Preliminary characteristics of some bottom sediments of the Baltic Sea*

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Abstract

Ten bottom sediments of the Baltic Sea have been investigated by the differential thermal analysis (DTA), thermogravimetry (TG) and X-ray diffraction method as well as by the Baline's method of measurement of specific surface area. On this basis the percentage of organic matter and the mineral composition of the sediments have been established. The results have been supplemented by elemental analyses.

1. Introduction

Chemical and physico-chemical processes occurring among trace elements residing in sea water and bottom sediments are of paramount importance in marine chemistry. The results of our previous [10] laboratory studies on the sorption and desorption of certain transition metal ions have shown that these processes are dependent on the nature of sediment, ion and conditions under which the study is carried out.

Sorption properties can be displayed by both organic and mineral components of the sediments. It would be of interest to demonstrate which components and to what extent are responsible for the sorption and desorption of trace elements. To do this, components of the bottom sediments, tested simultaneously for their sorption activity, should be identified [10].

Organic compounds [7] occurring in bottom sediments, consisting mostly of humic acids, are capable of chelate formation with trace metals at pH around 8. The chelates have various stability constants.
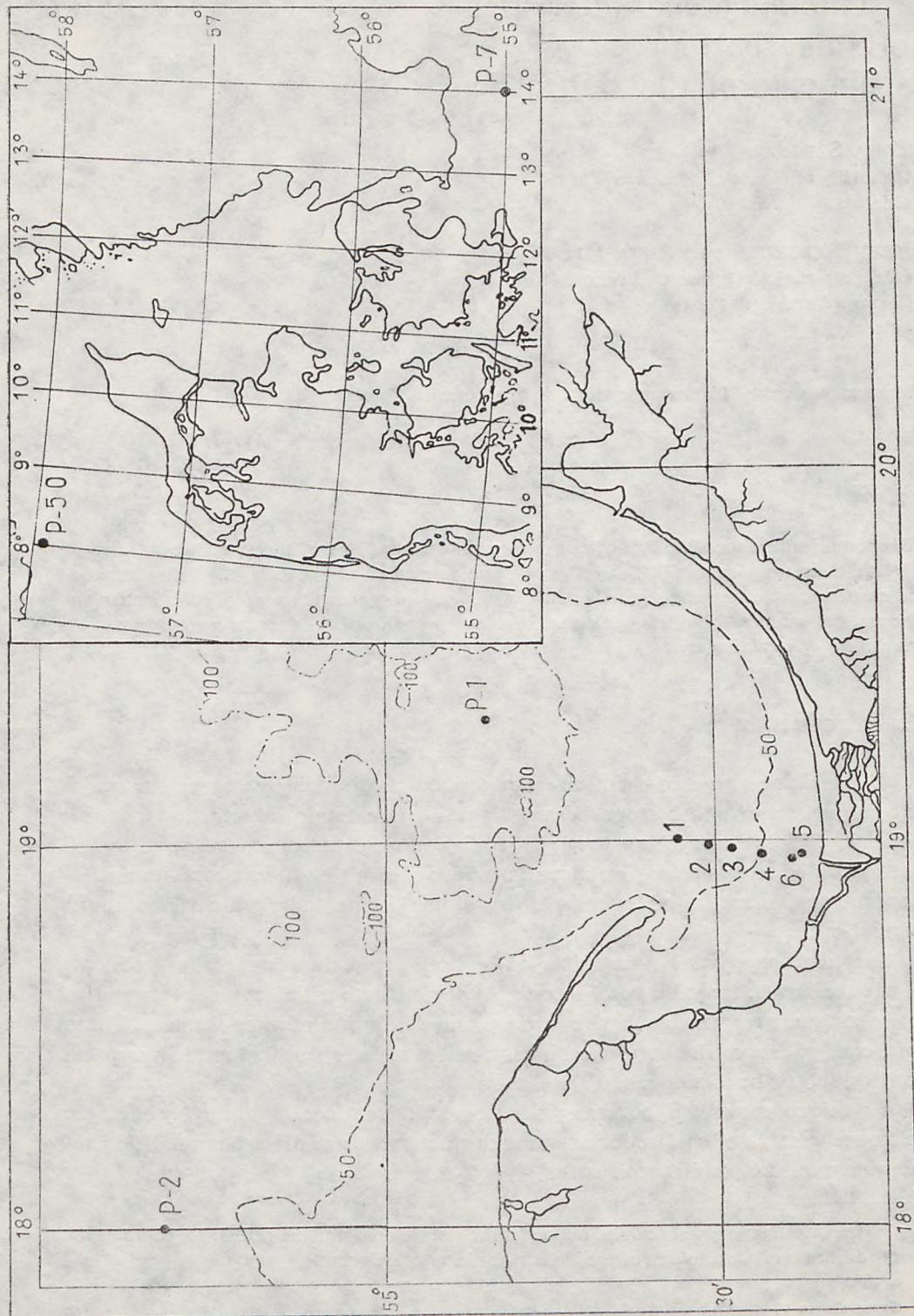
Fig. 1. Sampling sites

Among minerals constituting marine bottom sediments one can distinguish quartz and clay minerals such as montmorillonite, illite, micas, chlorite and kaolinite [8].

Quartz (SiO_2) consists of the SiO_4^{4-} tetrahedra dislocated in the elementary unit cell. Its sorption capacity depends on the orientation of the edges of outer tetrahedra carrying hydroxyl groups.

Clay minerals include layer-type aluminosilicates of differentiated chemical composition and structure. They are distinguished by specific properties such as high hydrophilicity, plasticity, ability to adsorb and exchange ions, etc. These all properties are governed by the internal structure. Ionic structures consist of two layers, tetrahedral and octahedral. The basic feature of the tetrahedral layer is a silicon--oxygen tetrahedron, and of the tetrahedral layer, an aluminium-oxygen-hydroxyl or magnesium-oxygen-hydroxyl octahedron. These layers are combined into clusters [3, 5].

From the foregoing it follows that all fundamental constituents of the bottom sediments can sorb or exchange metal ions, albeit to different extent. They can also desorb them under favourable conditions [9, 10]. These features account for the usefulness of a precise characterization of the sediments.

2. Experimental

2.1. Materials

Bottom sediments of the Baltic Sea analyzed here were marked with numbers 1 through 6 (the Gulf of Gdańsk), P-1, P-2, P-7 (open sea) and P-50 (Skagerrak). Sampling sites are shown in Figure 1.

Table 1. Geographical co-ordinates of the sampling sites and their characteristics

Sample designation	Geographical co-ordinates of the sampling site		Hygroscopic water content [%]	Carbonate content
	Lat. (N)	Long. (E)		
1	54°33.1'	19°00.4'	4.55	−
2	54°30.4'	18°59.5'	3.38	−
3	54°28.2'	18°58.9'	3.48	−
4	54°26.1'	18°58.3'	2.26	−
5	54°22.4'	18°57.9'	5.30	−
6	54°23.0'	18°57.4'	4.93	−
P−1	54°50.0'	19°20.0'	6.50	−
P−2	55°17.5'	18°00.0'	5.70	+
P−7	55°00.0'	14°05.0'	2.31	−
P−50	57°56.0'	08°00.0'	4.65	++

−   1 - 3% $CaCO_3$,
+   3 - 5% $CaCO_3$,
++   more than 5% $CaCO_3$

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Table 1 lists positions of the sampling sites, the content of hygroscopic water in air-dried samples and the results of testing for carbonates.

Both the manner of sampling and the preparation of the samples for investigations have been reported elsewhere [2, 8].

Organic matter contained in the bottom sediments made difficult recognition of other components in thermal analysis due to a very strong and broad exothermic peak. It also masked other minerals in the X-ray diffraction patterns. To improve the legibility of the results, before taking the X-ray spectrograms, the samples had been digested with a 30% hydrogen peroxide solution to destroy organic matter.

2.2. Equipment and analyses

Simultaneous differential thermal analysis (DTA) and thermography (TG) runs were made using derivatograph of the firm MOM, Budapest. The sample (200 mg) was heated at a rate of 10 deg/min, in static air, using the DTA sensitivity of 1/5.

The specific surface area was determined by the Blaine's method [4], the surface area of the sample being compared with that of the reference sample.

The qualitative mineral composition of the bottom sediments was estimated by the X-ray diffraction method by using a DRON 2 apparatus (U.S.S.R.) [11].

An automatic CHN analyzer (Carlo-Erba) has been applied also.

3. Results and discussion

Thermal methods of analysis enable to estimate changes occurring in sample with increasing temperature on the basis of endothermic and exothermic processes (DTA) and of the loss in weight (TG).

A typical DTA curve of bottom sediments enable to discern:

(i) an endothermic effect over the range $20 - 160°C$ associated with the loss in weight due to humidity;

(ii) exothermic effect over the range $200 - 500°C$ associated with the loss in weight due to pyrolysis and combustion of organic matter;

(iii) a slight endothermic effect over the range $570 - 590°C$ due to polymorphic transformation of β-quartz to α-quartz.

Heating of the samples to higher temperatures was considered useless, as the curves would have indicated overall changes occurring in mineral components. Their recognition is better by, for instance, the X-ray diffractometry.

The organic matter is characterized by an exothermic effect over the range $160 - 600°C$. The magnitude of this effect, together with characteristic points on the DTA curve, may indicate rough differences in the amount and composition of organic matter.

Organic matter appears to play an important or even decisive role in sorption phenomena of bottom sediments. For this reason an attempt was made to classify the

sediments into three basic groups on the basis of the magnitude of the exothermic effect in the temperature range indicated.

One of the groups includes sediments labelled 4, P-2 and P-50 (Fig. 2). A characteristic feature of this group is a weak exothermic effect with a characteristic temperature of 290—310°C. As the effect is well-shaped one may speculate that it is due to one type of organic compounds or to a group of compounds of similar structure.The group of these compounds predominates in the organic portion of the bottom sediments.

The second group of sediments is characterized by a stronger thermal effect (Fig. 3). This group includes samples no. 1—3,5 and 6. Another characteristic feature of this group are two distinct peaks within 280—300 and 410—420°C. One may thus conclude that the organic matter of these sediments consists of two groups of compounds of similar structure. Compounds with the characteristic pyrolysis peak of 280—300°C occur in larger amounts than those with the pyrolysis peak of 410 — 420°C. The presence of the latter compounds in the first group of the previously discussed sediments is supported by the DTA curves, although the corresponding effect is weak.

The third group of sediments includes samples P-1 and P-7 characterized by strong exothermic effects and of similar shapes of the DTA curves (Fig. 4). In this group of sediments the basic thermal effect occurs over the range 280 — 310°C. The DTA curves suggest that organic matter includes also a group of compounds of a higher temperature of pyrolysis, their amount being, however, much smaller than that in the two preceding groups of sediments.

As it was impossible to separate organic components from the bottom sediments, their characteristics has been given with reference to all sediments. In Table 2 the magnitude of the exothermic effect over the range 140 — 160°C is given.
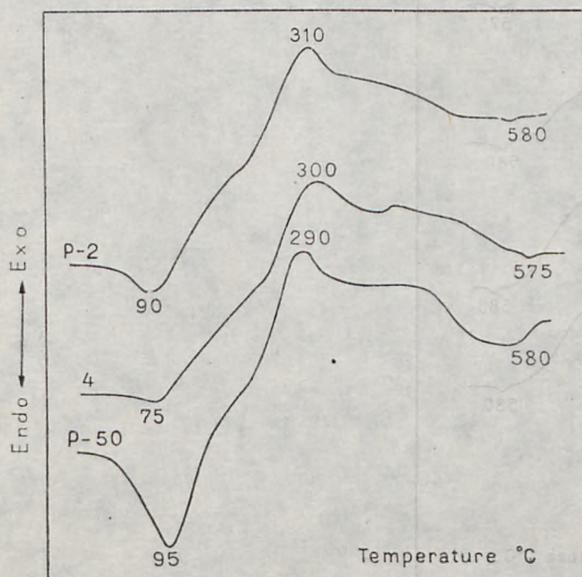
Fig. 2. DTA curves of samples 4, P-2 and P-50

As predicted, samples P-1, P-7, 1 2, 3, 5 and 6 gave the largest thermal effects. Sample 4, taken in the Gulf of Gdańsk, had a very low content of organic matter, hence its thermal effect differs from those of the remaining samples.

The thermal investigations were supplemented by the measurement of the loss in weight of air-dry samples from the TG curves (Table 3). The loss over the range 20 — — 140°C corresponds to sample humidity. A difference between this loss for air-dry samples stored under identical conditions during about 6 months corresponds to the water sorption capacity of these sediments. This sorption depends mostly on the specific surface area of samples, and indirectly and additionally on the chemical and mineral composition.

It might be predicted that sample 4 would have the smallest specific surface, while sample P-1 the largest specific surface. The loss of humidity upon heating manifests itself in the DTA curve in an endothermic effect with a peak over the range 75 — 100°C.
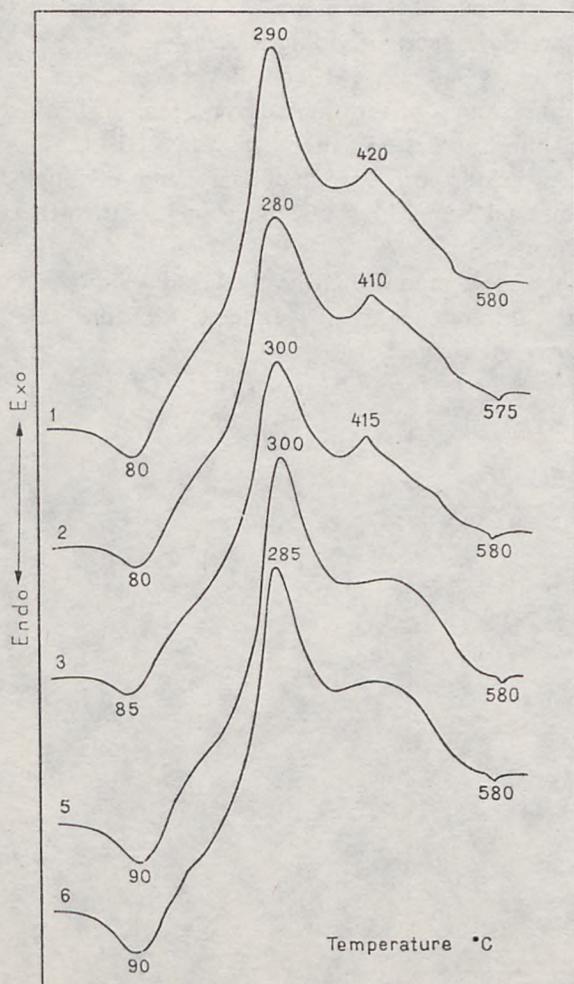
Fig. 3. DTA curves of samples 1 — 3, 5 and 6
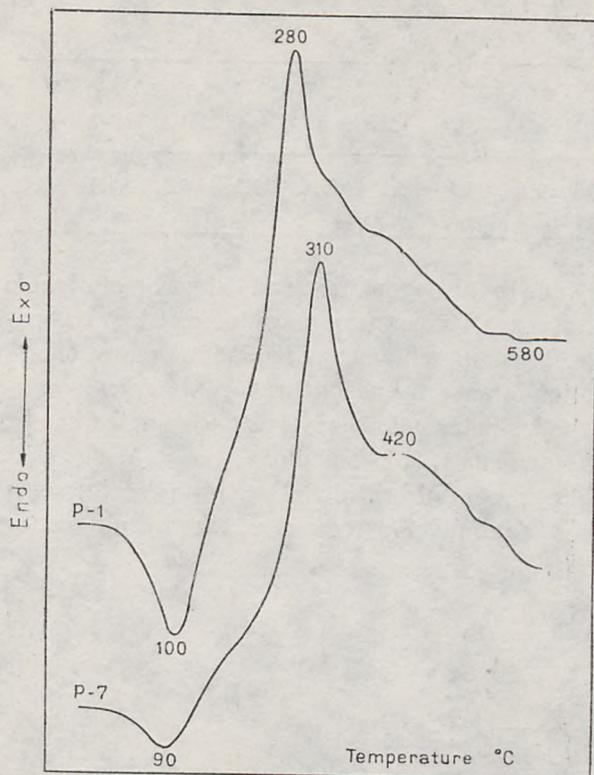
Fig. 4. DTA curves of samples P-1 and P-7

The loss in weight within 140 — 160°C is due to the degradation and oxidation of organic matter, these giving exothermic response in the DTA curves, and to further loss in humidity, dehydration and dehydroxylation which are endothermic processes. Thermogravimetric investigations give over-all results. The DTA curves indi-

Table 2. Magnitudes of the exothermic effects over the temperature range 140 — — 600°C

Sample designation	Exothermic effect [J/g]
1	1654
2	1631
3	1507
4	1036
5	1825
6	1713
P-1	2732
P-2	1177
P-7	2096
P-50	1183

Table 3. Loss in weight of the samples

Loss in weight [%] within the temperature range	Sample designation									
	1	2	3	4	5	6	P-1	P-2	P-7	P-50
20−140°C	4.5	4.0	3.5	2.5	5.5	5.5	21.5	9.5	5.0	8.0
140−600°C	9.3	7.5	7.0	4.5	9.5	22.5	22.5	10.0	21.5	11.8

cate that the loss in weight is mostly due to the degradation and oxidation of organic matter. This process predominates over the temperature range indicated. A comparison of samples 4, P-2 and P-50 of a comparable magnitude of the heat effects (Table 2) suggests, that the contribution of water to the loss in weight is larger in samples P-2 and P-50 than in sample 4. A similar statement relative to sample 6 can be expressed in relation to a group of sediments 1, 2, 3, 5 and 6.

An additional confirmation of the amount of organic matter in the sediments is their elemental analysis giving a more accurate chracteristics of the organic matter (Table 4).

Table 4. Results of elemental analyses

Sample designation	Content of chemical elements		
	C	H	N
1	4.3	1.04	—
2	3.4	0.87	—
3	3.5	0.86	—
4	2.6	0.73	—
5	4.3	1.00	—
6	4.6	1.07	—
P-1	4.4	1.3	1.0
P-2	2.1	0.5	0.9
P-7	5.3	1.0	1.3
P-50	3.3	1.12	—

Sediments P-1, P-2 and P-7 contain nitrogen which is supposedly present in amino groups. The remaining sediments are free of nitrogen. The richest in carbon is sediment P-7, sediments 6 and P-1 being somewhat poorer, and P-2 is the poorest in this element.

To arrive at a better legibility of measurements, qualitative X-ray analysis of the non-digested and digested samples was carried out. Recognizable were those constituents of the sediments whose percentage exceeded 3 based on the digested sample weight. The main mineral component of all samples was quartz. Further, felspars and illite as a representative of clay minerals were identified. The results of this investigation are shown in Table 5.

Relative amounts of a particular mineral show that the poorest in quartz and felspar are samples P-1 and P-50. Illite is missing in sample P-1. Montmorillonite occurs in sample 4 only. A characteristic feature of the bottom sediments is their grain

Table 5. Qualitative X-ray spectrographic evaluation of the mineral composition of the bottom sediments

Sample designation	Quartz	Felspars	Illite	Montmorillonite
1	+++	++	+	−
2	+++	+	+	−
3	+++	++	++	−
4	+++	++	++	+
5	+++	++	+	−
6	+++	+++	+++	−
P-1	+	+	−	−
P-2	+++	++	+++	−
P-7	++	++	+	−
P-50	+	+	+	−

+++ High content,
++ low content,
+ very low content,
− missing

Table 6. Specific surface area of the bottom sediments

Sample designation	1	2	3	4	5	6	P-1	P-2	P-7	P-50
Specific surface area [cm²/g]	4310	3380	3240	2040	4410	3510	7420	5510	5940	4500

size distribution. Owing to the small grain size of the samples and their content, this parameter was evaluated from the measurements of the specific surface area (Table 6).

The intensity of all surface phenomena, including sorption, depends on the subdivision of the particles. The experimental evidence suggests that in this respect the most active should be sample P-1 and the least active sample 4. These results largely support the earlier finding that the humidity of air-dry samples, due to sorption of water, is dependent on the specific surface area. Samples 4 and P-1 have the smallest and the largest specific surface areas, respectively, and possess correspondingly the lowest and the highest humidity (Table 3).

The open-sea sediments (P-1, P-2, P-7 and P-50) have markedly larger specific surface area as compared with those from the Gulf of Gdańsk. Among the latter, sample 4 has the smallest specific surface area.

References

1. Blazek A., 1973, *Thermal Analysis*, Van Nostrand Reinhold Co., London.
2. Bojanowski R., Podwalska-Sobiecka H., Szponar Z., 1979, *Określenie właściwości sorpcyjnej osadów dennych w stosunku do wybranych jonów metali alkalicznych i ziem alkalicznych*, Stud. i Mater. Oceanolog. KBM PAN, 25.

3. Grabowska-Olszewska B., 1980, *Metody badań gruntów spoistych*, Wyd. Geol., War-
szawa.
4. Lehmann H., Koltermann A., 1961, *Die Messung der Specifischen Oberfleische mit
dem Gereit von Blaine*, Tonindustrie Ztg., 10, p. 233.
5. Pempkowiak J., 1975, *Substancje humusowe w morskich osadach dennych*, Stud. i Mater.
Oceanolog. KBM PAN, 8.
6. Popiel B., 1980, *Wpływ kationów wymiennych na mechanizm adsorpcji polarnych związków
organicznych na montmoryllonicie*, Wiad. Chem., 34.
7. Riley J. P., Chester R., 1971, *Introduction to Marine Chemistry*, Acad. Press, London—
—New York.
8. Stoch L., 1974, *Minerały ilaste*, Wyd. Geol., Warszawa.
9. Szponar Z., Bojanowski R., Podwalska-Sobiecka H., 1979, *Określenie właści-
wości sorpcyjnych osadów dennych w zależności od pH środowiska*, Stud. i Mater. Oceanolog.
KBM PAN, 26.
10. Szponar Z., Bojanowski R., *Własności sorpcyjne osadów dennych w odniesieniu do
niklu, miedzi i kobaltu*, (in preparation).
11. Thorez J., 1975, *Phyllosilicates and Clay Minerals*, Editor G. Lelette, Dison.