Properties of selected bottom sediments of the Baltic Sea and their sorption ability towards cobalt (II) ions*
(Part I)

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Sediments
Cobalt (II) ions
Sorption ability
Baltic Sea

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Abstract

We studied sorption of Co^{2+} ions on 12 bottom sediments of the Baltic Sea devoid of organic substances. The results were compared with those obtained for non-mineralized sediments. Infrared spectra were recorded in addition to investigations carried out by means of DTA, TG, X-ray diffraction, specific surface, and elemental analysis. Sorption of cobalt (II) ions on some sediments previously saturated with copper (II) or nickel (II) ions was also investigated.

1. Introduction

This paper is part of a comprehensive study dealing with sorption properties of selected bottom sediments of the Baltic Sea with respect to cobalt (II) ions. Previously (Szponar *et al*, 1984) we have presented investigations carried out on 8 sediments of the Gulf of Gdańsk, 3 from the open sea and 1 from the Skagerrak, dealing with the kinetics of cobalt (II) ions sorption. We found out that the extent of sorption depends on the type of sediment. The relationship between concentration of the Co^{2+} ions adsorbed in an equilibrium state and the initial concentration of these ions are linear with the straight line passing through the origin the co-ordinate system. The stronger sorption properties of the sediment, the longer it takes to reach a state of equilibrium. It would be interesting to find out which components of sediments, mineral or organic, and to what degree are responsible for sorption. Investigations of mineralogical characteristics of bottom sediments

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by mean of DTA, TG, X-ray diffraction, specific surface and elemental analysis were carried out previously (Szponar *et al*; 1985). In this paper we present sorption properties of sediments freed of organic substances through mineralization. The results supplementing thermal analyses and also characterizing sediments may be obtained from investigations of infra-red spectra. They may reveal interatomic bonds inside silicate layers or hydrogen bonds formed in the outer layers; they may also indicate the presence of certain groups or suggest location of ion binding or exchange. The spectra can also serve for identification of particular sediments. On selected sediments, saturated previously with copper (II) or nickel (II) ions, ivestigations of cobalt (II) ions sorption were carried out.

2. Material and methods

The sediments from the Gulf of Gdańsk were designated with symbols 1 – 8, those from the open sea – P-1, P-2, P-7, and the one from the Skagerrak P-50. Sampling sites are shown on a chart in Figure 1. Bottom sediment samples were collected by means of a Van Veen's clamshell bucket, which

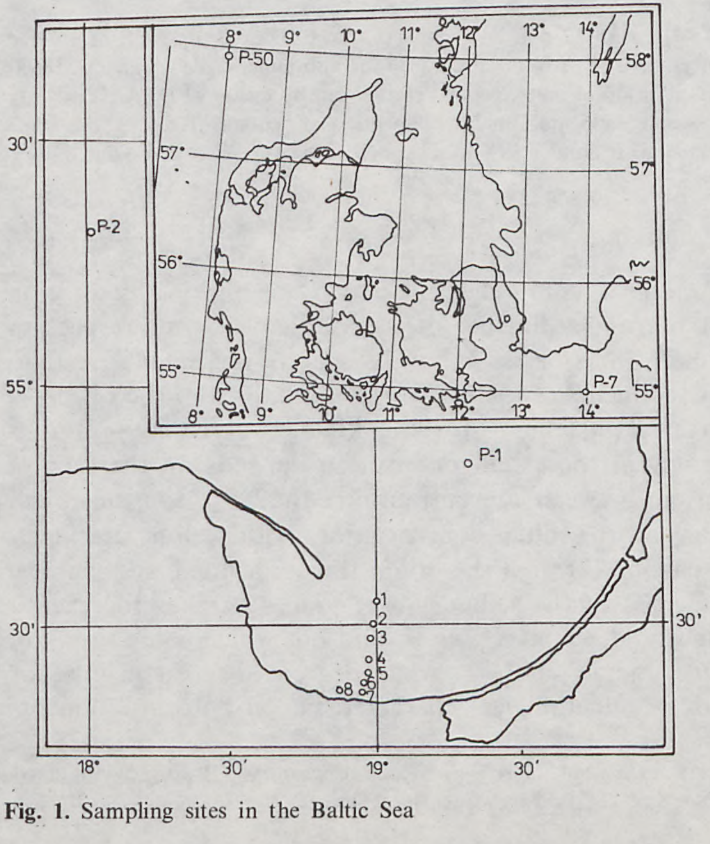

Fig. 1. Sampling sites in the Baltic Sea

grabbed a surface layer with a thickness of about 15 cm. The material was homogenized, dried, pulverized, and sieved through a screen with a mesh size of 0.071 M/M^2 (Szponar *et al*, 1984, 1985).

The sediments were mineralized by treatment with a 30$^0/_0$ hydrogen peroxide solution. When the reaction was over, the fraction which did not react with H_2O_2 was extracted in a soxhlet apparatus with n-propyl alcohol (Grabowska-Olszewska, 1980).

For the determination of concentration of cobalt (II) ions, a modified nitro-R-salt method was used (Szponar *et al*, 1984).

The spectra were recorded on a UV-VIS Perkin-Elmer 402 spectrometer and a Specord 71 IR instrument. A KBr pellet technique with identical concentration of 800/2 mg was used. Spectra of sediment suspensions were also investigated in nujol and 6-chlorobutadiene of deuterated and, for comparison, non-deuterated sediments.

Deuteration was carried out in the following way: 50 mg of sediment were added to 50 cm^3 of D_2O, followed by evaporation to dryness in a vacuum drier.

For the investigation of sorption 10.000 g weighed samples of dry sediments mineralized and, for comparison, non-mineralized were placed in polyethylene containers and the covered with 25 cm^3 of sea water. The salinity of sea water used determined by the argentomeric method was 7.15$^0/_{00}$. Next day 75 cm^3 of cobalt (II) salt solution in sea water were added; its concentration was 2600 ppb, so its concentration above the sediment was 1950 ppb. Saturation of sediments with sea water before the addition of cobalt salt was a condition for the repeatability of results. The sediment with solution was shaken and then, after it settled, 5 cm^3 of the solution were taken at intervals from above the sediment and the concentration of Co^{2+} was determined there until the state of equilibrium was reached.

For investigations of the effect of saturation of sediments with other ions on sorption of cobalt (II) ions, 1.000 g samples of sediments P-1, P-7, and P-50 dried and non-mineralized were treated with solutions of nickel (II) or copper (II) ions in sea water with a concentration of 2000 ppb. At the same time test samples were prepared by treating sediments with sea water only. The salinity of sea water was 7.15$^0/_{00}$. After reaching an equilibrium state saturated sediments were centrifuged and treated with a cobalt (II) salt solution with a concentration of 2000 ppb.

3. Kinetic investigations of cobalt (II) ion sorption by mineralized sediments

The results of cobalt (II) sorption (Table 1) reveal that the measured values range from 30$^0/_0$ (sediment 1) to 86$^0/_0$ (sediment 8), that is are quite significant. In two cases, *ie* for the sediment P-50 the value equals to 101$^0/_0$

Table 1. Results of cobalt (II) ions sorption in an equilibrium state on mineralized (C_{e1}) and non-mineralized (C_{e2}) sediments, C_{e1}/C_{e2} ratio, sorption coefficient C_0/C_{e1} for mineralized sediments, time t necessary to achieve an equilibrium state on mineralized sediments, and values of sorption by the mineral part of the sediments expressed in percent. C_0 of $Co^{2+} = 1950$ ppb

Sediment	C_{e1} [ppb]	C_{e2} [ppb]	C_{e1}/C_{e2}	C_0/C_{e1}	t [h]	% of mineral part sorption
1	70	235	0.298	27.85	72	30
2	1260	1470	0.857	1.17	240	86
3	490	1100	0.445	3.98	168	45
4	330	470	0.702	5.90	144	40
5	960	1160	0.827	2.03	192	83
6	920	1070	0.860	2.12	198	86
7	850	1210	0.702	2.3	144	70
8	650	1710	0.380	3.0	264	38
P-1	580	240	2.42	3.36	216	241
P-2	1440	1860	0.774	1.35	168	77
P-7	980	1340	0.731	2.0	168	73
P-50	1830	1800	1.017	1.06	144	101

and in the sediment P-1 it is equal to as much as 241%. Large sorption on mineral components is a result of the presence of negative oxygen charges on the surface of silicates. In the sediments there might occur minerals possessing the properties of exchange sorption (Aston, Duursma, 1970; Fijał *et al*, 1979; Hull *et al*, 1982; Popiel, Żyła, 1976; Żyła, 1977) and swelling under the influence of polar substances. This confirms the fact that the repeatability of results may be achieved only when the dry sediment is covered with water for at least 24 hours prior to treating it with the cobalt ion solution. In that case water molecules may penetrate interparticle spaces and only after attaining an equilibrium an exchange or sorption of cobalt ions occurs. Kaolinite has neither the property of cation exchange nor does it undergo swelling. It has, however, hydroxyl groups on its outer surfaces in which hydrogen may be replaced by metal ions. Illite, a laminar silicate, does not undergo swelling and exchanges cations with great difficulty; it also has a very small specific surface are which does not promote sorption. Montmorillonite (Hodgson, 1960) is also a laminar silicate but it exchanges cations quite easily and undergoes swelling. Its specific surface area is very large (depends on the type and origin) which results in great sorption properties. Feldspars being potassium-sodium-calcium aluminosilicates do not have exchange properties. It is, however, difficult to determine simple relations between the presence of particular minerals in sediments, their specific surface area, and the extent of sorption. The time needed to achieve a state of equilibrium is generally shorter in the case of mineralized sediments. The exception is sediment 4 and especially P-1 in which it was much longer. It is possible that after removal of the organic part minerals exhibiting large sorption properties were exposed, *eg* montmorillonite (which was a component of sediment 4) and the organic substance of this sediment bound mineral granules in condensed, compact aggregates as may be seen from previous investigations (Szponar *et al*, 1985). After mineralization the specific surface area of this sediment increases from 2040 cm^2/g to 4910 cm^2/g, that is by a factor of 2.4. Sediment P-1 contains negligible amounts of quartz and feldspars and has no illite at all. In its organic part there are nitrogen and carbon in quite substantial quantities (1.0 and 4.4⁰/₀, respectively – see Szponar *et al*, 1985). The removal of organic compunds through mineralization exposes the minerals, their very large surface is uncovered which might have an impact on much greater sorption but also influences the time needed for achieving the equilibrium.

Sediment 1 is characterized by the smallest percentage of sorption by its mineral part. Its specific surface area after mineralization almost does not differ from the surface of non-mineralized sediment (4360 and 4480 cm^2/g, respectively). The organic substance is very dispersed throughout this sediment and, as may be seen from TG and DTA analyses (Szponar *et al*, 1985), it is abundant consisting of two groups of compounds with a similar structure. In this case the organic part has a decisive influence on sorption of cobalt ions. Chelate complexes of various stability constants may be formed. The time needed for achieving a state of equilibrium depends on the sum of reactions taking place, *ie* on the formation of complexes, access to the mineral or organic part, penetration inside the minerals, and exchange reactions.

4. Measurements of infra-red spectra

Measurements of infra-red spectra of 12 bottom sediments (air dry, non-mineralized) were made by means of the KBr pellet technique (Colthup *et al*, 1975; Farmer, Russel, 1979; Hull *et al*, 1982). Sediments saturated with cobalt (II) ions with an initial concentration $C_0 = 1950$ ppb were also tested. These spectra revealed characteristic bands and inflections, which can be ascribed to the following vibrations:

(i) in-plane bending vibrations of the —OH group between 780 and 810 cm^{-1},

(ii) bending vibrations connected with the presence of a $Al^{3+}-Fe^{3+}$ pair at 845 – 890 cm^{-1}; when the sample contains large amounts of iron they tend to occur at 890 cm^{-1},

(iii) small inflections corresponding to bending vibrations connected with the presence of two Al^{3+} ions, *eg* in montmorillonite at 920 cm^{-1},

(iv) stretching vibrations in the Si—O—Si plane degenerate at about

1100 cm^{-1} and perpendicular vibrations $Si=O$ between 1050 and 1100 cm^{-1},

(v) bands at 1640 cm^{-1} and possibily at 1450 cm^{-1} associated with the presence of water,

(vi) at 2850 cm^{-1} a band of water taking part in hydrogen bonding in the outer co-ordination sphere,

(vii) at 3300 cm^{-1} a water band co-ordinated with cations, taking part in a strong hydrogen bonding with water in the outer co-ordination sphere and other overlapping bands of the —OH group,

(viii) vibrations corresponding to the hydrogen bond of the —OH group bound with oxygen of the silicate group in the latice with water in the range of 3630 cm^{-1} together with the previous frequencies,

(ix) at 3700 – 3100 cm^{-1} vibrations of the —NH group may occur although weaker than those of the —OH groups.

The sediments investigated differed with respect to the location of individual bands and their intensity. This is illustrated in Table 2. An exemplary spectrum is presented in Figure 2.

Two symmetrical vibrations with lower frequency and asymmetrical with higher frequency correspond to Si—O—Si groups at about 1020 – 1100 cm^{-1}. In some minerals these vibrations might be degenerate and observed as a single band. In the spectra of the sediments tested usually two bands are observed, *ie* vibrations occur in the octahedral plane. There is only one band for sediments 1 and 4.

A band at 890 cm^{-1}, corresponding to vibrations connected with the

Table 2. Infra-red spectra recorded by KBr pellet technique*

Sediment	790-810**		890	920	1050	1100	1450 – 1470	1640	2880	3300	3600
	[cm^{-1}]										
1	S	S	–	VW	–	VS	–	VW	VW	M	VW
2	M	M	M	W	VS	VS	S	VW	VW	S	VW
3	M	M	–	VW	S	S	VW	VW	W	M	VW
4	M	M	–	VW	–	S	–	VW	VW	M	VW
5	M	M	–	VW	S	S	–	VW	VW	VW	VW
6	W	W	–	VW	S	S	–	VW	VW	M	VW
7	M	M	–	VW	VS	VS	VW	W	VW	M	VW
8	M	M	–	VW	VS	VS	VW	W	W	S	W
P-1	W	M	–	VW	VS	VS	W	M	VW	S	VW
P-2	M	M	–	VW	VS	VS	–	W	VW	M	–
P-7	W	W	–	VW	S	S	–	W	VW	W	–
P-50	W	W	W	M	S	S	M	W	–	W	–

* Peak sizes denoted in the following way: VW – very weak, W – weak, M – medium, S – strong, VS – very strong.

** 2 peaks

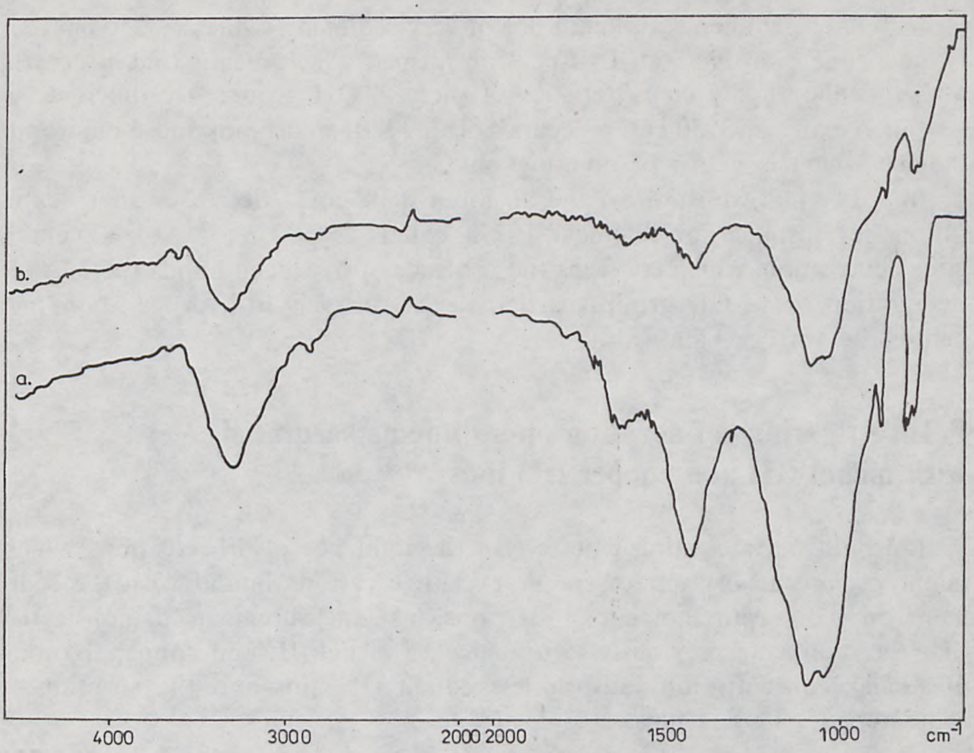

Fig. 2. IR spectra of sediment 2 before (line a) and after saturation with cobalt (II) ions (line b)

presence of iron and aluminium in the lattice, occurs only for sediments 2 and P-50. These bands are reduced considerably in the spectra of sediments saturated with cobalt (II) ions (Fig. 2).

A band at 1450 – 1470 cm^{-1} occurs for sediments 2 and P-50 as a strong one while it is quite weak for sediments 3, 7, 8 and P-1. After saturating the sediments with cobalt (II) ions these bands disappear or are greatly reduced. The exception is sediment P-50. It should be emphasized that this sediment has a different mineral composition than the others. It contains very little quartz, feldspars, and illite and has no montmorillonite at all.

Band intensity at 3300 and 3630 cm^{-1} is smaller for sediments saturated with cobalt (II) ions, which suggests that the —OH groups of the minerals might be replaced with Co^{2+} ions (De Mumbrum, Jackson, 1956; Sawhney, 1972).

In order to characterize the sediments studied in more detail infra-red spectra of suspensions of deuterated and normal sediments were recorded in nujol and 6-chlorobutadiene. The spectra exhibited the following features:

(i). At about 3600 cm^{-1} the bands often not revealed in KBr in both media, and at about 3250 ± 20 cm^{-1} the bands corresponding to the —OH groups in a given hydrogen bond. The band at about 3600 cm^{-1} disappears in deuterated sediments although not in very sediment, while at 3250 cm^{-1} it is independent of deuterated suspension formed which means that structural and crystallographic characteristics of these —OH groups are different.

(ii). A band at 3250 cm^{-1} occurs both in KBr and nujol and 6-chlorobutadiene which is worth of pointing out.

(iii). The half-width of a band at about 3600 cm^{-1} decreases after deuteration; for instance for sediment P-1 it equals to 500 cm^{-1} and 420 cm^{-1} after deuteration, which confirms the presence of hydrogen bonds there. After deuteration the —OD groups participate less actively in hydrogen bonding; hence, the smaller bandwidth.

5. Investigations of sorption on sediments saturated with nickel (II) and copper (II) ions

It would be interesting to establish the influence of other cations which might occupy adsorption centra or exchange cations bound with the sediment on the sorption of cobalt (II) ions. The measurements demonstrated that the sediments previously saturated with nickel (II) and copper (II) ions of similar concentrations adsorb less cobalt (II) ions and the sorption is characteristic. This is illustrated in Table 3.

Table 3. Sorption of cobalt (II) ions from sea water at an equilibrium state (C_e) by sediments previously saturated with nickel (II) or copper (II) ions. Initial concentration C_0 of Co^{2+}, Ni^{2+}, and Cu^{2+} ions = 2000 ppb

Sediment	Saturation with	C_e [ppb]	% of sorption
P-1	sea water	246	100
	Ni^{2+}	236	96
	Cu^{2+}	210	85
P-7	sea water	1370	100
	Ni^{2+}	1264	92
	Cu^{2+}	1220	89
P-50	sea water	1850	100
	Ni^{2+}	1770	96
	Cu^{2+}	1700	92

Similar investigations were carried out on sediment P-2 using higher concentrations of cobalt (II) and copper (II) ions corresponding to the sum of exchangeable bases (Bojanowski *et al*, 1978). A sample of 1.0000 g of sediment was treated with a solution of Cu^{2+} ions of a concentrations of 23.4 ppm. After a state of equilibrium was reached it was observed that the sediment adsorbed 13.4 ppm Cu^{2+}. The sorption coefficient C_0/C_e was thus

1.7. The sediment was then centrifuged and treated with a solution of cobalt (II) ions of a concentration of 21.8 ppm. At equilibrium the sediment adsorbed 6 ppm of Co^{2+} ions. The same sediment not saturated with copper ions sorbed 7 ppm of Co^{2+} ions. Thus, the percentage of saturation of cobalt (II) ions on a sediment saturated previously with copper (II) ions was the same as in earlier investigations amounting to $85.7^{0}/_{0}$.

It may be, therefore, said that sorption of ions is a selective process. Similar observation was made by other authors (Cavallaro, Mc Bride, 1978; Duursma, 1973). The extent of sorption is only slightly influenced by the presence of other cations in comparable concentrations and this influence depends on the kind of cations. In cases investigated by us the influence was smaller when sediments were saturated with nickel (II) ions ($92-96^{0}/_{0}$) and greater when they were saturated with copper (II) ions ($85-92^{0}/_{0}$).

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