $NaCl$ solution. Then the $Zn_2(OH)_2CO_3$ suspension (10 ml) was added to this solution. Before the analysis the samples were stored in the dark place at $t = +4\text{ }^\circ C$. The first sample was filtered every other day, the resulting filtrate ($<0.45\text{ }\mu m$) and the filter with the precipitation were analyzed each using four absorbers. These absorbers were changed every 30 minutes of the hydrogen sulfide distillation. Before the first absorber, 15 ml of 6N HCl was added to the sample, before the third one — 15 ml of 12N HCl and 30 ml of 1M $CrCl_2$. According to the method (Fig. 1), 15 ml of 6N HCl is not added to the filtrate. However, in the experiment we were interested in the amount of hydrogen sulfide that is released without reducing $CrCl_2$ and corresponds to the ZnS fraction that passed through the $0.45\text{ }\mu m$ filter. The second sample was analyzed after 3 days, the third one – after 6 days. In all three samples, only sulfide was identified (absorber 1, filter with precipitation). In the filtrate (absorber 1), the sulfide form of sulfur is lower than the detection limit. This indicates the completeness of the transfer of hydrogen sulfide to the precipitation (absorber 1) (Table 1). As the hydrogen sulfide is oxidizing, the amount of other reduced species of sulfur – the sum of thiosulfates and sulfites (absorber 3, filtrate) and zero-valent sulfur (absorber 3, precipitation) increased. A decrease in the H_2S concentration in the solution leads to a decrease in its trace amounts (absorber 2, precipitation, to $6.9\text{ }\mu g$ of sulfur). These traces of hydrogen sulfide could have been previously interpreted as elemental sulfur.

The appearance of hydrogen sulfide while treating the filtrate with 6N HCl without a reducing agent may be associated with the decomposition of thiosulfate when boiling into hydrogen sulfide and tetrathionate [19]:



T a b l e 2

The influence of the completeness of co-precipitation of sulfide by a suspension of zinc hydroxocarbonate on the determination of trace amounts of thiosulfate in the filtrate

Experiment	Initial composition of the reduced forms of sulfur in the 2%-solution of NaCl	Exposure time of filtrate before analysis, hours	Introduced amount of the thiosulfate sulfur, μg	The obtained amount of sulfur in absorbers, μg				Total amount of the obtained sulfur, μg	Yield, obtained/introduced, %
				1 $\text{S H}_2\text{S}$	2 $\text{S H}_2\text{S}$	3 $\text{S S}_2\text{O}_3$	4 $\text{S S}_2\text{O}_3$		
1	1.05 $\mu\text{mol Na}_2\text{S}_2\text{O}_3$	1	67.4	9.9	0.4	59.8	2.1	67.1	100
2	1.05 $\mu\text{mol Na}_2\text{S}_2\text{O}_3$	1	67.4	7.9	0.6	60.2	1.0	66.5	99
3	1.05 $\mu\text{mol Na}_2\text{S}_2\text{O}_3$	1	67.4	9.3	0.4	54.2	3.5	59.6	88
4	60 $\mu\text{mol H}_2\text{S} + 0.90 \mu\text{mol Na}_2\text{S}_2\text{O}_3$	18	57.3	9.7	0.4	53.4	2.4	60.3	105
5	60 $\mu\text{mol H}_2\text{S} + 1.00 \mu\text{mol Na}_2\text{S}_2\text{O}_3$	42	64.1	8.4	0.4	65.0	2.9	70.1	109
6	60 $\mu\text{mol H}_2\text{S} + 1.26 \mu\text{mol Na}_2\text{S}_2\text{O}_3$	66	80.9	9.5	0.6	82.2	3.1	87.9	109
Mean									
Standard deviation									

Note. Presented data are the mean value and the standard deviation for hydrogen sulfide (2nd absorber) and thiosulfate (4th absorber) trace amounts. The obtained sulfur is calculated by the formula $(C_1 - C_2) + (C_3 - C_4)$, where C_n is the sulfur content in the absorber 1–4.

To confirm this conclusion, the filtrate of 2% NaCl solution containing S_2O_3 in an amount close to its concentration in the Black Sea water (about 1 μmol) was distilled off using four absorbers (Tabl. 2). Hydrogen sulfide in the first three experiments was not introduced. As a result, it was shown that hydrogen sulfide appears in the first absorber in an amount approximately equal to the theoretical ratio of sulfur in hydrogen sulfide to sulfur in thiosulfate – 1/9. Addition of hydrogen sulfide to the system (experiments 4–6) did not change this ratio (Tab. 2). The detection limit of hydrogen sulfide was 0.03 μmol and the one of thiosulfate – 0.05 μmol . In seawater samples, when, according to the method (Fig. 1), the determination of sulfide sulfur in the filtrate is not carried out, the detection limit was 0.03 μM per thiosulfate. Experiments have shown that H_2S is effectively removed into the precipitation with zinc hydroxocarbonate in the form of ZnS . Taking into account the blank experiments in absorbers 2 and 4 (Tab. 2), the yield of S_2O_3 was 88–109%.

Determination of the accuracy of elemental sulfur analysis

In the works devoted to the method [1, 14 and 15], there is no data on the verification of the method for determining zero-valent sulfur. Its accuracy was checked, and the limit of zero-valent sulfur detection in 2% NaCl solution was determined. The reagent blank (0.002 μmol (H_2S) and 0.004 μmol (S^0)) turned out to be an order of magnitude below the detection limit (Tabel 3). Zero-valent sulfur was dissolved in acetone (1 $\mu\text{mol}/\text{ml}$). Then 1 ml of the sulfur solution in acetone was added into 2% NaCl solution. After adding the $Zn_2(OH)_2CO_3$ suspension, the solution was kept for 1 h prior to the filtration procedure (0.45 μm). Zero-valent sulfur was determined in the filtrate and on the filter after heating to boiling with 1M $CrCl_2$ and 12N HCl . About 0.1 μmol of sulfur remained in the filtrate, which accounted for approximately 20% of the added concentrations (Fig. 4). The remaining sulfur was found on the filter (approximately 80%), the deviation of the amount of suspended and dissolved sulfur from the added one did not exceed 10% (Tab.3).

Table 3

Results of determining the elemental sulfur, μmol , obtained for filtrate and precipitation on the filter after filtering suspension of the zinc hydroxocarbonate in the 2% NaCl solution

Experiment	Added sulfur	Sulfur concentration				the obtained sulfur	Deviation, %
		in filtrate		in precipitation on the filter			
		Absorbers					
		1	2	1	2		
1	0.55	0.117	0.002	0.432	0.008	0.55	0.3
2	0.46	0.106	0.001	0.347	0.005	0.45	-1.6
3	0.66	0.148	0.003	0.572	0.009	0.72	9.9
4	0.64	0.126	0.004	0.549	0.011	0.67	4.7
5	0.38	0.104	0.003	0.245	0.009	0.35	-8.1
6	0.61	0.128	0.002	0.525	0.007	0.65	7.3
Mean		-	0.003	-	0.008	-	-
Standard deviation		-	0.001	-	0.002	-	-
Limit of determination		-	0.009	-	0.027	-	-

Note. Solution and precipitation were analyzed for two absorbers: the 1st – 30 min, the 2nd – 30 min.

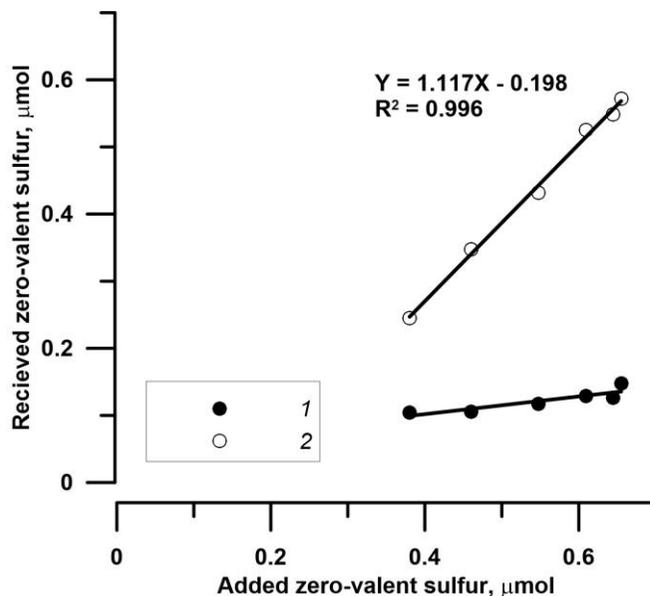


Fig. 4. Determination of zero-valent sulfur in the 2%-solution of NaCl: 1 – filtrate, 2 – precipitation

Effect of filling the Niskin bottles with argon on the concentration of hydrogen sulfide, thiosulfate and zero-valent sulfur

The method for the determination of reduced forms of sulfur [14, 15] provided for the filling of chemical glassware before analysis with argon to prevent oxidation of samples. Water sampling from the Niskin bottle when filling it with argon for this type of analysis was not previously carried out. The subsequent operation of $Zn_2(OH)_2CO_3$ suspension filtering in the air could lead to oxidation of the reduced forms of sulfur in the sample. Filling of the Niskin bottles with argon [17, 20] showed that at the low H_2S concentration the sensitivity of the determination method ($0.3 \mu M$) is not enough to assess the effect of atmospheric oxygen on the hydrogen sulfide content in water. At the same time, the amount of oxygen to be determined in the suboxic layer depends significantly on the filling of Niskin bottles on shipboard with inert gas [21].

At the Ashamba-7 station, two Niskin bottles were closed on each of eight depths, conducting sampling when filled with argon and the air, respectively. Water for determining the forms of sulfur were sampled in closed bottles (volume 1.0 l), which $Zn_2(OH)_2CO_3$ suspension was added on the shore in advance. Then they were filled with argon. Samples taken from the Niskin bottle when it was filled with argon or the air were filtered, in the argon or air atmosphere, respectively.

Data for hydrogen sulfide, obtained by sampling in two ways, are given in Tab. 4 and Fig. 5. On Fig. 5 it can be seen that the air oxygen does not affect the H_2S content within the sensitivity limits of the applied method of analysis ($0.3 \mu M$) [17]. A different result was obtained for thiosulfate (Fig. 6a). Obviously, the data on the concentration of thiosulfate and sulfite, obtained without filling the Niskin bottle with argon, is higher when the H_2S content is greater than $9 \mu M$ (Tab. 4). When water is taken from the Niskin bottle, H_2S is partially oxidized. When the hydrogen sulfide concentration is $74 \mu M$, the addition reaches 65% (Tab. 4). The effect of the sampling method from the Niskin bottle on the concentrations of zero-valent sulfur is significantly less (Fig. 6b), the differences between the contents are within the limits of the analytical error (Tab. 4).

Table 4

Effect of filling the Niskin bottles with argon and air during water sampling upon determining the reduced species of sulfur (hydrogen sulfide, thiosulfate, zero-valent sulfur), μmol , in the Black Sea water at the Ashamba-7 station (09.07.2016)

Depth, m	$t, ^\circ C$ ¹	$\theta, ^\circ C$ ²	Salinity, psu	Density, kg/m^3 ³	Content of the sulfur species during filling with					
					argon			air		
					H_2S	S^0	S_2O_3	H_2S	S^0	S_2O_3
150	8.65	8.64	20.71	16.00	< 0.01	nd ³	HO / nd	< 0.01	nd	nd
160	8.,8	8.67	20.88	16.12	< 0.01	nd	HO / nd	< 0.01	nd	nd
166	8.69	8.68	20.93	16.16	0.12	0.03	0.04	0.26	0.03	0.03
175	8.67	8.66	21.02	16.24	7.07	0.09	0.04	6.86	0.09	0.04
180	8.67	8.65	21.05	16.26	7.70	0.11	0.05	7.50	0.10	0.04
190	8.67	8.66	21.14	16.34	11.9	0.11	0.03	12.1	0.12	0.06
200	8.68	8.67	21.21	16.39	17.4	0.17	0.05	16.8	0.12	0.07
250	8.76	8.73	21.50	16.61	43.6	0.23	0.08	43.1	0.19	0.13
280	8.79	8.77	21.62	16.69	57.0	0.26	0.07	58.7	0.30	0.22
320	8.82	8.80	21.73	16.78	74.1	0.29	0.15	73.6	0.33	0.45

¹ – temperature

² – potential temperature

³ – no determined

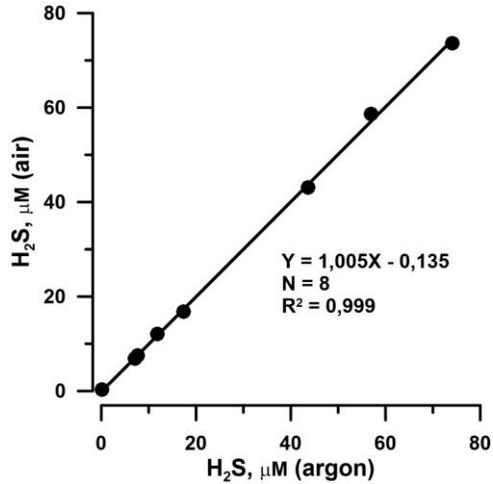


Fig. 5. Comparison of the hydrogen sulfide concentration (μM) in the simultaneously closed Niskin bottles filled with air and argon during sampling

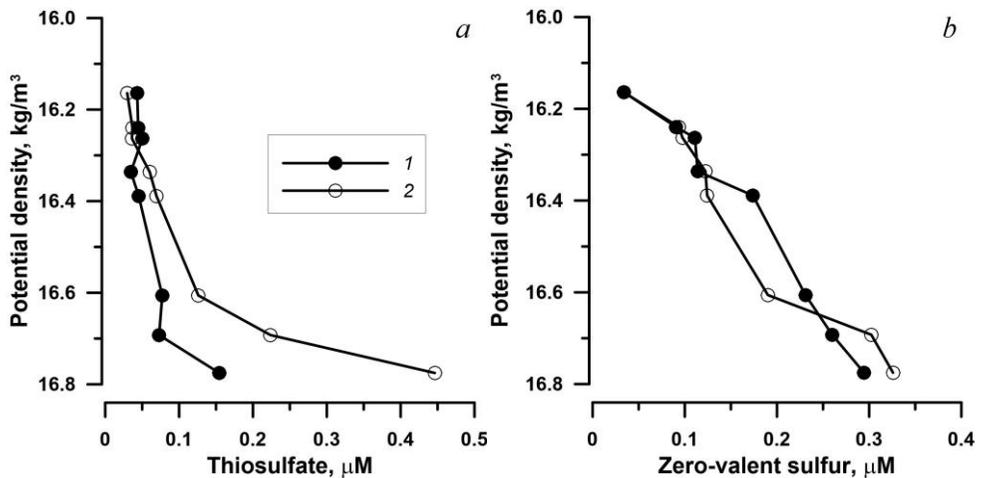


Fig. 6. Comparison of the thiosulfate (a) and zero-valent sulfur (b) concentrations in the simultaneously closed Niskin bottles filled with argon (1) and air (2) during sampling

Filtration of samples with $\text{Zn}_2(\text{OH})_2\text{CO}_3$ suspension in the air can lead to the oxidation of reduced forms of sulfur. At the Ashamba-9 station, all samples were taken from the Niskin bottles using argon to fill them (Tab. 5). The samples were filtered in an argon atmosphere, and three of them – additionally in air. No significant differences in the data on the thiosulfate concentrations in samples filtered in an atmosphere of argon and air were found. Zero-valent sulfur data during filtration in air turned out to be systematically lower than the results obtained during filtration in an argon atmosphere (Tab. 5). The resulting systematic error may indicate the oxidation of sulfur during filtration in air. These results do not contradict the zero-valent sulfur data given in Tab. 4 and Fig. 6b. Air filling of

the Niskin bottles leads to the oxidation of part of H₂S and the appearance of the newly formed S⁰. During the filtration procedure, partial oxidation of S⁰ takes place.

Table 5

Concentrations of the reduced sulfur species (hydrogen sulfide, thiosulfate, zero-valent sulfur), μM, in the Black Sea water at the Ashamba-9 station (13.07.2016)

Depth, m	<i>t</i> , °C ¹	<i>θ</i> , °C ²	Salinity, psu	Density, kg/m ³	H ₂ S	S ₂ O ₃	S ⁰
145	8.66	8.65	20.70	15.99	< 0.01	< 0.03	0.03
156	8.67	8.66	20.88	16.13	< 0.01	0.06	< 0.02
159	8.65	8.64	20.92	16.16	< 0.01	0.06	< 0.02
164	8.66	8.64	20.95	16.18	0.31	0.06	0.03
170	8.65	8.63	21.01	16.23	4.61	0.03 (0.04) ³	0.10 (0.06)
181	8.66	8.65	21.13	16.33	12.7	< 0.03	0.09
202	8.70	8.68	21.30	16.45	24.4	0.06	0.16
230	8.75	8.73	21.48	16.59	38.0	0.07 (0.06)	0.19 (0.16)
250	8.77	8.75	21.55	16.64	46.4	0.09	0.25
280	8.80	8.77	21.64	16.71	57.8	0.08	0.28
300	8.82	8.79	21.70	16.76	71.4	nd ⁴	0.42
321	8.83	8.80	21.75	16.79	75.5	0.10 (0.13)	0.34 (0.25)

¹ – temperature

² – potential temperature

³ – the results in brackets are obtained after filtering in the air

⁴ – no determined

Based on the analysis of samples of blank experiments, the detection limits were calculated. The detection limit for H₂S and S⁰, calculated as the sum of the mean and three standard deviations, was 0.01 and 0.02 μM, respectively. The detection limit (S₂O₃ + SO₃) is 0.03 μM.

Conclusion

This research showed that the method for determining the reduced sulfur species, proposed in [14, 15], has good sensitivity for the sum of the forms (S₂O₃²⁻ + SO₃²⁻) and (S⁰ + S⁰ polysulfides). The detection limit for the sum of thiosulfates and sulfites (S₂O₃²⁻ + SO₃²⁻), defined as the sum of the mean value and the three standard deviations for blank experiments in the analysis of seawater, was 0.03 μM, and for the sum of elemental sulfur and sulfur polysulfides (S⁰ + S⁰ polysulfides) – 0.02 μM. The detection limit of H₂S is 0.01 μM, which is 30 times better than the result obtained using the standard spectrophotometric method for the H₂S determination in seawater [17].

The accuracy of the method and measurement results was verified using 2% NaCl solutions with introduced concentrations of thiosulfate (0.5–1.5 μmol), sulfite (1 μmol), zero-valent sulfur (up to 1 μmol) against the background of much higher hydrogen sulfide concentrations (60 μmol). The selection of the concentrations corresponds to the ratio of these sulfur species in the Black Sea

water. It was shown that the presented method of analysis adequately reflects the presence of these forms in solutions, and a large amount of H₂S is effectively removed into the precipitation by Zn₂(OH)₂CO₃ suspension, without interfering the determination of trace amounts of other reduced sulfur species. To analyze them, it is necessary to fill the Niskin bottles with inert gas and filter in an inert atmosphere.

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Lybov' S. Semilova – sampling, filtration, carried out analysis of forms of sulfur

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