FOLIA MALACOLOGICA
Folia Malacol. 5: 119–130
Cracow, 1993
http://dx.doi.org/10.12657/folmal.005.007

CHEMICAL COMPOSITION OF *DREISSENA POLYMORPHA* (PALLAS, 1771) SHELLS IN THE LAKE DĄBIE (WESTERN POMERANIA)

STANISŁAW PIOTROWSKI, TOM OCHMAN

Faculty of Biology, University of Szczecin, Wąska 13, 71-415 Szczecin, Poland

ABSTRACT: The paper presents results of derivatographic analysis applied to determine the basic chemical composition (organic matter and calcium carbonate) of *Dreissena polymorpha* (Pallas, 1771) shells. Derivatographic analysis was supplemented in the present study with assays of organic carbon (C_{org}), SiO_2, Al, Fe, Mg, K, Pb, Co, Zn, Cu, Ni, Cd, Mn and S in homogenised samples.

KEY WORDS: Bivalvia, Dreissenidae, shell composition, element content

Folia Malacologica 5/1993 was originally published as No. 1462 of Scientific Bulletins of University of Mining and Metallurgy, Cracow. This digitalised version was prepared by the Association of Polish Malacologists and first published on-line on December 30th, 2016.

Ministry of Science and Higher Education
Republic of Poland

This digitalised version of Folia Malacologica is funded by the Ministry of Science and Higher Education, Republic of Poland under the agreement no. 646/P-DUN/2016 allocated to the activities of disseminating science and by the courtesy of the Rector of the AGH University of Science and Technology, Cracow

STANISŁAW PIOTROWSKI, TOM OCHMAN *

Chemical Composition of *Dreissena polymorpha* (PALLAS, 1771) Shells in the Lake Dąbie (Western Pomerania)

1. Introduction

Dreissena polymorpha (PALLAS, 1771) is a bivalve common in Polish waters and is very important in aquatic communities due to its role in biofiltration and biosedimentation (e.g. STAŃCZYKOWSKA 1968, 1977, WIKTOR 1969, PIESIK 1983). For these reasons, it is important to know the chemical composition of the shell. WIKTOR (1969) touched upon that problem in his paper.

Shells of bivalves and gastropods are important in formation of lacustrine carbonate sediments. Thus the knowledge on the basic chemical composition of shells, particularly in terms of thermal properties of organic matter, of as many species as possible, will contribute to elucidation of the origins of these sediments.

The paper was aimed at determining changes in chemical composition of *Dreissena polymorpha* shells in relation to their length, and at presenting statistical relationships between the chemical components and shell length as well as between various components themselves. An attempt was also made to relate shell chemistry to that of unconsolidated lacustrine sediments *Dreissena* populations dwell on.

2. Material and methods

Materials were collected, with a vanVeen grab operated on board the SNB-1 motor boat, from the bottom of the Lake Dąbie in late July/early August 1988.

Well preserved shells (i.e. devoid of any sign of a mechanical damage) of dead bivalves were selected for the analysis. The shells were thoroughly rinsed in distilled water, fouling organisms and sediment remains being carefully removed. As the shells tended to break down in two halves, these were taken for the analyses. The clean shells were dried at 105°C to constant weight, which took about 4 h. Then the shells were divided into length classes, each class containing the same number of left and right halves; the same number of shells was ascribed to each length interval (0.1 mm). The samples were subsequently weighted to obtain the mean shell weight in a length class. The length classes up to 20 mm contained 100 shell halves each,

* Stettin University, Szczecin

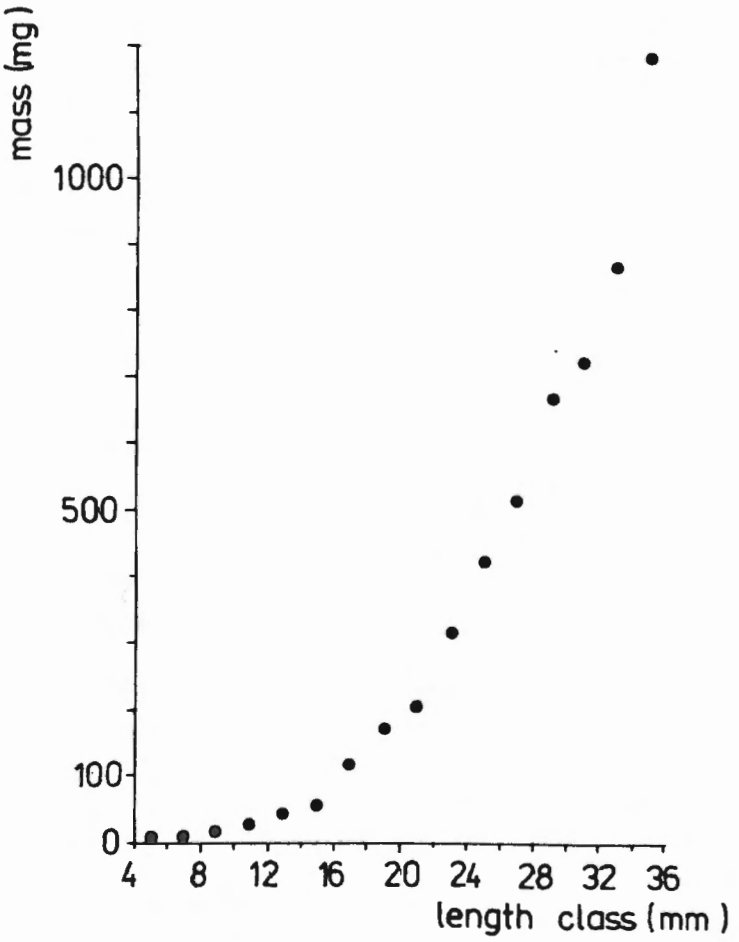

Fig. 1. *Dreissena* shell half mean weight distribution in length classes

50 halves being assigned to each of the remaining classes. Finally, the shell halves were pulverised and homogenised in an agate mortar. The pulverised samples were stored in tightly closed containers.

The derivatographic analyses were performed in a 1500 D Derivatograph (MOM Budapest) with a simultaneous recording of differential thermal (DTA), thermogravimetric (TG), derivative thermogravimetric (DTG), and temperature (T) curves. The latter is an auxillary curve used to determine temperatures of individual reactions and is not shown in the derivatogram enclosed. The derivatographic analyses were carried out under the following constant conditions: sample weight of 400 mg; curve sensitivity: 200 mg for TG, 500 V DTA, 250 V for DTG (500 V from 600°C up); heating rate of 10°C/min; atmospheric air; ceramic crucible; Al_2O_3 as inert substance.

Organic carbon (C_{org}) was determined with Tiurin's method at the Szczecin University's Chemical Laboratory.

Assays to determine SiO_2, Al, Fe, Mg, K, Pb, Co, Zn, Cu, Ni, Cd, Mn, and S contents were performed in an ICP Spectrophotometer (Baird, The Netherlands) at the Chemical Laboratory of ZD "Cuprum" KGHM Lubin.

3. Results

Due to insufficient amount of material available, *Dreissena* shells smaller than 4 mm were not studied. The derivatographic analysis can be run on any sample weight. However, it is purposeful to use equal sample weights in every analysis. The approach adopted in the present study was to analyse averaged samples consisting of a number of shells rather than analysing individual shells or their halves. The mean shell weight changes exponentially with shell length, from 6.3 mg at the smallest class (4 to 5.9 mm) to 1182.1 mg in the largest class (34 to 35.9 mm). The 400 mg sample weight used in the assays makes it possible to analyse single halves measuring 24 mm and more.

The derivatograms obtained make it possible to calculate the amounts of physically bound water, organic matter, and calcium carbonate in the *Dreissena* shells. All the derivatograms obtained do not differ significantly from one another, therefore a single derivatogram is presented only (Fig. 2). The most legible curve is the DTG one; its interpretation will serve as a basis for further considerations.The DTA curve which incorporates both endo- and exothermic effects is less legible, particularly the part that records the transfer between the loss of physically bound water and organic matter combustion. The derivatogram is presented in its original, unchanged form, hence different lengths of various sections in spite of the assumed constant temperature increase. The constant temperature increase is seldom attained in practice and depends on both the properties of a substance tested and characteristics of the apparatus used.

The DTG curve shows three effects of mass loss. The first is related to the loss of the physically bound water and occurs at 25 - 30°C to 130 - 170°C with a maximum at 70 - 90°C. This effect is interpreted as a result of dehydratation. The water content is equal to the weight loss as read from the TG curve. The second, broad effect is related to organic matter combustion and proceeds at 130 - 170°C to 539 - 580°C with a maximum at 283 - 302°C. The weight loss related to this effect and read from the TG curve identifies the organic matter content. More precisely, the content of solids remaining after the organic matter combustion is regarded as negligible and confined to the measurement error limits. The third, very conspicuous effect is brought about by $CaCO_3$ breakdown as in the reaction:

$$CaCO_3 = CaO + CO_2$$

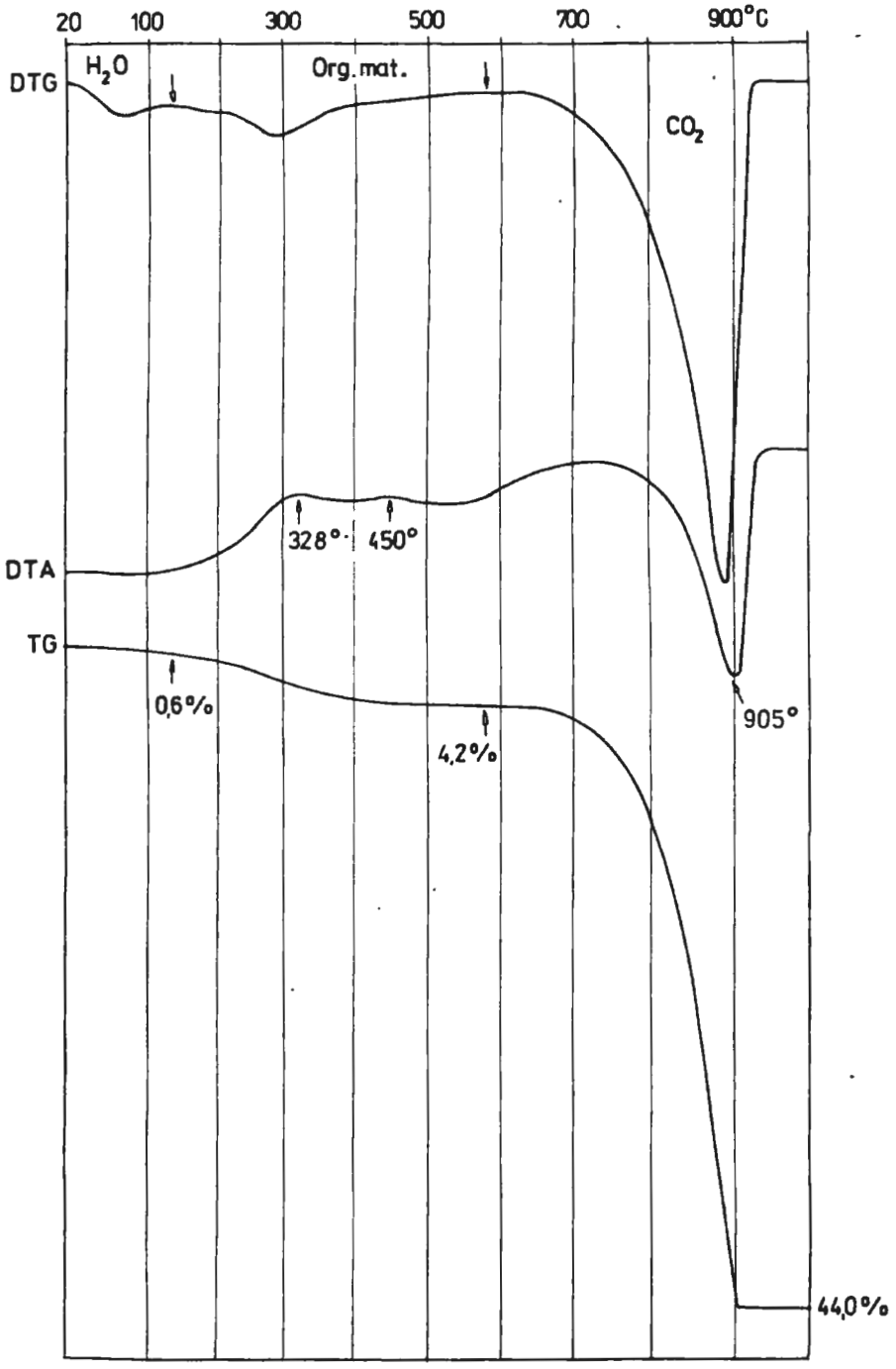

Fig. 2. *Dreissena* shell derivatogram (8.0 - 9.9 mm shell length class)

Table 1.

Chemical composition (weight %) of *Dreissena* shells as shown by derivatographic

Length class (mm) of *Dreissena* shell	H_2O	organic matter	$CaCO_3$	organic matter + $CaCO_3$
4.0 - 7.9	0.6	3.6	88.7	92.3
8.0 - 9.9	0.6	3.6	90.5	94.1
10.0 - 11.9	0.5	2.6	90.4	93.0
12.0 - 13.9	0.6	2.4	93.7	96.1
14.0 - 15.9	0.4	2.6	93.3	94.9
16.0 - 17.9	0.4	2.5	92.9	95.4
18.0 - 19.9	0.8	2.6	93.7	96.3
20,0 - 21.9	0.4	2.6	93.7	96.3
22.0 - 23.9	0.6	2.6	94.1	96.7
24.0 - 25.9	0.8	2.0	94.1	96.1
26.0 - 27.9	0.8	2.0	96.4	98.4
28.0 - 29.9	0.4	2.0	96.4	98.4
30.0 - 31.9	0.4	2.0	95.1	97.1
32.0 - 33.9	0.4	1.8	95.1	96.9
34.0 - 35.9	0.4	2.4	94.6	97.0

Table 2.

Organic matter and C_{org} content (weight %) and organic matter : C_{org} ratio in *Dreissena*

Length class (mm) of *Dreissena* shell	organic matter	C_{org}	organic matter C_{org}
8.0 - 9.9	3.6	1.22	2.95
24.0 - 25.9	2.0	0.49	4.08
26.0 - 27.9	2.0	0.40	5.00
28.0 - 29.9	2.0	0.49	4.08
30.0 - 31.9	2.0	0.41	4.88
34.0 - 35.9	2.4	0.64	3.75

Table 3.

Chemical composition of *Dreissena* shells (24.0 - 25.9 mm shell length class) and bottom sediments (weight %) and concentration coefficients; for explanation see text

element	Dreissena	sediments	K_A	K_B
SiO_2	1.400	50.490	——	——
Al	0.071	0.947	0.075	0.008
Fe	0.203	2.618	0.078	0.040
Mg	0.056	1.700	0.033	0.027
K	0.000	0.075	0.000	0.000
Pb	0.004	0.025	0.160	2.500
Co	0.013	0.160	0.081	4.330
Zn	0.010	0.064	0.156	2.000
Cu	0.024	0.024	1.000	2.400
Ni	0.001	0.006	0.167	0.125
Cd	0.000	0.001	0.000	?
Mn	0.054	0.495	0.109	0.600
S	0.016	0.352	0.045	0.320

The effect is visible at 535 - 580°C to 920 - 930°C with a maximum at 895 - 905°C. The weight loss calculated from the TG curve results from CO_2 release and is multiplied by the gactor of 2.274 ($CaCO_3 : CO_2 = 2.274$) to obtain the $CaCO_3$ content.

The dehydratation reaction is reflected in the DTA curve as a poorly visible endothermic effect smoothly passing into organic matter combustion. The latter shows two peaks: the first at 328 - 355°C and the other at 435 - 465°C. While the latter is more pronounced on most derivatograms, the first is related to the principal weight loss effect (DTA curve). The $CaCO_3$ breakdown corresponds to an extensive asymmetric effect on the DTA curve with a maximum at 900 - 910°C.

Results of the derivatographic analyses are presented in Table 1. The content of physically bound water was found to range within 0.4 - 0.8% with a mean (15 samples) of 0.5%. The presence of water in the samples, in spite of drying them at 105°C, can be explained by the water absorption properties of the substance tested, the samples absorbing moisture while being prepared for the derivatographic analyses. The water content is disregarded in the further discussion.

The organic matter content was found to vary from 1.8% (32.0 - 33.9 mm length class) to 3.6% (4.0 - 7.9 mm and 8.0 - 9.9 mm classes) with a mean of 2.5%. The shell length versus organic matter content correlation was negative (r = -0.803). The regression equation showed that a shell length increase by one milimetre is accompanied by an organic matter content decrease by 0.047% (Fig. 3).

The minimum and maximum $CaCO_3$ contents were 88.7% (4.0 - 7.9 mm class) and 96.4% (26.0 - 27.9 mm and 28.0 - 29.9 mm classes), respectively, the mean content amounting to 93.4%. The shell length versus $CaCO_3$ content correlation was positive (r = 0.867). The regression equation showed a shell length increase by one milimetre to be accompanied by a $CaCO_3$ content increase by 0.21%.

The combined contents of organic matter and $CaCO_3$ ranged from 92.3% (4.0 - 7.9 mm class) to 98.4% (26.0 - 27.9 mm and 28.0 - 29.9 mm classes) with a mean of 95.9%. The correlation between the two components was clearly negative (r = -0.865). Organic matter and $CaCO_3$ are the basic components of each shell; an increase in the content of one of them brings about a decrease in the other. The regression equation showed a 1% increase in the $CaCO_3$ content to be accompanied by a decrease in organic matter by 0.21% (Fig. 4).

The organic carbon (C_{org}) content of *Dreissena* shells was found to vary from 0.4% (26.0 - 27.9 mm length class) to 1.22% (8.0 - 9.9 mm class) with a mean (six samples) of 0.61% (Table 2). Due to a small sample size, the C_{org} versus shell length relationships were not calculated. On the other hand, C_{org} correlated positively with organic matter (r = 0.993). The corresponding regression equation showed a 1% increase in the organic matter content to be accompanied by the organic carbon content increasing by 0.48% (Fig. 5). The organic matter to C_{org} ratio is not constant and varies from 2.95 to 5.00. Based on the regression equation for the two components, the ratio may be given as:

$$\text{organic matter} / C_{org} = 2.08 + 1.08 / C_{org}$$

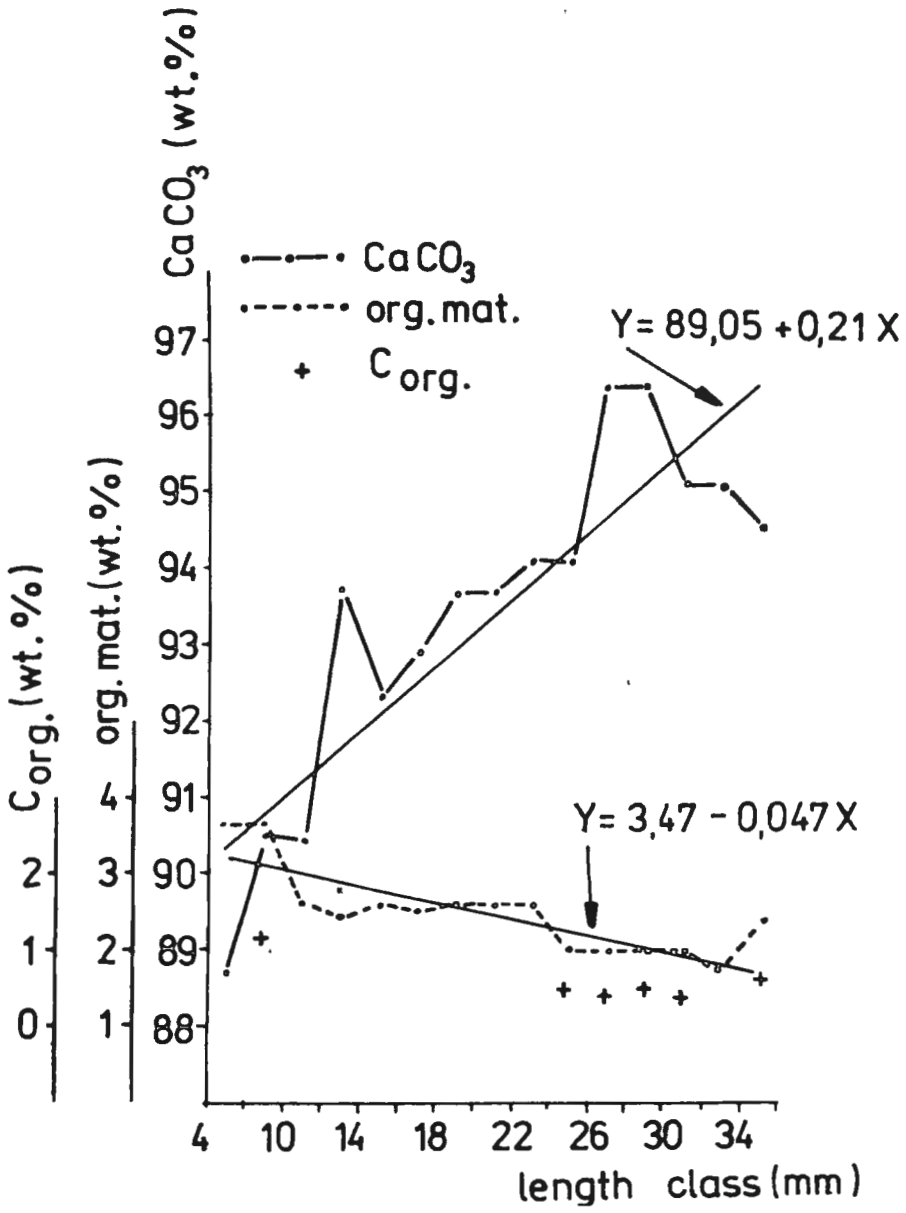

Fig. 3. Distribution of contents of $CaCO_3$, organic matter and C_{org} in *Dreissena* shells and regression equations for contents versus shell length relationships

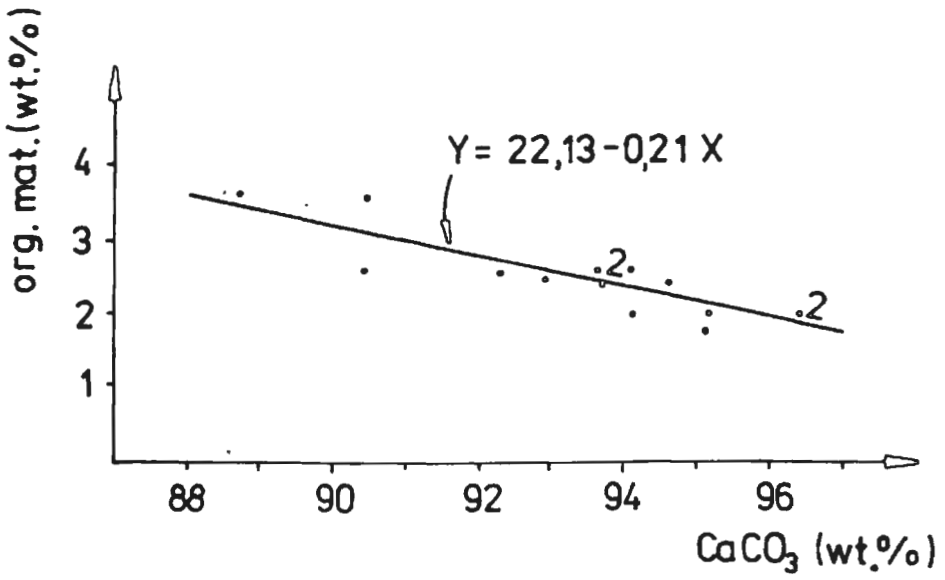

Fig. 4. Organic matter versus $CaCO_3$ content relationship regression line for *Dreissena* shells

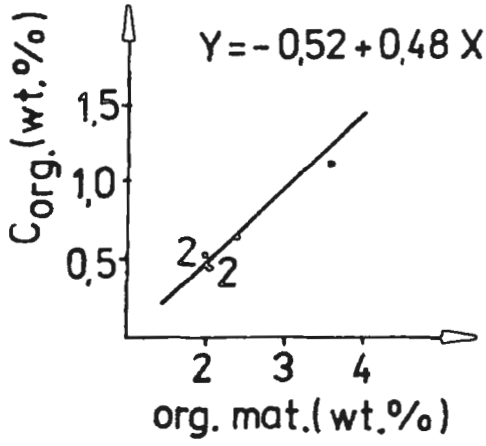

Fig. 5. C_{org} versus organic matter content relationship regression line for *Dreissena* shells

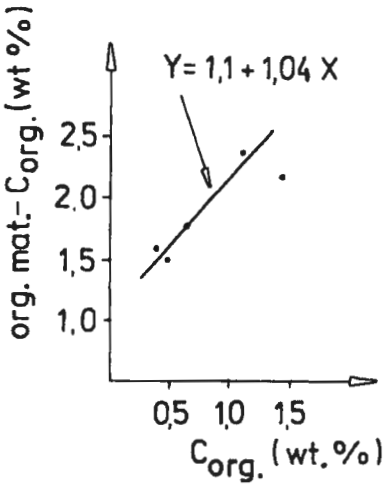

Fig. 6. (Organic matter - C_{org}) versus C_{org} relationship regression line in *Dreissena* shells

A relationship between C_{org} and organic matter residue after the removal of C_{org} (organic matter - C_{org}) was calculated as well. The correlation coefficient was r = 0.983. The corresponding regression equation showed a 1% increase in the content of C_{org} contained in organic matter to result in an increase of the remaining organic matter components by 1.04% (Fig. 6).

Table 3 summarizes data on contents of 13 chemical components of *Dreissena* shells. As a single analysis only was made (a 24.0 - 25.9 mm length class sample), the data should be treated as preliminary. The SiO_2 content was 1.4% and is interpreted as a contamination by mineral components of bottom sediments. The contents of K and Cd are given as zero values. As the elements were determined to 0.001%, the zero values should be taken as a possibility of K and Cd occurring in shells in amounts lower than 0.001%. Contents of the remaining elements varied from 0.001% (Ni) to 0.203% (Fe). The combined content of these components (without SiO_2) was 0.452%.

It is interesting to compare elemental composition of the *Dreissena* shells with that of unconsolidated sediments *Dreissena* populations dwell on. Mean values of three sediment samples (Ø « 0.25 mm fraction) are presented. The concentration coefficient (K_A) was calculated as a ratio between the mean shell content and the mean sediment content of an element. As SiO_2 in the *Dreissena* shells was assumed to be a contamination the concentration coefficient was not calculated in this case. Values of the coefficient for the remaining elements were very low (« 1) except for Cu (K_A = 1).

Another coefficient of concentration, K_B, was calculated as a ratio between the mean shell content of an element and its clarke. The K_B values for Pb, Co, Zn, and Cu were found to range from 2.00 to 4.33, the values being less than 1 for remaining elements.

4. Discussion

In view of the techniques used to prepair the materials for assays, the results presented in this paper are treated as mean values for the *Dreissena* shell length classes separated.

Statistical relationships presented are regarded as tentative only, to be verified by analysing à larger body of data. The conclusions resulting from interpretation of the regression equations should be treated as expected values which, in certain cases, may deviate from the true ones.

Several derivatograms were obtained for a single homogenous sample to verify the interpretation of the results of the derivatographic analysis. The between- - measurement differences were within the experimental error limits and amounted to 0.1%. The criteria of the derivatogram interpretation are given clearly

in the literature. For the purpose of this study the guidelines established by WYRWICKI (1988) are followed. However, it remains to be decided whether the organic matter content, determined in this way, may be equalled with the shell conchiolin content. WYRWICKI (1988) questions the validity of comparing the two substances. A bivalve shell is composed of three layers. The outer layer (periostracum) is made of organic matter called the conchiolin. It seems that the problem of comparing the devaritographically determined organic matter with conchiolin can be solved by employing other techniques, mainly X-raying.

The organic matter versus C_{org} content relationship presents an interesting problem. It seems probable that a low number of data has in some way affected the relations between the two components as presented in this paper. Nevertheless, the contents of the two components did not increase in proportion to each other. With the increase in both organic matter and C_{org} contents, their ratio was observed to decrease. Both substances were, without doubt, determined correctly. Generally, organic matter consists of organic carbon bound to elements such as hydrogen, nitrogen, and oxygen. As no proportion between increasing amounts of organic matter and C_{org} could be observed, a change in organic matter chemistry in terms of altered numerical relations between the components is a likely explanation. It is consequently assumed that *Dreissena* shells contain compounds other than C_{org} which produce thermal effects similar to those of C_{org} and are responsible for the disproportionate increase of the two components discussed.

In order to grow, a *Dreissena* shell needs certain chemicals. The chemistry of the shell reflects, to some degree, that of its environment. Unconsolidated lacustrine sediments form an active system in which proceed a number of biologically important processes. These processes provide for, and control transformation of numerous biogenic elements. Thus the coefficient of concentration K_A is interpreted as a measure of an element's ability to migrate out of the sediment into the shell structure. The very low values of the coefficient found may evidence an inhibited sediment-shell migration of all the elements except copper in which case the value of the coefficient may suggest an enhanced incorporation into the *Dreissena* shell.

The other coefficient calculated, K_B, compares the elemental content of the shell with that of the lithosphere (clarkes). Thus clarkes of various elements can be regarded as expected values typical of the environment. Four elements: Pb, Co, Zn, and Cu are concentrated in the *Dreissena* shells in amounts exceeding their clarkes. The contents of the remaining elements are lower than their clarkes. It was not possible to calculate the K_B value of Cd as the assays were made to $1x10^{-3}$%, while the Cd clarke is $5x10^{-5}$%.

The contents of several elements in the *Dreissena* shells are relatively low.

However, if their total amounts deposited in the shells of the entire *Dreissena* population in a water body were calculated, the values arrived might be quite substantial.

The chemistry of *D. polymorpha* shells was earlier presented by WIKTOR (1969). A direct comparison with his results is difficult because WIKTOR (1969) analysed pulverised unsorted bivalves 3 - 30 mm long. the results thus obtained describe the averaged chemical composition of a whole *Dreissena* individual (shell + soft parts). The shell chemistry versus length relationship presented in this paper may cast doubts on the validity of calculating amounts of $CaCO_3$ and other compounds, accumulated in the *Dreissena* shells, by the use of those averaged values.

5. Conclusions

The derivatographic analysis is a relatively simple and rapid method of simultaneous quantifying of several substances, provided these are thermally active and occur in appropriate amounts in the samples. The "appropriate amount", understood as a minimal quantifiable amount, as different for different substances and depends both on thermal properties of a substance and on thermal properties of the remaining compounds making up the sample and and their proportions in it. For example, assuming that the whole Mg amount determined in the *Dreissena* shell (Table 3) is bound as $MgCO_3$, the calculations yield 0.19% $MgCO_3$. This is too low for the derivatogram to record the thermal breakdown.

However, the method can be used to determine, with reasonable accuracy comparable to that of chemical procedures, contents of the basic chemical components, viz. organic matter and $CaCO_3$. For the purpose of this study, 400 mg samples were analysed. Much smaller samples, e.g. 40 mg, can be used as well, in which case referring to Fig. 1 - single shells or their parts can be analysed. Further work employing the derivatographic analysis will hopefully make it possible to select optimal procedures for studying molluscan shells.

The results of assays of the remaining chemical components, obtained with other analytical techniques, provide insights into the chemical composition of *Dreissena* shells and enable calculations of coefficients of concentration for various elements.

Further studies on molluscan shell chemistry, employing new research techniques and carried out in chemically different ecosystems may contribute to elucidation of the course of geochemical reactions in the respective environments, with a particular emphasis on relations between chemistry of shells and that of bottom sediments and water.

REFERENCES

PIESIK Z. 1983. Biology of *Dreissena* polymorpha (PALL.) settling on stylon nets and the note on this mollusc in eliminating the seston and the nutrients from the water-course. - *Polskie Archiwum Hydrobiologii*, **30**: 353-361.

STAŃCZYKOWSKA A. 1968. Możliwości filtracyjne populacji *Dreissena polymorpha* (PALL.) w różnych jeziorach, jako czynnik wpływający na obieg materii w jeziorze. [The filtration capacity of population of *Dreissena polymorpha* (PALL.) in different lakes, as factor affecting circulation of matter in the lake (in Polish, with English summary)] - *Ekologia Polska, Ser.* **B, 14**: 265-270.

STAŃCZYKOWSKA A. 1977. Ecology of *Dreissena polymorpha* PALL. (*Bivalvia*) in lakes. - *Polskie Archiwum Hydrobiologii*, **24**: 461-530.

WIKTOR J. 1969. Biologia *Dreissena polymorpha* (PALL.) i jej ekologiczne znaczenie w Zalewie Szczecińskim. [The biology of *Dreissena polymorpha* (PALL.) and its ecological importance in the Firth of Szczecin (in Polish, with English summary)] - *Studia i Materiały Morskiego Instytutu Rybackiego, Ser.* **A, 5**: 1-88.

WYRWICKI R. 1988. Derivatographic analysis of the lacustrine sediments of the Orle basin. - *Folia Quaternalia*, **58**: 75-93.

Reviewer: Prof. Stefan Witold Alexandrowicz D. Sc.