

Polish Academy of Sciences —  
Institute of Oceanology in Sopot

## OCCURRENCE OF METALORGANIC COMPLEXES IN WATER OF THE BALTIC SEA

Contents: 1. Introduction, 2. Experimental, 3. Results and discussion, 4. Significance of organometallic complexes; Streszczenie; References.

### 1. INTRODUCTION

A well known property of the Baltic Sea water is the relatively high concentration of organic substances. Expressed as organic carbon it is equal to 4–6 mgdm<sup>-3</sup> [5, 8, 17]. A considerable fraction of organic substances of the Baltic Sea water consists of humic substances. Their concentration attains the value of 2–3 mgdm<sup>-3</sup> in coastal waters and 1.5–2.5 mgdm<sup>-3</sup> in open sea waters [11, 13]. The chemical composition and properties of these substances indicate that they can act as ligands in organometallic complexes. It was also proved that humic substances actually form such complexes in fresh water [6] and in sea water [20]. Moreover, humic substances from the Baltic Sea bottom sediments form stable complexes with trace metal ions [12]. This clearly indicates that humic substances dissolved in sea water can interact with trace metal ions. The possibility was indicated by the authors of a number of papers [7, 10, 14, 19], but no quantitative data have been published so far. In order to find out whether humic substances dissolved in sea water bind trace metal ions and determine the magnitude of this phenomenon, a method of determination of concentration of metals bounded with humic substances was developed. A description of the method and the results of determination of concentration of organometallic forms in the Baltic Sea water are given in the present paper.

### 2. EXPERIMENTAL

The concentration of dissolved humic substances (DHS) was determined by a gravimetric method. A water sample with a volume of ca. 60 dm<sup>3</sup> was filtered through a Whatman GF/F glass fibre filter, acidified to pH

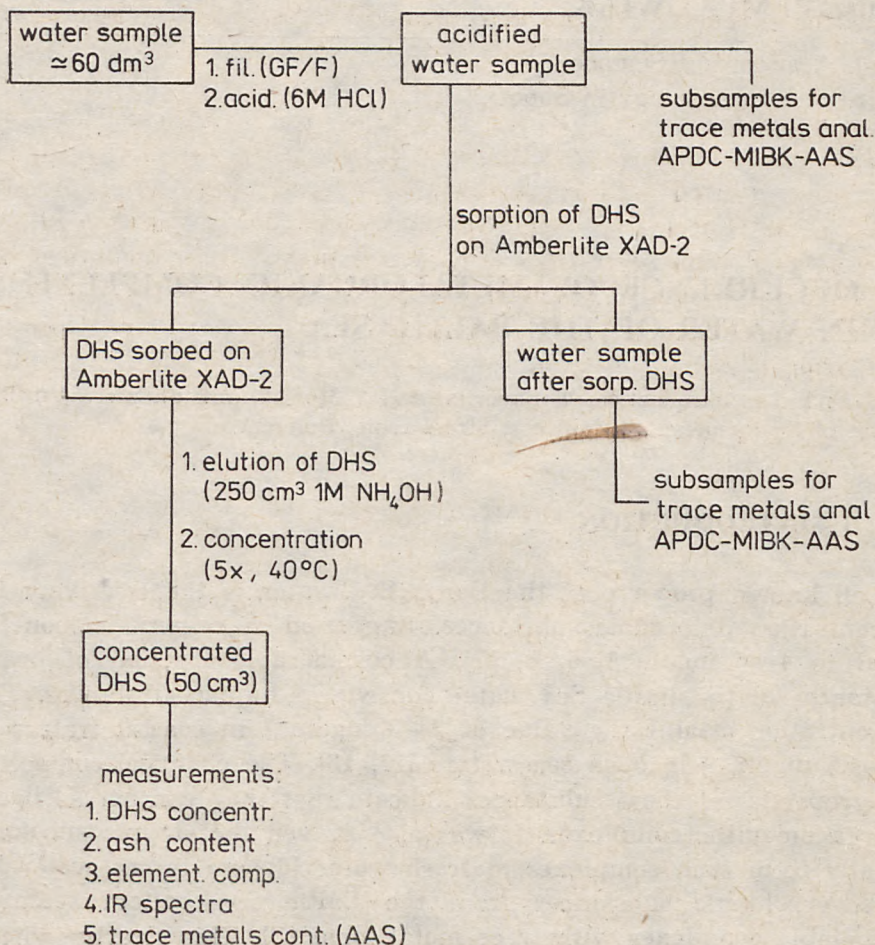


Fig. 1. Procedure of the determination of concentrations of dissolved humic substances (DHS) and organic complexes in water

Rys. 1. Schemat postępowania przy oznaczaniu stężenia rozpuszczonych substancji humusowych (DHS) i stężenia kompleksów metaloorganicznych w wodzie

2.0, weighed and passed through a glass column (2.0×30.0 cm) packed with Amberlite XAD-2 resin (Rohm & Haas, Serva) with a flow rate of 0.85 dm<sup>3</sup>/h. The column was washed with redistilled water until no Cl<sup>-</sup> ions were detected in the effluent (ca 250 cm<sup>3</sup>), and subsequently the adsorbed humic substances were eluted with 5 portions of 1 M ammonia solution (total volume of 250 cm<sup>3</sup>) over a period of 3 days. Ammonia was removed from the solution in a rotatory evaporator in the course of concentration of the effluent to 50 cm<sup>3</sup> at 50°C, 20 to 30 cm<sup>3</sup> of the concentrated effluent were evaporated to dryness, the mass of the solid residue was determined and the results calculated for the initial volume of water. The procedure is shown in Fig. 1, which also

shows the procedure for the determination of metals bounded with the organic substances. For this purpose the concentration of metals at the inlet and outlet of the column was determined using extraction of the complex of metal ions with ammonium pyrrolidylethylthiocarbamate (APDC) into methyl-isobutyl ketone (MIBK). Three parallel samples of water were shaken with 10 cm<sup>3</sup> of APDC solution and 20 cm<sup>3</sup> of MIBK for 5 min and the ketone layer was separated after the next 5 min. The concentration of metals was determined by atomic absorption spectroscopy (AAS) using an I 151 (International Instruments) spectrometer. The concentration of metals in concentrated effluent was determined by AAS after mineralization of HS by means of a mixture of HNO<sub>3</sub> and HClO<sub>4</sub> (5 : 1). The blanks were determined under identical condition, using similar amounts of the reagents.

### 3. RESULTS AND DISCUSSION

Isolation of humic substances from natural waters presents considerable difficulties. No method permitting quantitative isolation of DSH has been developed as yet. This also includes sorption on XAD-2 resin. However, the method is characterized by the highest recovery of DHS, since both during sorption and desorption steps the losses are small (recoveries 95% and 80—85%, respectively). The sorption of molecules of DHS occurs as a result of interaction by van der Waals forces and is particularly effective for compounds exhibiting hydrophobic properties. In order to decrease the dissociation of carboxyl and phenolic groups of DHS, water is acidified to pH 2. No change in the chemical properties of DHS was observed in an acidic solution [10]. Amberlite XAD-2 resin, being a copolymer of styrene and divinylbenzene, does not contain ion-exchange groups. This is a fundamental property which enables the investigation of the contents of organometallic complexes in water, as due to the lack of ion-exchange properties of XAD-2 the metal ions and their inorganic complexes will not be sorbed from the solution.

The concentration of selected trace metal ions in water was determined by the APDC-MIBK method. The results characterizing the precision of the adopted version of the method are listed in Table 1. It follows from Table 1 that the precision of the method is insufficient, particularly for lower concentrations of trace metals. However, no general method of simultaneous determination at several metals from one sample with high precision is available of present. Preliminary concentration of ion-exchange resins or anodic stripping voltammetry (ASV) could not be employed due to the lack of information on the behaviour of organometallic complexes under analytical conditions. Due to the high values of the standard deviation of concentration of individual

Table 1. Overall precision of APCD-MIBK trace metal extraction with atomic absorption analysis of water samples before and after sorption of humic substances on Amberlite XAD-2 resin

Tab. 1. Dane charakteryzujące precyzję oznaczeń stężenia metali śladowych w wodzie morskiej metodą spektrofotometrii atomowoabsorpcyjnej po ekstrakcji metali APCD-MIBK z próbek wody przed i po sorpcji substancji humusowych na Amberlicie XAD-2

Element Oznaczony metal	Mean <sup>a</sup>	Concentrations ( $\mu\text{gdm}^{-3}$ ) of trace metal in water samples					
	Średnia wartość <sup>a</sup>	Stężenie analizowanych metali ( $\mu\text{gdm}^{-3}$ ) w badanych próbkach wody					
	Standard deviation Odchylenia standardowe	1	1'	2	2'	3	3'
Fe	mean	3.4	1.8	4.7	4.5	3.6	3.4
	s.d.	0.5	0.3	0.6	0.6	0.8	0.6
Zn	mean	18.5	11.3	10.1	10.5	17.9	19.2
	s.d.	2.0	1.1	1.0	0.9	1.8	1.9
Ni	mean	3.2	2.3	4.8	5.1	3.2	3.0
	s.d.	0.5	0.4	0.6	0.7	0.7	0.6
Pb	mean	0.95	0.21	1.1	1.0	0.90	0.95
	s.d.	0.3	0.1	0.35	0.3	0.3	0.35
Cu	mean	3.9	2.8	4.7	5.0	4.1	3.8
	s.d.	0.6	0.4	0.85	0.9	0.7	0.6

1 - coastal water

2 - distilled water spiked with  $5 \mu\text{gdm}^{-3}$  of Fe, Ni, Cu;  $10 \mu\text{gdm}^{-3}$  - Zn and  $1 \mu\text{gdm}^{-3}$  - Pb

3 - coastal water boiled with  $\text{K}_2\text{S}_2\text{O}_8 + \text{H}_3\text{PO}_4$

1', 2', 3' - samples 1, 2, 3 after sorption of humic substances on Amberlite XAD-2 resin

<sup>a</sup> mean of five determinations

1 - woda przybrzeżna

2 - woda destylowana wzbogacona  $5 \mu\text{gdm}^{-3}$  Fe, Ni, Cu;  $10 \mu\text{gdm}^{-3}$  - Zn;  $1 \mu\text{gdm}^{-3}$  - Pb

3 - woda przybrzeżna po zmineralizowaniu substancji organicznych (ogrzewanie z  $\text{K}_2\text{D}_2\text{O}_8 + \text{H}_3\text{PO}_4$ )

1', 2', 3' - próbki 1, 2, 3 po sorpcji substancji humusowych na Amberlicie XAD-2

<sup>a</sup> średnia z pięciu analiz równoległych.

metals, the test was used to check whether the differences between the two average values are statistically significant. The t test was chosen, as the most suitable for statistical evaluation of small sets of data [2]. The null hypothesis that the mean values of the following sets of data from Table 1 are equal was tested for: a) the concentration of metals in sea water at the inlet and outlet of the column; b) the concentration of metals in distilled water at the inlet and outlet of the column, and c) the concentration of metals in sea water after decomposition of organic substances at the inlet and outlet of the column. The results of the test were negative for case a) and positive for cases b) and c) at the confidence level  $\alpha=0.05$ . This means that the hypothesis as to the equality of the mean values of the concentration of metals in samples of sea water at the inlet and outlet of the column should be rejected. On the other hand, there is no basis for questioning the hypothesis in cases

where the determinations were carried out with water not containing organic matter. The data from Table 1 and the results of statistical test permit the assumptions that, firstly, metals do not sorb on XAD-2 and secondly, that the presence of organic substances in sea water does not affect the value of concentration of metals determined by the APDC-MIBK method. A decrease of concentration of metals in water passed through the column packed with XAD-2 was observed. This phenomenon

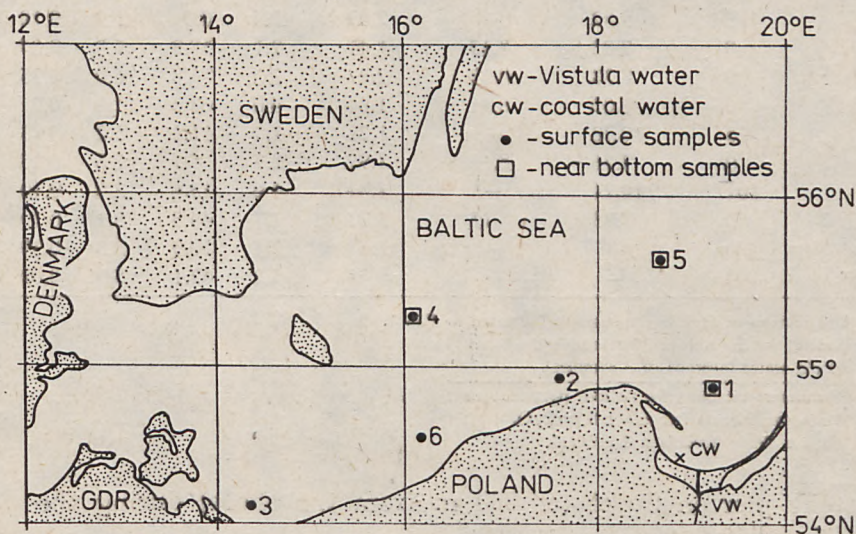


Fig. 2. Map of the southern Baltic showing stations where water samples were collected

Rys. 2. Rozmieszczenie punktów poboru prób wody do oznaczeń stężenia kompleksów metaloorganicznych

should be attributed to the sorption of DHS and trace metal ions bound to them on the surface of the resin. Naturally, only the complexes which are stable under experimental conditions (at  $\text{pH}=2.0$ ) are sorbed on XAD-2. In an acidic medium, the dissociation of carboxyl and phenolic groups decreases, which can explain the dependence between  $\text{pH}$  and the amount of organically bounded iron observed in fresh waters [6]. At a  $\text{pH}$  of water of less than 3, only 50% of the initial amount remains in the organically bounded form.

Using the procedure shown in Fig. 1, the content of DHS, the concentration of selected trace metals and the percentage of organically bounded metals was determined for 10 samples of sea water collected from the region of the southern Baltic in October 1979. The location of sampling sites is shown in Fig. 2. General characteristics of collected samples are given in Table 2 together with the data for water sampled from the Vistula in June 1979 and for the Baltic Sea water collected

Table 2. Results of analyses of water samples from the southern Baltic  
 Tab. 2. Charakterystyka próbek wody pobranych z Bałtyku Południowego

Station <sup>a</sup> No. Punkt poboru <sup>a</sup> nr	Depth Głębokość [m]	Salinity Zasolenie	pH	DHS mgdm <sup>-3</sup>	Fe	Zn	Ni	Pb	Cu
					μg dm <sup>-3</sup>				
1	0	7.75	8.21	1.75	3.6	10.1	11.7	0.41	2.5
1'	115	9.82	—	2.09	2.4	8.3	1.9	0.10	4.1
2	0	7.85	8.15	1.41	2.1	18.9	6.3	0.37	1.9
3	0	8.33	8.13	2.07	3.2	73.8	6.0	0.35	2.0
4	0	8.00	8.11	1.84	4.6	68.3	11.1	0.21	2.5
4'	75	10.78	—	1.21	1.9	11.1	5.2	0.43	2.1
5	0	7.76	8.19	1.99	2.2	5.1	2.6	0.25	1.3
5'	101	10.21	—	1.84	1.6	13.4	2.2	0.10	1.1
6	0	7.95	8.11	1.77	1.7	44.3	3.1	0.19	1.9
CW <sup>b</sup>	0	—	—	2.45	2.1	30.3	3.6	0.39	3.8
VW <sup>c</sup>	0	—	—	6.74	5.2	42.1	5.9	0.89	4.2

<sup>a</sup> Distribution of sampling stations is indicated in Fig. 1.

<sup>b</sup> Coastal water (average of 8 samples).

<sup>c</sup> Vistula water (average of 3 samples).

<sup>a</sup> Rozmieszczenie punktów poboru pokazano na rys. 1.

<sup>b</sup> Woda przybrzeżna (średnia z 8 próbek).

<sup>c</sup> Woda z Wisły (średnia z 3 próbek).

from the pier in Sopot (ca 300 m from the shore) during the period June–November 1979.

The results obtained indicate that the concentration of DHS in open sea water ranges from 1.4 to 2.1 mgdm<sup>-3</sup>. These values are significantly higher than those reported earlier [11] for the same region. In coastal water the concentration of DHS is equal to 2.5 mgdm<sup>-3</sup>, the value being characteristic for coastal water [13]. Vistula water also exhibits a concentration of DHS agreeing with that reported earlier — 6.1 mgdm<sup>-3</sup> [13]. The concentrations of Fe, Cu, Cd, Ni and Pb are characteristic for the Baltic Sea Water [3, 4], a noticeable exception in two cases being an unusually high concentration of zinc, which indicates the possibility of secondary contamination of the samples.

The data characterizing the percentage fraction of organometallic forms in the total concentration of metals in filtered water are summarized in Table 3. The relatively small fraction of organometallic complexes of copper (28%) is worth noting, as the measurements of the stability constants of complexes of copper with fresh water DHS indicate considerable stability of these complexes [10], similar to the case of HS from bottom sediments [12].

The percentage of metal-humus complexes in the total contents of individual metals in water varies substantially (22–57% for Zn, 23–61% for Fe, 28–61% for Pb). This phenomenon can be explained only

Table 3. The percentage of the total amount of trace metals occurring in water as organic complexes

Tab. 3. Procentowy udział kompleksów metaloorganicznych w ogólnej zawartości metali w wodzie

Station No. Punkt poboru nr	Percentage of organic complexes Procentowa zawartość kompleksów metaloorganicznych w ogólnym stężeniu metali				
	Fe	Zn	Ni	Pb	Cu
1	61	42	62	38	35
2	42	39	69	28	78
3	36	22	20	33	27
4	28	35	18	39	22
5	55	57	50	30	47
6	23	34	22	35	19
average średnio	41	38	40	34	28
1'	47	37	24	43	35
4'	41	58	35	61	33
5'	54	33	42	39	27
average średnio	47	43	34	48	32
CW <sup>a</sup>	33	35	39	35	27
VW <sup>b</sup>	28	30	29	37	24

<sup>b</sup> coastal water (average of 8 samples).

<sup>b</sup> Vistula water (average of 3 samples).

<sup>a</sup> woda przybrzeżna (średnia z 8 próbek).

<sup>b</sup> woda z Wisły (średnia z 3 próbek).

by the heterogeneity of DHS carried with river run-off. Investigations of the contents of organics or of metals in natural waters proved there to be a considerable fraction in the total contents of metals. For example, it was established that 60–90% of Fe, Mn, Co, Zn and Al is bounded with fresh water DHS [6]. In this case also, the percentage of organo-metallic forms depends on the pH of the water. In addition, it was found that over 80% of Fe in oceanic water occurs in the form of organometallic complexes [20]. However, little is known about the nature of these chemical combinations. The possibility of complex formation as a result of the presence in DHS of the electron-donating functional groups has been suggested. Another possibility is sorption of DHS on colloidal suspensions [6, 19]. The latter phenomenon cannot be excluded even in the case of filtered water. This is indicated by among other things the relatively high ash content in DHS isolated from Baltic Sea water (Tabl. 4). Knowing the average ash content in DHS and assuming that it is caused by the sorption on colloidal mineral suspensions, than assuming further that the average contents of Zn, Cu, Pb and Fe in the suspension from the southern Baltic are 900, 1000, 100 and 13 000 µg/g, respectively

Table 4. Elementary composition of dissolved humic substances isolated from Baltic water  
 Tab. 4. Skład elementarny rozpuszczonych substancji humusowych wyodrębnionych z wody Morza Bałtyckiego

Water sample No. Próbka wody nr	Ash content % Popiół %	Elementary composition Skład elementarny			C/H	C/N
		C %	H %	N %		
		1	9.2	46.21		
1'	8.5	48.73	7.05	6.42	6.9	7.6
4	9.2	47.35	7.41	6.38	6.4	7.4
4'	9.4	48.91	6.93	6.85	7.1	7.2

[1], and the average concentration of DHS in sea water to be equal to  $2 \text{ mg dm}^{-3}$ , the potential concentration of these elements in colloidal suspension associated with DHS was calculated. The following contents of such forms of metals in  $1 \text{ dm}^3$  were obtained: Zn — 0.20; Cu — 0.22; Pb — 0.022; Fe —  $2.9 \mu\text{g}$ . Thus a value comparable to the content found for the complex was obtained only for iron. Hence, the association with suspensions cannot be excluded as a primary mechanism of formation of organometallic complexes of iron. In the remaining cases the presence of organometallic forms in water can be explained only to a small extent by the formation of associates with the colloidal suspension. Considerable contents of trace metals in DHS can thus be attributed to the formation

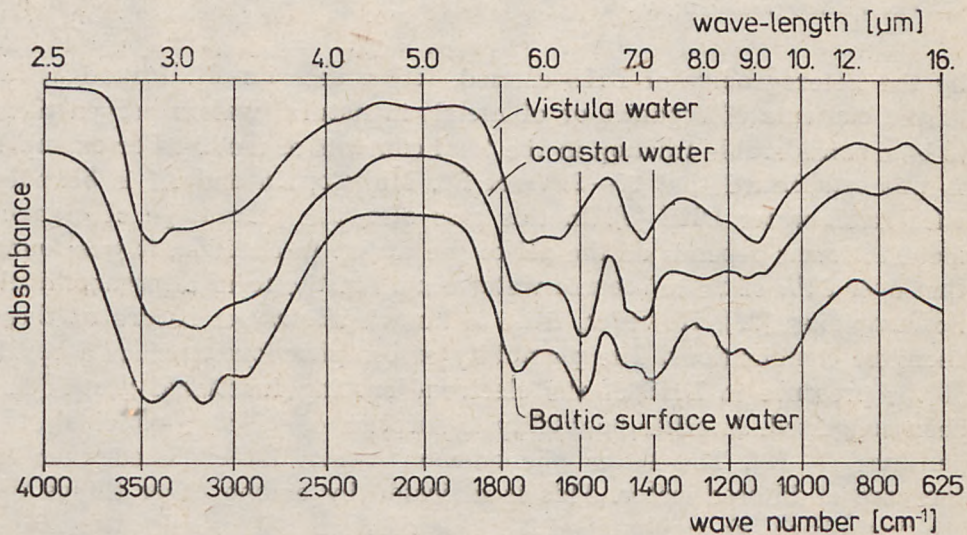


Fig. 3. Typical ir absorption spectra of dissolved humic substances (DHS) isolated from water of various origin

Rys. 3. Typowe widma absorpcyjne w podczerwieni rozpuszczonych substancji humusowych (DHS) wyodrębnionych z różnorodnych próbek wody



of complexes. Both the results of elemental analyses listed in Table 4 and their absorption spectra shown in Fig. 3 indicate that DHS isolated from sea water contain functional groups (hydroxyl, amine, carbonyl) capable of complex formation. It should be pointed out that the high content of nitrogen in DHS from sea water results partly from the fact the elementary composition presented in Table 4 refers to ammonium salts. The ir absorption spectra shown in Fig. 3 exhibit considerable similarity to the spectra described earlier for DHS isolated from oceanic water [18] and the Gdańsk Bay water [13].

#### 4. SIGNIFICANCE OF ORGANOMETALLIC COMPLEXES

The results presented indicate that the organometallic forms, probably complexes with DHS, constitute a significant fraction of the total concentration of metal ions in the Baltic Sea water. The fact that the presence of these forms was observed in water with a pH=2 indicates their high stability. A considerable fraction of stable organometallic complexes in the total concentration of metals in water determines their behaviour to a large degree since it can be assumed that they will participate in the processes occurring with the contribution of DHS. For example, they will be transferred to the bottom sediments together with DHS due to effective sedimentation processes of DHS. This phenomenon influences the concentration of metals in sea water and their average time of residence in water. Moreover, it can be anticipated that the stability of complexes will vary depending on the properties of the water (salinity, redox, potential). This will lead to the migration of metals in reservoirs with diversified properties of water in various layers. The processes of migration of DHS will be of great significance for self-purification of reservoirs from toxic metal ions. The concentration of these metals resulting in definite biological changes will be higher in water with a high content of DHS. It should also be mentioned that the reactions of deamination, decarboxylation and oxidation are catalyzed by metal ions bounded in the form of complexes with organic substances [16]. Therefore, it can not be excluded that formation of humic-type substances in sea water depends in part on the presence of metal ions bounded to molecules of humic substances.

## WYSTĘPOWANIE KOMPLEKSÓW METALOOGRANICZNYCH W WODZIE MORZA BAŁTYCKIEGO

### Streszczenie

Próby wody morskiej i wody z Wisły, pobrane w punktach pokazanych na rys. 2, sączono przez sączek szklany GF/F (Whatman), a następnie oznaczano w wodzie stężenie substancji humusowych (DHS) oraz metali śladowych (Cu, Zn, Fe, Pb, Ni) przed i po przepuszczeniu przez kolumnę wypełnioną Amberlitem XAD 2 (Serva). Sposób postępowania przedstawiony jest schematycznie na rys. 1. Stwierdzono, że stężenie DHS w próbkach wody morskiej wahało się w granicach 1,21—2,45 mg/dm<sup>3</sup>. Stężenia Fe, Zn, Ni, Pb i Cu wynosiły odpowiednio 1,6—3,6 μgdm<sup>-3</sup>; 5,1—73,8 μgdm<sup>-3</sup>; 1,9—11,7 μgdm<sup>-3</sup>; 0,10—0,43 μgdm<sup>-3</sup> i 1,1—4,1 μgdm<sup>-3</sup> (tab. 2). W próbkach wody przepuszczonych przez kolumnę wypełnioną Amberlitem XAD-2 stężenia oznaczonych metali śladowych były znacznie niższe. Średnie obniżenia stężenia Fe, Zn, Ni, Pb i Cu wyniosło odpowiednio 41, 38, 40, 34 i 28% w wodzie powierzchniowej oraz 47, 43, 34, 48 i 32% w wodzie przydennej (tab. 3). Efekt ten przypisano sorpcji kompleksów metaloorganicznych na Amberlicie XAD-2. Podane wartości charakteryzują więc udział stabilnych przy pH=2,0 kompleksów metaloorganicznych w ogólnym stężeniu metali w wodzie morskiej. Taką interpretację uzasadniają wyniki oznaczeń stężenia metali w wodzie przed i po przepuszczeniu przez kolumnę z Amberlitem XAD-2 przedstawione w tab. 1. Skład elementarny DHS (tab. 4) i ich widma absorpcyjne w podczerwieni (rys. 3) wskazują na obecność tlenowych grup funkcyjnych zdolnych do spełniania roli donorów w kompleksach z metalami śladowymi.

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