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EXAMINATION OF CONTEMPORARY LAKE SEDIMENTS BY MEANS OF THERMAL ANALYSIS
The Dabie lake near Szczecin

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Abstract

An attempt was made to use thermal analysis (DTA, TG, DTG) for identification of the mineralogical composition of contemporary lake sediments. Sediments were investigated both in the natural state and after ignition at 300°C. Selected fractions of the sediments in the natural state were also studied. The thermoanalytical curves of mollusca shells, reed and plankton were also recorded for use in the interpretation of the thermoanalytical curves of sediments.

Keywords: chemical composition, Dabie lake, mollusca, north-west of Poland, Odra river estuary, plankton, reed, sediments, thermal analysis (DTA, TG, DTG)

Introduction

Contemporary lake sediments are mixtures of two phases: an organic and an inorganic phase. The way of separation of the sediments into these two phases is determined theoretically in limnology, but actually various techniques are employed, depending on the objective of an examination. For many years the method of determination and elimination of the organic matter contained in sediments has stirred up disputes [1]. This paper constitutes an attempt to determine the mineralogical and petrographic composition of contemporary lake sediments on the basis of thermal analysis supplemented by chemical and X-ray structural analyses.

Investigation area characteristics

The Dabie lake is situated in the lower Odra River Valley (in the north-west of Poland) in the region of the Odra river estuary and in the close neighbourhood of the Szczecin agglomeration. The geographic coordinates of the lake centre are as follows: $\Phi=53^{o}27'$; $\lambda=14^{o}40'$. In terms of the area which covers 56 km^2, the Dabie lake takes fourth place among the Polish lakes [2]. The lake subjected to investigations can be classified as a shallow and polymictic reservoir. The average depth is 2.7 m [3].

The Dabie lake constitutes the last inland element of the estuarial complex of the Pomorska Gulf and Szczeciński Lagoon [4], (Fig. 1). This is an open type lake with

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a river flowing through it, rinsed very intensively by the waters of the Regalica river. At the same time it acts as a transitional accumulation reservoir for a major part of the Odra river waters. It is characterized by an extremely intensive exchange of the

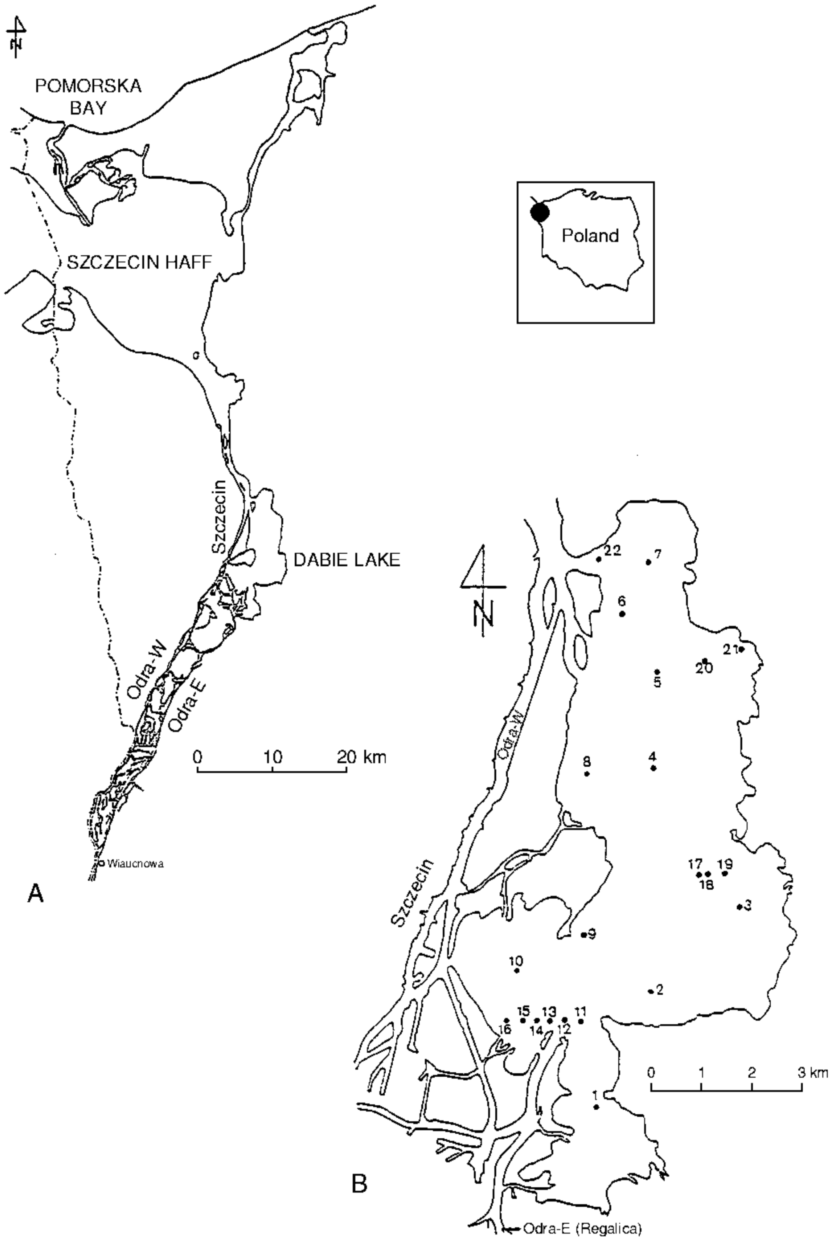

Fig. 1 The investigation area: A – the Odra river estuary, B – the Dabie lake: locations where the sediments' samples were taken

river waters, over fifty times a year. The rate of formation of bottom sediment calculated on the basis of comparing the Dabie lake bathymetric maps drawn in 1963 and 1981 indicates a range varying from 1.05 to 2.63 cm per year.

Material and method

The sediment samples were taken with the help of a Van Veen type sampler in late July and early August in 1988 and 1992 (Fig. 1). Determination of the mineralogical and petrographic composition was carried out for the fraction above 2 mm (22 samples).

Thermal analysis was made by means of a Derivatograph Q-1500 D (MOM Hungary). Curves were obtained of the particular sediment fractions: 1–2; 0.5–1.0; 0.25–0.50; 0.125–0.25; 0.063–0.125 and below 0.063 mm for 12 samples: samples No. 11 to 22. For 10 samples with size grade below 2 mm, samples No. 1 to 10, curves were obtained for the material both in the natural state and after ignition of the samples at a temperature of 300°C to a constant mass (for approximately 4 h). Thermal analysis was also carried out for samples of mollusca shells, plankton and reed. Thermal analysis was made under the following constant conditions – TG: 200 or 100 mg, DTA and DTG: 500 μV, heating rate: 10°C min^{-1}, atmosphere: air. Ceramic crucibles were used throughout the study. The masses of particular samples are given in the figure legends.

Supplementary X-ray structure investigations of the sediment and mollusca shell samples were carried out with a HZG-4 X-ray diffractometer (Germany).

Chemical analyses were made with a plasma spectrometer made by BAIRD (the Netherlands). Mercury was determined by means of a hydride generator (cold-vapour method) and the organic carbon content by means of the conventional Tiurin method.

Sediment characteristics

In this paper ‘sediments’ mean semi-liquid black sapropel muds which if dried, take on a khaki colour. In many locations within the lake the sapropel muds resemble formations of a gytia type. There is a considerable amount of recognizable parts of plant and animal origin present in them, mainly mollusca shells. Locally in isolated parts of the lake, where the pH of the sediments is strongly acid and organic life hardly develops and there is plenty of organic matter, very black and clammy sapropel muds can be observed with a distinct smell of H_2S. Moreover, locally sandy formations can be discovered. Most likely their presence is connected with silting works.

Mollusca shells represented mainly by the Dreissena polymorpha shells as well as a vegetable detritus (Table 1) prevail in the sapropel sediment fraction above 2 mm. The share of other components is smaller.

In the classification given in [5] the sapropel muds of the Dabie lake are represented by:

– clay muds (samples No. 1, 4, 5, 10),
– sandy clay muds (samples No. 2, 3, 7, 8, 9).

Table 1 Average composition of the Dabie lake sediment fraction above 2 mm (22 samples)

Organic components:	Average/%	Range/%
1. Dreissena polymorpha shells	57.0	0–95.7
2. Mollusca shells except D. polymorpha	9.6	0–50.8
3. Mollusca shells fragments	11.0	0–76.1
4. Wood, stem and foliage fragments, seeds	18.1	0.1–98.6
5. Fish scales, bone fragments, snail operculums, byssus	1.7 0.2	0–20.0 0– 1.6
6. Chironomidae	0.1	0– 0.4
7. Oligochaeta	0.1	0– 0.1
8. Ostracoda		
Mineral components: quartz, feldspar, quartzite, granite, slag, charcoal, coal, peat	2.2	0–20.0
Total	100.0	

Results

Apart from thermal effects attributed to various minerals, the burning of organic matter is manifested very distinctly in the thermoanalytical curves of the Dabie lake sediments. Therefore over a dozen thermal analyses were made of the materials containing mollusca shells and vegetable debris and plankton, thus obtaining ‘pattern’ curves useful in the interpretation of the curves of the sediments.

Molluscs

In the DTG curve of Dreissena polymorpha shell the mass decrease related to the sample dehydration taking place at the temperature up to 145°C with the maximum at 90°C, can be observed as the first process. The second effect related to the burning of organic matter (conchiolin) appears as an asymmetric peak (within the range from 145 to 560°C) with a distinct maximum at 295°C and a less distinct one at 450°C. The decomposition of $CaCO_3$ occurs in the range from 560 to 920°C with the maximum at 900°C. In the DTA curve the burning of conchiolin indicated by a wide exothermic range with a distinct maximum at 460°C and a less distinct one at 305°C. The decomposition of $CaCO_3$ is accompanied by a wide asymmetric endothermic effect with the maximum at 905°C (Fig. 2). The average organic matter content of Dreissena polymorpha shells in the Dabie lake is 2.8% and the $CaCO_3$ content is 94.6%. The concentration of $CaCO_3$ in the shells of this species depends on their length and the $CaCO_3$ content increases by 0.21% per each 1 mm increase in the shell dimensions. The opposite trend was observed for the organic matter: when the organic matter content decreased by 0.047% per each 1 mm increase in the shell dimensions [6].

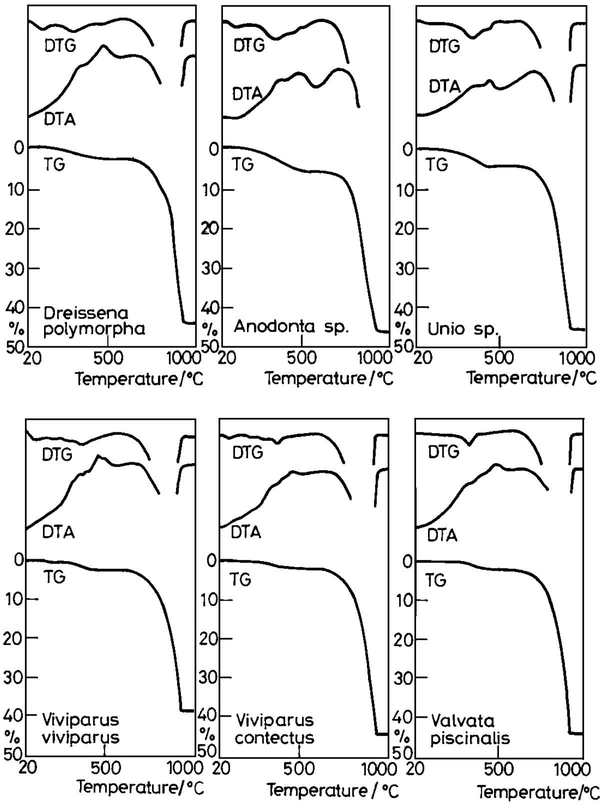

Fig. 2 Thermoanalytical curves of mollusca shells. Experimental conditions: m_s=400 mg, TG: 200 mg, DTA and DTG: 500 μV

The curves of other taxons, both bivalves and snails, are similar in terms of the effects related to the dehydration and decomposition of $CaCO_3$. Greater differences occur only for the effects related to the burning of organic matter. The ratio of the two main components, i.e. organic matter and $CaCO_3$ in the mollusca shells differs for each particular species (Table 2). In the mollusca shells, both bivalves and snails, calcium carbonate can be found in the form of aragonite.

Plankton

For the plankton a considerable mass decrease related to sample dehydration is shown by the DTG curve. The process takes place up to 245°C with the maximum at 128°C. The burning of organic matter occurs in the range from 245 to 880 with the maximum at 275°C. In the DTA curve a great endothermic effect with the maximum at 140°C corresponds to the dehydration and a wide exothermic range corresponds to the burning of organic matter up to a temperature of 875°C and within this range two smaller but distinct effects occur at 412 and 455°C (Fig. 3).

Table 2 Organic matter and $CaCO_3$ (mass%) contents of mollusca shells from the Szczecińki Lagoon (on the basis of thermal analysis)

	Organic matter	$CaCO_3$
Theodoxus fluviatilis	2.2	96.9
Viviparus viviparus	3.2	95.1
Viviparus contectus	1.8	96.2
Valvata piscinalis	2.2	93.9
Bithynia tentaculata	1.6	96.6
Lymnaea stagnalis	1.6	96.6
Lymnaea peregra	2.0	96.4
Lymnaea auricularia	1.6	97.3
Planorbarius corneus	2.4	95.7
Unio tumidus	4.4	94.6
Unio pictorum	5.0	93.0
Anodonta anatina	4.8	93.5
Anodonta cygnea	4.8	93.0
Dreissena polymorpha	2.8–3.3	94.6–96.2
Dreissena polymorpha*	1.6	97.3

* after a partial removal of conchiolin 10% KOH

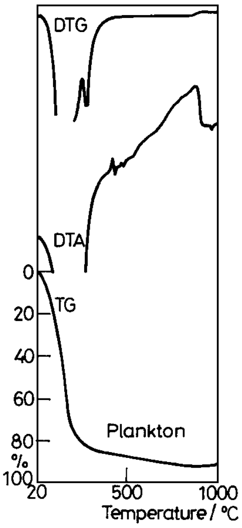

Fig. 3 Thermoanalytical curves of planktons. Experimental conditions: m_s=1000 mg, TG: 1000 mg, DTA and DTG: 500 μV

Reed

For the reed sample the DTG curve shows that dehydration takes place up to 155 with the maximum at 90°C. The burning of organic matter occurs up to 800 with two strong effects at 260 and 305°C. In the range from 800 to 905°C the decomposition of $CaCO_3$ is indicated. In the DTA curve a very distinct exothermic peak with the maximum at a temperature of 365°C corresponds to a considerable mass decrease related to a rapid burning of the organic matter. Above this temperature and up to 900°C another large exothermic peak appears connected with considerably smaller mass decrease. The $CaCO_3$ decomposition of $CaCO_3$ is shown as a small depression at a temperature of 855°C (Fig. 4).

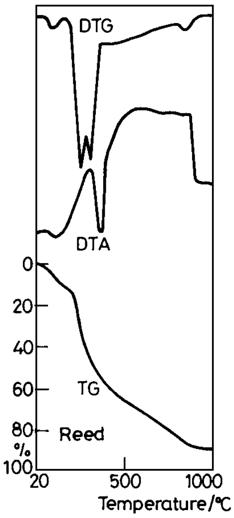

Fig. 4 Thermoanalytical curves of reeds. Experimental conditions: m_s= 200 mg, TG: 200 mg, DTA and DTG: 500 μV

Sediments

In the DTA curves of the clay muds from the Dabie lake sediments (Fig. 5: samples No. 1, 4, 5, 10) a wide exothermic effect appears within the range from 150 to 780–900°C. Within the limits of this effect smaller endothermic depressions can be observed at the following temperatures: (1) 290 to 355°C, (2) 505 to 515°C and (3) 300 to 805°C. The endothermic effect at 505–515°C is caused by the dehydroxylation of clay minerals. The presence of an endothermic depression at 800–900°C in some curves as well as a dome-shaped exotherm appearing between 900 and 1000°C might indicate the presence of potassium alumino-silicate. The effect at a temperature between 700 and 805°C is caused by the decomposition of $CaCO_3$. The DTG curves indicate a mass decrease caused by the dehydration of the sample which occurs up to 170–190 with the maximum at 95 to 140°C. The burning of organic matter occurs up to 640–730°C and produces a wide and asymmetric effect with a maxi-

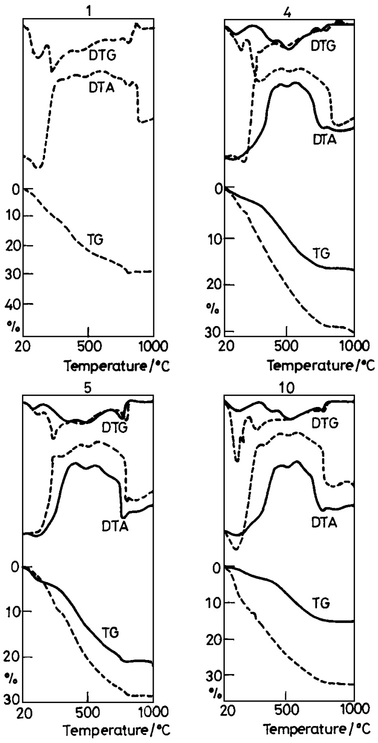

Fig. 5 Thermoanalytical curves of clay mud, fraction <2 mm. The dashed line stands for a sample in the natural state; the solid line stands for a sample previously heated at a temperature of 300°C. Experimental conditions: m_s (natural state)=1: 400 mg, 4: 350 mg, 5: 300 mg, 10: 327 mg; m_s (sample previously heated at a temperature of 300°C)=4, 5, 10: 350 mg, 1: not analysed, TG: 200 mg, DTA and DTG: 500 μV

mum between 230 and 258°C. It is probably caused by the burning of the plant detritus (see the curve of reed). The second and less distinct effect appears at a temperature between 475 and 500°C and is caused by the dehydroxylation of clay minerals. The decomposition of $CaCO_3$ takes place in the temperature range from 710–780 to 800–850°C with the maximum at 780 to 805°C. Despite the predominant effects connected with the burning of organic matter, the presence of goethite and gypsum may be assumed in the sediments studied. The presence of goethite is indicated in some curves by an endothermic effect at about 300°C. The mass decrease in the DTG curve is less distinct because it is included in the main effect of the burning of organic matter (e.g. sample No. 1). A small fold in the DTA curve at about 160°C and a bipartite effect of the mass decrease in the DTG curve may evidence the presence of gypsum (e.g. the sample No. 10). The observed mass gain at a temperature of almost 900°C (e.g. for sample No. 1) is most likely the result of the oxidation of Fe^{2+} to Fe^{3+} [7]. The thermal curves of the same sediments which had been ignited at 300°C to a constant mass (for about 4 h, marked with dotted curves in the figures)

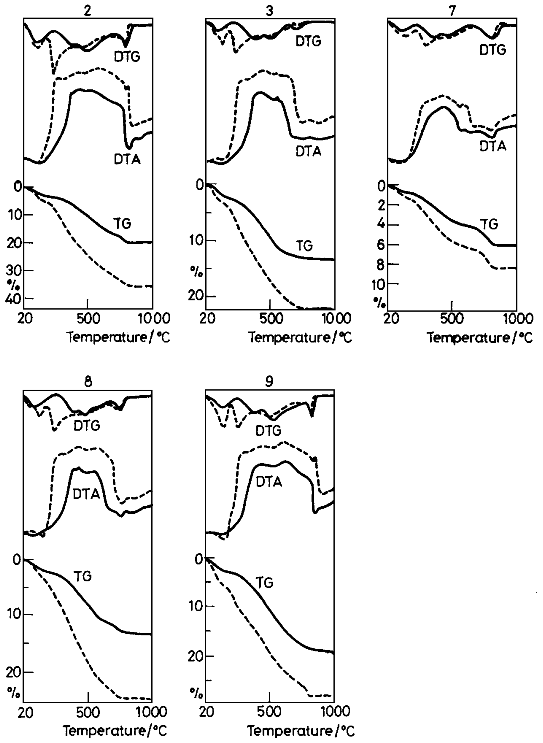

Fig. 6 Thermoanalytical curves of sandy clay mud, fraction <2 mm. The dashed line stands for a sample in the natural state; the solid line stands for a sample previously heated at a temperature of 300°C. Experimental conditions: m_s (natural state)=2, 3: 300 mg, 7: 700 mg, 8: 311 mg, 9: 332 mg; m_s (sample previously heated at a temperature of 300°C)=2: 372 mg, 3: 350 mg, 7: 701 mg, 8, 9: 350 mg, TG: 200 mg, DTA and DTG: 500 μV

first of all show narrower exothermic effects connected with the burning of organic matter. In the DTA curves the exothermic effects occur at temperatures from 200 to 740–755°C. The decomposition of clay minerals is indicated by a depression of the exotherm at a temperature of 500 to 515°C. The decomposition of $CaCO_3$ appears as an endothermic peak at 750 to 780°C. In the DTG curves the dehydration of the sample is shown to occur up to 200–250°C with the maximum at 95–100°C. The burning of organic matter takes place up to 650 to 700°C with the maximum at 350 to 400°C. In this wide range of mass decrease the dehydroxylation of clay minerals is shown as an inserted effect at 495 to 510°C. The decomposition of $CaCO_3$ takes place in the temperature range from 650–700 to 800°C with the maximum at 740 to 775°C. The mass loss connected with the burning of organic matter as well as with the decomposition of clay minerals is 18.7–22.7%. The mass change connected with the dehydroxylation of clay minerals calculated for the range of 400 to 600°C, is 7.0–8.5%. The mass decrease due to the dehydroxylation of potassium alumino-silicate in this temperature range is 4% [7]. The comparison of these two values reveals that the decomposition of clay minerals takes place simultaneously with the burning of organic matter and, in consequence, the mass decrease is the resultant of these two processes. The $CaCO_3$ content of the sediments studied is 1.1–4.8%. For the ignited samples the mass decrease connected with the burning of organic matter is 10.9–14.0% corresponding to 57–61% of the value calculated for the samples in the natural state.

The thermoanalytical curves of sandy clay muds (samples No. 2, 3, 7, 8, 9) show similar thermal effects to those described above (Fig. 6). In the curves of the samples in the natural state the burning of organic matter is indicated by a wide exotherm in the temperature range from 200 to 650–850°C. The dehydroxylation of clay minerals is manifested by a small depression within the range of the exotherm at temperatures between 470 to 505°C. The decomposition of carbonates takes place in the temperature range 730–800°C and is indicated by a distinct endothermic peak. For samples with lower share of organic matter, a quartz peak appears in the DTA curves at 565–580°C. The DTG curves indicate that the dehydration of the samples takes place up to 190–200 with the maximum between 100 and 150°C. The burning of organic matter takes place up to 650–700 with the maximum at 245–280°C. The dehydroxylation of clay minerals appears at 450–500°C. The decomposition of $CaCO_3$ takes place in the temperature range from 725 to 810°C. The DTA curves of the samples ignited at 300°C exotherms in the temperature range from 200–250 to 570–800°C. The dehydroxylation of clay minerals appears at 520–525°C. The decomposition of $CaCO_3$ takes place in the temperature range from 745 to 805°C. The DTG curves indicate that dehydration occurs up to 200–250°C with the maximum at 90 to 105°C. A mass decrease observed up to 620–700 with the maximum at 330 to 405°C corresponds to the burning of organic matter. Dehydroxylation takes place in the range 450–518°C. The decomposition of $CaCO_3$ takes place at 700–800°C. For samples in the natural state the mass decrease connected with the dehydration is between 1.2 and 5.7%. The mass loss caused by the burning of organic matter was found to be between 4.7 and 26.1% and the calculated $CaCO_3$ content between 1.8 and 8.6%. In the ignited samples the organic matter is between 50 and 71% of the value calculated for the samples in the natural state.

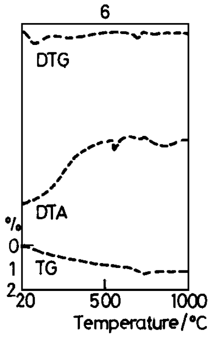

Fig. 7 Thermoanalytical curves of sand. Experimental conditions: m_s=600 mg, TG: 100 mg, DTA and DTG: 500 µV

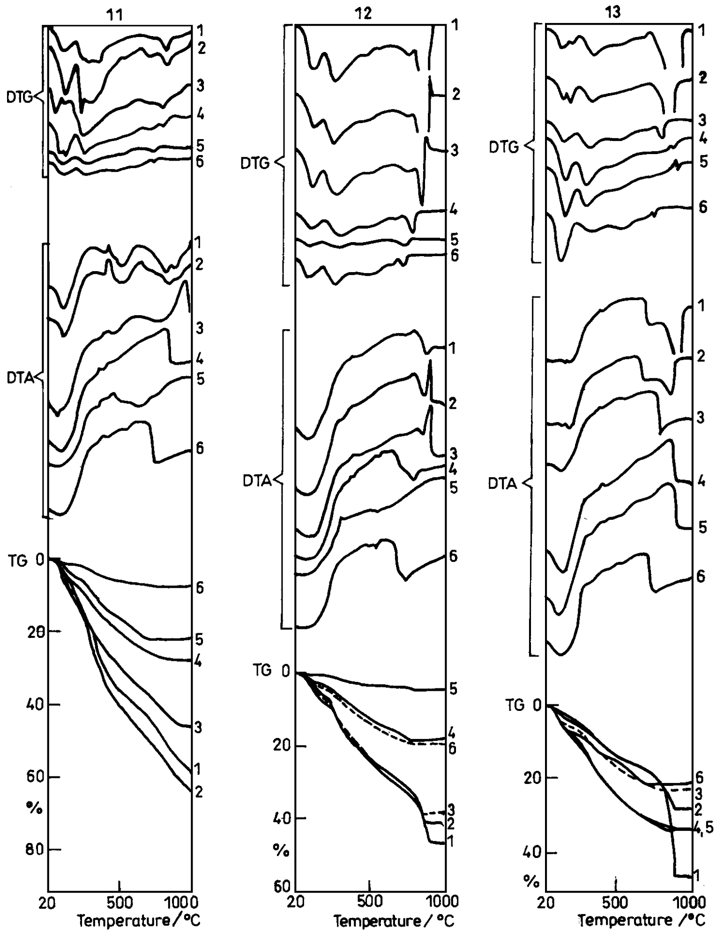

Fig. 8 Thermoanalytical curves of selected fractions of sediments: 1: 1–2 mm, 2: 0.5–1.0 mm, 3: 0.25–0.5 mm, 4: 0.125–0.25 mm, 5: 0.063–0.125 mm, 6: <0.063 mm. Experimental conditions: m_s=500 mg, TG: 200 mg, DTA and DTG: 500 µV

The curves of sand (sample No. 6) clearly indicate very small organic matter and $CaCO_3$ contents i.e. below 0.5 and 0.6%, respectively (Fig. 7).

Regularities similar to those described above can be observed for the thermoanalytical curves of selected fractions of the sediments (Figs 8, 9 and 10). The burning of organic matter is represented by a vast and asymmetric effect with the maximum between 200 and 350°C. In some samples, especially in the 0.25–0.125 mm fraction, the amount of the organic matter is so large that the burning takes place up to 1000°C with an assumed sample heating rate, of 10°C min^{-1} (e.g. samples 14, 15 and 16). In such cases the decomposition of carbonates takes place simultaneously with the burning of organic matter leading to the formation of coke at the cost of the latter. For the fractions above 0.25 mm a mass gain can often be observed at about 900°C

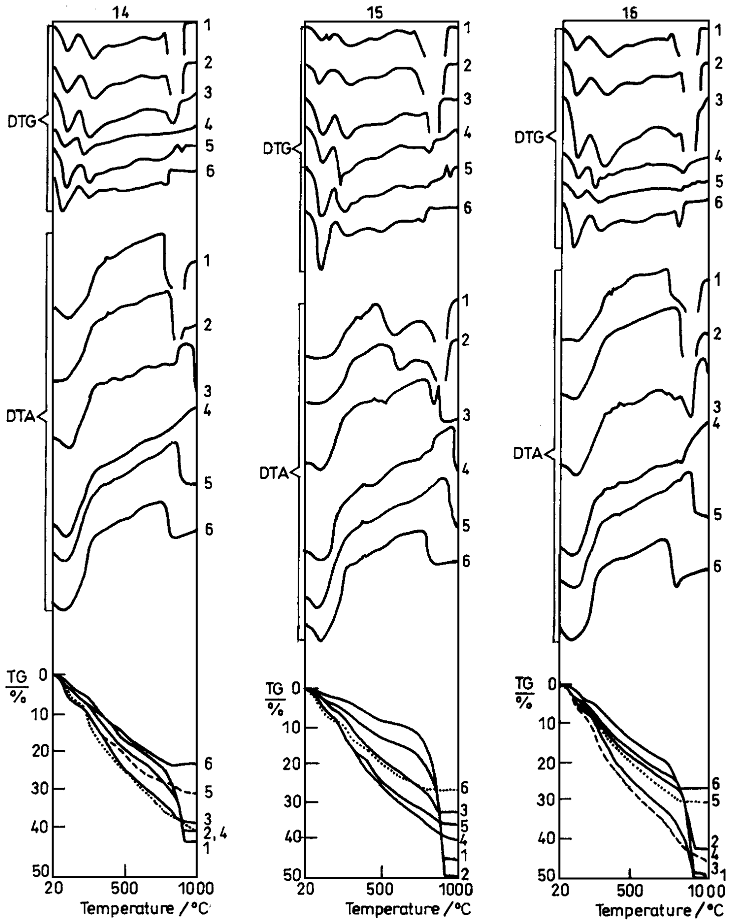

Fig. 9 Thermoanalytical curves of selected fractions of sediments. Explanation as in Fig. 8

which, as mentioned before, is most likely the result of the oxidation of Fe^{2+} to Fe^{3+}. The oxidation of Fe^{2+} to Fe^{3+} does not cause any change in the mass but on account of the oxidation, the transformation of e.g. Fe_3O_4 into Fe_2O_3 or other compounds containing Fe^{2+} into Fe_3O_4 takes place. For the size grade 0.5–0.25 mm effects can occasionally be observed that evidence the presence of iron sulphides. Then, in the fraction 0.125–0.063 mm distinct effects of the burning of coal dust can be observed. In the samples studied carbonates are probably present as $CaCO_3$ in the form of aragonite which comes from crumbled mollusca shells and is the main component of these shells. It was found in all the sediment fractions analysed. However, in the size grades above 0.25 mm a dual effect can be observed in the thermal decomposition of carbonates (e.g. samples 11, 12, 15, 16 and 22), which is caused by the decomposition of aragonite, magnesite and dolomite. The X-ray photographs of the selected grain fractions indicate the presence of these carbonates in the sediments. For the

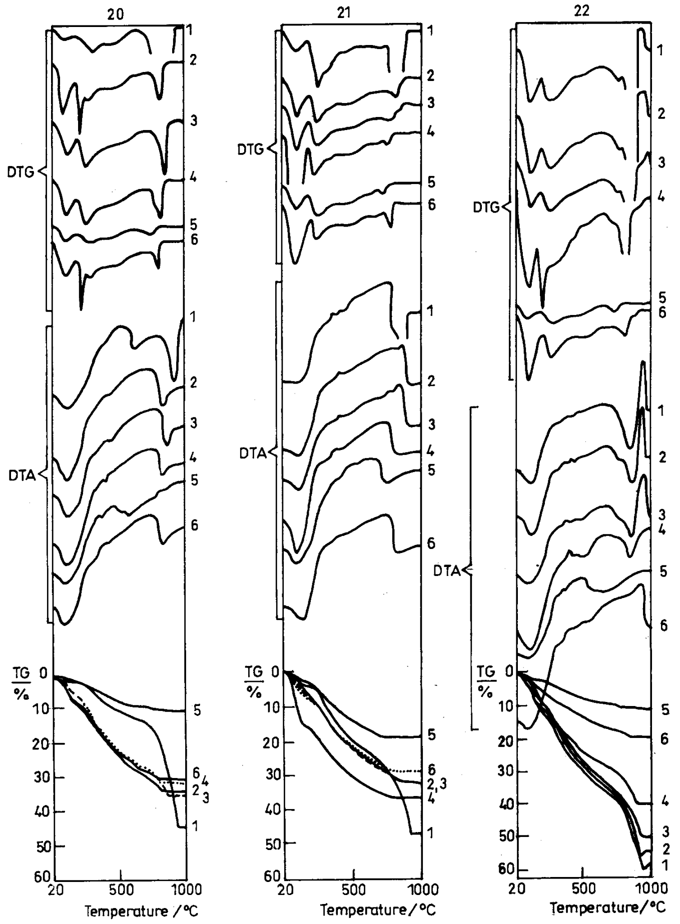

Fig. 10 Thermoanalytical curves of selected fractions of sediments. Explanation as in Fig. 8

fraction below 0.063 mm hardly any sign of the dehydroxylation of clay minerals appeared about 500°C. The approximate carbonate and organic matter contents of individual fractions of the sediments are presented in Table 3. The smaller the fraction of the sediment the lower the $CaCO_3$ content. The organic matter content was the highest in the size grade 0.25–0.125 mm and the lowest in the 0.125–0.063 mm fraction.

Conclusions

In the present work an attempt was made to use thermal analysis (DTA, TG and DTG) for the determination of the mineralogical and petrographic composition of contemporary lake sediments. Thermal analysis allowed identification and determination of the basic components of contemporary lake sediments, i.e. the organic mat-

Table 3 Average organic matter, $CaCO_3$ and $MgCO_3$ (mass%) contents depending on the fraction of the Dabie lake sediment

Fraction/mm	Organic matter	$CaCO_3$	$MgCO_3$
2–1	20.1	50.1	7.3
1–0.5	21.9	27.3	2.5
0.5–0.25	23.0	12.1	3.4
0.25–0.125	24.6	6.8	0
0.125–0.063	14.8	2.0	0
<0.063	16.0	3.4	0

ter and carbonates, and indication of the presence of clay minerals and iron compounds, gypsum and quartz. The results obtained may be used in the planning of further mineralogical and petrographic investigations aimed mainly at elaboration of ‘some patterns’ that may be useful in the interpretation of the thermoanalytical curves of fossil lake sediments. Such an attempt has been made earlier [8]. At present further thermal investigations are focused mainly on the analysis. of the organic components of lake sediments. At the first stage of these investigations special attention was paid to the thermal analysis of the contemporary fresh water mollusca shells.

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