The complexing capacities of humic substances isolated from Baltic sediments and their molecular weight fractions towards copper(II) and iron(III)*

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Abstract

Humic substances were isolated from sediments collected from the Gdańsk Deep, separated into humic acids and fulvic acids, and further separated into molecular weight fractions by ultrafiltration. The respective complexing capacities of the fractions towards copper(II) and iron(III) lie in the 0.067–0.240 $\mu g\,mg^{-1}$ and 0.094–0.240 $\mu g\,mg^{-1}$ ranges. The complexing capacity increased with decreasing molecular weight of the fractions. Examination of the IR spectra of humic substances and their precipitates obtained after addition of excess metals revealed that the absorption band at 1710 cm^{-1} (carbonyl of carboxylic groups) had shifted to 1600 cm^{-1} (carboxylate ions), indicating the participation of carboxyl groups in the bonding of metal ions. The decreasing intensity of the DTG peak at 365°C supported this conclusion.

1. Introduction

Many trace metals are found in soils and sediments in concentrations exceeding their average content in the Earth's crust (Förstner and Wittmann, 1981). This is due to various natural and anthropogenic causes. One of the factors influencing the distribution of trace metals in the environment is organic matter (Rashid, 1971). Humic substances are the fraction of organic matter most actively affecting the migration and accumulation of these elements (Förstner and Wittmann, 1981; Schnitzer and Khan, 1972; Wright and Schnitzer, 1963). This is brought about not only by the relatively large proportion of humic substances in natural organic matter but also by the high content of oxygen-containing functional groups in humic substances (Rashid, 1971). These functional groups are responsible for the considerable complexing capacity of humic substances and their affinity towards many di- and trivalent metals (Rashid, 1971; Szponar, 1991).

Despite the large number of studies on the interactions of humic substances with trace metals, not very much is known about the quantities of such metals complexed to humic substances. This is particularly true about humic substances derived from marine sediments. The subject was investigated in the early 1970s (Rashid and King, 1969; Rashid, 1971), but the studies in question dealt with humic substances from only one sampling site, off the Nova Scotia coast. More data are needed in order to evaluate the complexing properties of humic substances in sediments originating under a variety of sedimentation regimes, for example, in humus-abundant coastal regions. The Baltic Sea is a typical semi-enclosed sea with a very large concentration of humic substances in both water and sediments (Pempkowiak, 1989), and these substances are thought to play a major role in the distribution of heavy metals in the Baltic (Szponar *et al.*, 1985; Szponar and Przewocka, 1988).

The purpose of this study was to determine the metal complexing ability of humic acids isolated from Baltic Sea sediments and to evaluate the role of various molecular weight fractions in the overall complexing ability of these acids.

2. Materials and methods

The sediment samples used in this study were collected from the Gdańsk Deep by means of a gravity corer. Humic substances were extracted from the upper 0–5 cm portions of the cores. The sedimentation rates in this area were found to be 1.72 ± 0.21 mm year^{-1} (Pempkowiak, 1991a).

After collection, the samples were treated with 0.05 M HCl to remove carbonates. Humic substances were extracted from the sediments by repeated treatment with 0.2 M NaOH (60° C, under nitrogen). Humic acids

were separated from fulvic acids by acidifying the extract to pH 2.5 with conc. HCl and centrifuging the precipitated humic acids. To lower the ash content, the humic acids were then redissolved in 0.2 M NaOH several times, centrifuged (25 000 g) and precipitated with HCl. The fulvic acids were sorbed on Amberlite XAD–2 resin (Serva), desorbed with 0.2M $NH_3 \cdot H_2O$ and concentrated in a rotary evaporator.

The solutions of humic and fulvic acids were fractionated on the basis of their molecular weight by ultrafiltration. A 402 type cell (Amicon) was used with XM100, PM10, YM5, YM2 type Diaflo membranes (Amicon) characterised by the respective cut-off ranges of 10^5, 3×10^4, 10^4, 5×10^3, 1×10^3 D (molecular weight units). The molecular weight distribution of the humic and fulvic acids investigated is given in Tab. 1. The metals dealt with in this study were iron(III) and copper(II). The initial solutions of the metal nitrates were prepared from reagent-grade salts. The procedure used to determine the complexing ability of humic substances followed that used in colloid chemistry (Schnitzer and Khan, 1972), as well as in soil organic matter (Wright and Schnitzer, 1963) and sedimentary organic matter (Rashid, 1971) studies. Small volumes (0.1–0.2 cm^3) of the metal solutions were added to 25 cm^3 of solutions containing appropriate fractions of humic substances (concentration 2 mg cm^{-3}). After each addition, the samples were shaken vigorously. The metal solution continued to be added until signs of precipitation were observed. After 2 days the precipitate was separated by centrifuging and filtration, and the metal concentrations were determined in this and the supernatant liquid (after wet digestion with HNO_3–$HClO_4$) by atomic absorption spectroscopy. Blanks were also run. The amount of metal bound to humic substances was calculated from the difference between the added and the found concentrations in solution after removal of the humate precipitate. This was compared to the metal content found by direct analysis of the precipitate. The complexing capacities of the investigated fractions of humic substances thus obtained are listed in Tab. 2.

Infrared (IR) spectra, thermogravimetric (TG and DTG) curves, and the elemental composition of both humic substances fractions and the precipitated metal humates were also recorded.

3. Results and discussion

The concentration of humic substances in the sediments analysed, equal to 1.05 %, is typical of Baltic Sea sediments (Pempkowiak, 1989). The proportion of humic and fulvic acids found in the humic substances investigated (2:1) is characteristic of the Gdańsk Deep sediments. It is higher in other areas of the Baltic owing to the influence of the high fulvic acid load brought to the Baltic with the river run-off (Poutanen, 1985b).

Humic substances are a mixture of a large number of compounds whose chemical and physical properties differ over a broad range (Schnitzer and Khan, 1972; Pempkowiak, 1989). Before the complexing capacities were measured, the substances were separated into molecular weight fractions in order to obtain substances with more uniform properties than the unfractionated acids. This approach was first used in the case of marine humus by Rashid (1971), who applied gel filtration to obtain fractions more homogeneous than the unfractionated substances. Fractionation according to molecular weight was also applied to the humic substances from Baltic sediments, although no interactions of the fractions with trace metals were investigated (Naik and Poutanen, 1984; Poutanen, 1985a,b).

Table 1. Molecular weight distribution of the investigated humic and fulvic acids

Humus fraction	Percentage of fraction					
	$< 100 \times 10^4$	$< 10 \times 10^4$	$< 5 \times 10^4$	$< 3 \times 10^4$	$< 1 \times 10^4$	$< 0.1 \times 10^4$
HA*	45	41	6.2	4.3	2.0	1.5
FA*	1.2	2.4	36	12	19	28
HA**	62	31	3	1	1	2
FA**	–	3.2	28	31	27	11
HA***	27	49	10	5	4	5
FA***	5	7	40	18	20	10

* this paper,
** Poutanen, 1985b,
*** Rashid, 1971.

Tab. 1 shows the molecular weight distribution of the investigated fulvic and humic acids. It is characteristic of fulvic acids that they comprise molecules of molecular weight less than 50 000 and that the percentage distribution of molecules among the various fractions is relatively even. Humic acids comprise substances with molecular weights up to 10^6, and the high molecular weight fractions predominate. This is in agreement with earlier findings of the molecular weight distribution of humic substances isolated from the Baltic Sea (Poutanen, 1985b).

The complexing capacities of the fractions towards the investigated metals are given in Tab. 2. The complexing capacities of fulvic acids are much higher than those of humic acids. This was attributed to the lower ash

and higher carboxyl-group contents in the fulvic acids isolated from soil (Schnitzer and Khan, 1972) and marine sediments (Rashid, 1971). The complexing capacity of unfractionated humic substances should be the simple sum of the complexing capacities of the fractions multiplied by their proportion in the acids. However, the values of the calculated and measured complexing capacities differ by as much as 18%. The most obvious explanation for the difference is the difficulty in establishing the end point in the titration of humic substances with metal solutions, caused by the unhomogeneity of the acid molecules. Difficulties in establishing the end point were also encountered in earlier studies (Rashid, 1971). Another cause of the difference is the loss of some organic substances due to sorption on the ultrafiltration membranes. This could have led to unrealistic proportions of the various fractions and caused the difference between the experimentally found complexing capacities and those calculated from the capacities assigned to the fractions. Sorption on the ultrafiltration membranes, although much less important than in gel filtration, was reported for humic substances (Pempkowiak, 1989).

Table 2. Complexing capacities of the fractions towards Cu(II) and Fe(III)

Molecular range	Complexing capacity $(mg\,mg^{-1})$							
	Humic acids				Fulvic acids			
	A*		B*		A*		B*	
	Fe	Cu	Fe	Cu	Fe	Cu	Fe	Cu
$< 100 \times 10^4$	0.060	0.071	nd	0.062	nd	nd	nd	nd
$< 10 \times 10^4$	0.047	0.090	nd	0.060	0.186	nd	0.180	nd
$< 5 \times 10^4$	0.147	0.098	0.208	0.086	0.177	0.085	0.212	0.063
$< 3 \times 10^4$	0.161	0.121	0.142	0.112	0.094	0.107	0.102	0.102
$< 1 \times 10^4$	0.240	0.142	0.242	0.128	0.240	0.163	nd	0.141
$< 0.1 \times 10^4$	0.216	0.070	0.178	0.063	0.221	0.121	nd	0.132
S	0.076	0.082	nd	0.090	0.200	0.135	0.217	0.127

*A – according to the end point titration,
*B – according to aas measurements,
nd – not determined,
S – unfractionated.

Two features of the interactions between humic substances and trace metals are of particular interest, namely the stability of organometal complexes and the quantity of metals complexed by unit mass of humic sub-

stances. The former is best characterised by the apparent stability constants, the latter by the complexing capacities of these substances (Pempkowiak, 1989; Warwick and Hull, 1992). These constants are much larger with respect to the copper complexes of the Baltic humic substances than to their nickel and chromium complexes (Szpakowska et $al.$, 1986; Pempkowiak, 1989). No data on the complexing capacities of humic substances from the Baltic sediments are available. The complexing capacities of humic substances isolated from the Baltic sediments found in this study are much greater than those of the acids from the Scotian Shelf (Rashid, 1971). This could be attributed to the large proportion (50%) of land-derived humic substances in the Baltic Sea sediments (Pempkowiak, 1989; Pempkowiak and Pocklington, 1984). The complexing capacities of soil humic substances lie in the 2.1–3.7 mval g^{-1} range, whereas those of marine sedimentary humic substances are in the 0.4–1.3 mval g^{-1} range (Schnitzer and Khan, 1972; Rashid, 1971; Pempkowiak, 1989). The complexing capacities found are also much larger than those of humic substances isolated from the sea water in the same region (Pempkowiak, 1991a). This suggests that at least part of the sedimentary humic substances is formed within the sediments and confirms earlier conclusions based on stable carbon isotope studies (Pempkowiak, 1989). The decreasing complexing capacity with increasing molecular weight of the fractions (Tab. 2) can be put down to the decreasing content of oxygen-containing functional groups. The complexing capacities of the fulvic and humic acid fractions of the same molecular range do not differ much. The greater complexing capacity of unfractionated fulvic acids is caused by the larger proportion of low molecular weight fractions.

The contribution of oxygen-containing functional groups in the complexation of copper(II) ions was established by comparing the IR spectra of humic acids, fulvic acids and the precipitated copper humates (Fig. 1). The absorption bands in these spectra are very broad – a characteristic feature of humic substances (Schnitzer and Khan, 1972; Szponar, 1991). This makes quantitative analysis impossible and qualitative analysis difficult. Some absorption bands can be attributed to the presence of the following functional groups: hydroxyl and amino groups ($\approx$3400 cm^{-1}) methyl and methylene groups ($\approx$2950 cm^{-1}), carbonyl groups (1710 cm^{-1}), aromatic rings ($\approx$1600 cm^{-1}) (Schnitzer and Khan 1972; Pempkowiak, 1989; Szponar, 1991). In the spectra of copper humates, an additional broad absorption band in the 1540–1600 cm^{-1} range appears, whereas absorption at 1710 cm^{-1} decreases substantially owing to the formation of carboxylic anions during chelation (Szponar, 1991). Similar differences between the IR spectra of humic substances and their insoluble precipitates with copper were found in the case of the humic substances isolated from the Scotian Shelf (Rashid, 1971).
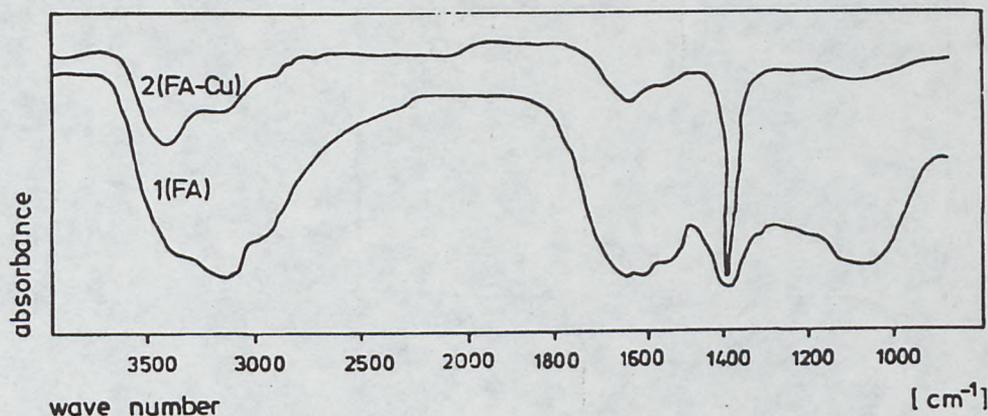
Fig. 1. Infrared spectra of fulvic acids (10^3 < fraction <10^4) before (FA) and after (FA – Cu) saturation with Cu

The complexing capacities of the investigated humic substances towards copper(II) and iron(III) are shown in Tab. 2. Two methods of assessing these capacities were used: (A) – observation of the precipitation of humic substances, and (B) – measurement of the quantities of metals in the supernatant liquid. Of the two methods, the latter is better suited for evaluating complexing capacities since it accounts for the uncomplexed metal ions in the solution. However, the differences are not great, and can be put down to difficulties in establishing the end point of the titration.

Humic substances exhibit greater complexing capacities towards iron(III). The relation between the complexing capacities towards iron and copper ranges from 0.8 to 3.0 (mass) and 0.9–3.3 (molar). This is in agreement with the complexing capacities of humic substances isolated from soil (Schnitzer and Khan, 1972) and from the sediments off the Scotian Shelf (Rashid, 1971). This difference has usually been attributed to differing ionic radii (Szponar, 1991; Pempkowiak, 1989a) and/or the valency of copper and iron (Rashid, 1971).

TG and DTG analyses of the investigated humic substances revealed more peaks on the DTG curves of fulvic acids and their fractions than on those of humic acids. The DTG curves of both iron and copper humates revealed a shift of the major peaks towards lower temperatures, as well as the disappearance of some peaks in the 280–350°C temperature range. Typical DTG curves illustrating the phenomena are presented in Fig. 2. The formation of metal humates leads to increased thermal dissociation energies
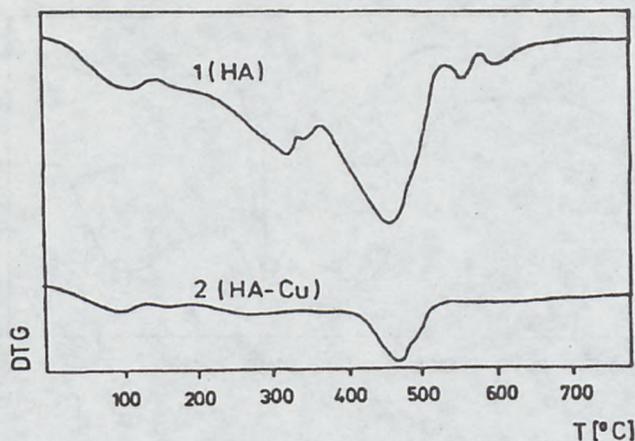
Fig. 2. DTG curves of humic acids (fraction $<10^5$) before (HA), and after (HA – Cu) saturation with Cu

of functional groups, which supports the conclusion that the complexes are formed via oxygen-containing functional groups (Campanella *et al.*, 1990).

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