

The application of IR spectra and TG and DTA curves in testing the sorption of selected trace metals on certain components of bottom sediments*

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Humic acids
Bottom sediments
Sorption of cations
on minerals
Complexes of cations
with humic acids

ZOFIA SZPONAR

Institute of Chemistry,

University of Gdańsk,

Gdańsk

ul. Jana Sobieskiego 18

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Abstract

Studies were carried out on the sorption of the cations Ni^{2+} , Cu^{2+} , Co^{2+} , Fe^{2+} , Hg^{2+} , Zn^{2+} , Cr^{3+} and Pb^{2+} on the main components of the Baltic bottom sediments - quartz, illite, montmorillonite, kaolinite, humic acids and mixtures of humic acids with bentonite. The IR spectra method, differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) were applied. It was found that sorption is mainly by humic acids and montmorillonite, which is illustrated by changes in the spectra.

1. Introduction

The physical and chemical processes taking place between the trace elements present in sea water and the bottom sediments are of considerable importance in marine chemistry. Previous laboratory studies of sorption and desorption of trace element ions showed these properties to depend on the type of sediment, type of ion, and conditions under which the studies were conducted (Bojanowski *et al.*, 1978; Sawhney, 1972; Szponar *et al.*, 1979, 1984; Szponar and Przewocka, 1987, 1988a,b).

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Sorption of cations by sediments in a solution may take the form of ion exchange, surface adsorption, chelation, coagulation or peptization (Schnitzer and Khan, 1972). Sorption properties are exhibited by both organic and inorganic compounds. These organic compounds are mainly humic acids, which may assimilate substantial quantities of metal ions (Pempkowiak *et al.*, 1984). They may constitute material with which to obtain certain trace metals and influence the nutritional capacity of the flora and fauna of the marine environment (Elderfield, 1976). The metals, particularly in larger quantities, may be toxic (Buffle, 1984). The minerals most frequently occurring in bottom sediments are quartz, illite, montmorillonite and kaolinite. Some of these may adsorb metal ions and also form complexes with humic substances (Duursma and Dawson, 1981).

Studies of the mechanisms of these reactions are important in marine geochemistry (Elderfield, 1976) and environmental protection.

2. Instruments and reagents

DTA, TG and DTG measurements were carried out using a Hungarian OD-103 derivatograph (Paulik, Paulik and Erdey system). 100 g of sediments were compared with an Al_2O_3 standard in platinum crucibles; the rate of temperature increase was $10^\circ\text{C}/\text{min.}$, the air was atmosphere-static, and the instrument sensitivities were set at: TG 50 mg, DTG 1/5, DTA 1/5.

IR measurements were done on a Perkin-Elmer 257 IR spectrophotometer. The technique of KBr pellets of equal strength of 800/2 mg was applied. Materials:

- Montmorillonite mud (bentonite) from Milewice
 $(\frac{1}{2} \text{Ca}, \text{Na})_{0.7} (\text{Al}, \text{Mg}, \text{Fe})_4 (\text{SiAl}/_8 \text{O}_{20})\text{OH}_{4x} \cdot n\text{H}_2\text{O}$.
- Austrian quartz $3(\text{SiO}_2)$.
- Kaolin from Siedlce (CSFR) $2 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.
- Hungarian illite $(\text{H}_2\text{O}, \text{K})_4\text{Al}_8(\text{Si}, \text{Al})_{16}\text{O}_{40}(\text{OH})_8$.

Assumed as pure, these minerals of uniform composition were dried, granulated and sifted through a 0.071 mm/mm mesh sieve. Air-dry minerals with a particle size smaller than the sieve mesh were used.

Humic substances were separated from Baltic bottom sediments. A 10 cm layer of sediment was removed with the aid of a Peterson - type scoop. The average age of the analyzed sediments was about 10 years.

Sediment samples with a natural moisture content were centrifuged for 20 minutes, after which the water was discarded. The remaining sediment was stirred continuously with the same volume of 0.01 M HCl, and then

brought to pH 2 with 1 M HCl. After being stirred for 16 hours in a polythene container, the mixture was centrifuged, the aqueous phase discarded and the sediment treated with a 0.5 M solution of KOH, the extraction being carried out as previously. The solution obtained was acidified with concentrated HCl to pH 2.0 and left to stand for 24 hours to enable the total precipitation of the humic acids. The precipitated sediment was decanted, centrifuged and put aside for analysis (Pempkowiak, 1989).

3. Solutions

Saline water from the Baltic and triply distilled water were used to prepare solutions.

The sea water was filtered through a soft filter to separate the fine suspended matter. It was stored in the dark, in hermetically sealed polythene containers. 0.002 mol · dm⁻³ solutions of NiCl₂, CuCl₂, CoCl₂, FeCl₂, HgCl₂, ZnCl₂, Cr₂(SO₄)₃ and Pb(CH₃COO)₂ were prepared in sea water. Dilution of these yielded solutions for treating the samples of bottom sediments, at concentrations of

- 1.10⁻⁷ mol · dm⁻³,
- 2.10⁻⁵ mol · dm⁻³.

4. Methods

For examination, 1.0000 g samples of minerals were weighed, and 50 cm³ of sea water were added. After 24 hours, the samples were treated with 50 cm³ of the above salt solutions. The samples were stored in polythene containers previously treated with 1.5 M HNO₃ and were agitated from time to time. After 14 days, the samples were centrifuged and the sediments dried in air. In all cases the IR spectra and the TG and DTA curves were first determined for pure substances, and then for these substances treated with solutions of metal ions.

0.5 cm³ of humic acid suspension was placed in a tared container and dried at 60°C. It was found that 25.0 mg of acids were present in 0.5 cm³ of humic acid suspension, their concentration thus amounting to 50.0 mg · cm⁻³. 4.0 cm³ of suspension was set aside for further studies.

5. Method of producing complexes¹

90 cm³ of triply distilled water was added, to 4.0 cm³ of humic acid suspension and mixed. A few drops of 1 M NaOH solution were then added

¹Rashid (1972).

the mixture being stirred continuously until the suspension was completely dissolved; care was taken that the pH of the solution did not exceed 8. The solution was strained through a hard filter, drops of 0.2 M salt solution of the cation studied being added until the suspension was precipitated. After 24 hours, the sediment was centrifuged, rinsed twice with triply distilled water, dried in air, and the IR spectrum and the TG and DTA curves were determined. Complexes of humic acids with trace metals ions were obtained when the ionic concentration was

Ion	Concentration (mol · dm ⁻³)
Cr ³⁺	2.1 · 10 ⁻³
Pb ²⁺	2.5 · 10 ⁻³
Cu ²⁺	4.5 · 10 ⁻³
Zn ²⁺	6.3 · 10 ⁻³
Fe ²⁺	6.7 · 10 ⁻³
Ni ²⁺	7.1 · 10 ⁻³
Co ²⁺	8.7 · 10 ⁻³
Hg ²⁺	0.1 · 10 ⁻²

Samples of humic acids with bentonite were also prepared: 1 g of bentonite was mixed with 1 cm³ humic acid suspension and 90 cm³ of 3 x distilled water. After mixing, 1 M NaOH and then 0.2 M salt solution of the cation studied were added drop by drop until the suspension was precipitated. After 14 days, the samples were centrifuged, dried in air, and the IR spectra, as well as the TG and DTA curves were recorded. In this case, for the complex of humic acids to form, the respective metal ion concentrations were

Ion	Concentration (mol · cm ⁻³)
Cr ³⁺	1.1 · 10 ⁻³
Pb ²⁺	1.3 · 10 ⁻³
Cu ²⁺	1.5 · 10 ⁻³
Zn ²⁺	2.8 · 10 ⁻³
Fe ²⁺	3.2 · 10 ⁻³
Ni ²⁺	4.0 · 10 ⁻³
Co ²⁺	4.7 · 10 ⁻³
Hg ²⁺	6.6 · 10 ⁻³

The complexing capacity differs for various ions and is similar to the results obtained by other authors (Rashid, 1971).

The following were calculated from the thermal analysis curves:

- Loss of mass in relation to 100 mg over a given temperature range (TH).

- Energy, based on the DTA curve peak surfaces compared with the standard surface. K_2SO_4 (analytical reagent grade) was taken as the standard (DTA energy).

6. Discussion of results and conclusions

The IR spectra for minerals are in agreement with those in the literature (Gadsen, 1975).

Analysis of IR curves indicates that distinct differences in bands occur in the case of bentonite when spectra of the pure mineral and its spectra with the ions studied are compared, but at the same time, the greater the concentration of the ion, the greater the reduction of the bands, particularly in the 1025 cm^{-1} band, which can be attributed to vibrations in the Si-O-Si plane, and degenerate and parallel Si = O vibrations in the $1050\text{--}1100\text{ cm}^{-1}$ range.

The IR spectra of samples of humic acids, similar to those described in the literature (Farmer and Russel, 1979; Nissenbaum and Swaine, 1976; Rashid, 1972, 1974; Schnitzer and Khan, 1972), were characterized by strong and extensive absorption bands, which could be assigned to various functional groups. The complex structure of humic acid molecules, and the fact that these acids are a mixture of compounds whose composition and properties change substantially, usually causes broadening of the absorption bands. Analysis of the IR spectra reveals greater intensity of absorption bands at wave numbers 2939 cm^{-1} , 2850 cm^{-1} (methyl and methine groups) and 1050 cm^{-1} (Si-O-Si). A wide band caused by the presence of hydroxyl and amino groups participating in hydrogen bonds occurs in the $3400\text{--}3100\text{ cm}^{-1}$ range. A weak band intensity is observed at the wave number 1390 cm^{-1} , indicating a relatively low carboxyl group content.

Analysis of the IR curves obtained after adding metal ions shows that there is band shortening at the wave number 1700 cm^{-1} and, in certain cases, lengthening at the wave number 1390 cm^{-1} . This indicated a higher number of carboxyl ions in relation to pure acids. Examples of spectra are presented in Figure 1.

For complexes of humic acids, the lowering of band intensity at 1700 cm^{-1} in relation to pure acids, may be due to the formation of a strong complex. The conclusion from these observations may be that carboxyl ions participate in the bonding of metal ions. This is confirmed by literature data, which indicates that the formation of permanent complexes of metal ions with organic ligands is due to the formation of coordination and ionic bonds (Rashid, 1974; Schnitzer and Khan, 1972).

Taking into account the kind of ion for bentonite, humic acids and their mixtures, the results can be arranged in series in order of the diminishing

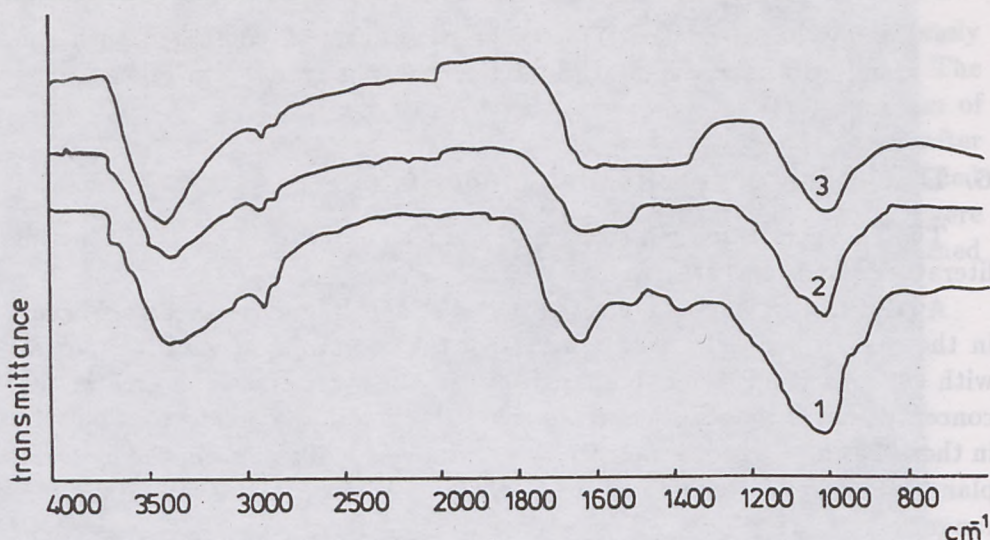


Fig. 1. IR spectra for pure humic acids (curve 1) and with adsorbed Co^{2+} ions (curve 2) and Cr^{3+} ions (curve 3).

band shortening corresponding to the valency oscillations of the Si-O-Si groups (Tab. 1).

Table 1. The relationship between the DTA energy and the ionic radius

Bentonite	Humic acids	Type of ion and length of ion-oxygen bond	Mixture of humic acids with bentonite
Co^{2+}	Pb^{2+}	Pb-O 0.23	Fe^{2+}
Cu^{2+}	Zn^{2+}	Zn-O 0.21	Ni^{2+}
Hg^{2+}	Co^{2+}	Co-O 0.205	Hg^{2+}
Zn^{2+}	Hg^{2+}	Hg-O 0.20	Pb^{2+}
Cr^{3+}	Cr^{3+}	Cr-O 0.198	Co^{2+}
Ni^{2+}	Ni^{2+}	Ni-O 0.203	Cu^{2+}
Fe^{2+}	Cu^{2+}	Cu-O 0.185	Cr^{3+}
Pb^{2+}	Fe^{2+}	Fe-O 0.194	Zn^{2+}

These series differ for different components of marine bottom sediments, but for the same component, the sequence is the same no matter what the ion concentration was.

In the case of humic acids, a certain relationship exists between the length of the ion-oxygen bond and the band shortening corresponding to the valency oscillations of the Si-O-Si group. The greater the length of the band, the greater the shortening of the band analyzed (Tab. 1).

Thus the humic acids and bentonite are mainly responsible for sorption of trace elements. The TG and DTA curves also confirm this. Quartz does

not exhibit changes in the thermal analysis curves after treatment with solutions of the metal ions studied, which indicates that sorption is minimal or non-existent.

In the case of kaolin, bentonite, humic acids and mixtures of bentonite and humic acids, the energy values calculated from the DTA curves are greater than for samples with adsorbed ions. The following relationship can be inferred: the greater the concentration of the ion studied, the greater its DTA energy. In the case of kaolin with the ions studied and kaolin alone, the loss of mass is identical, and amounts to 10 mg per 100 mg sample in the 500–680°C temperature range. However, the DTA energy values of these ions differ slightly, indicating very little sorption; this varies slightly depending upon the ion.

The situation is similar for illite: there are similar losses of mass (4 mg/100 mg samples) in the 600–800°C temperature range, irrespective of the ion. The energy values differ very slightly, which indicates minimal sorption, differing slightly depending upon the ions studied.

The following relationship is found in bentonite samples: the greater the concentration of the ion studied, the greater the loss of mass in the 600–700°C temperature range.

The DTA energy values are greater for humic acids, as compared with the bentonite mixtures, most probably because of the formation of complexes between them.

The results show that the greater the DTA energy, the more strongly the given ion is bonded to the sediment component.

Ion series can be arranged in order of decreasing DTA energies for different sediment components (Tab. 2).

Table 2. Ions in order of decreasing DTA energies for different sediment components

Illite	Kaolin	Bentonite	Humic acids	Mixture of bentonite and humic acids
Ni ²⁺	Ni ²⁺	Hg ²⁺	Cr ³⁺	Ni ²⁺
Zn ²⁺	Zn ²⁺	Zn ²⁺	Cu ²⁺	Co ²⁺
Cr ³⁺	Hg ²⁺	Cr ³⁺	Ni ²⁺	Zn ²⁺
Cu ²⁺	Cu ²⁺	Cu ²⁺	Zn ²⁺	Fe ²⁺
Hg ²⁺	Pb ²⁺	Co ²⁺	Fe ²⁺	Hg ²⁺
Co ²⁺	Fe ²⁺	Pb ²⁺	Co ²⁺	Cu ²⁺
Pb ²⁺	Cr ²⁺	Ni ²⁺	Pb ²⁺	Cr ³⁺
Fe ²⁺	Co ²⁺	Fe ²⁺	Hg ²⁺	Pb ²⁺

The sequence differs slightly for different components of sediments, but in the case of different concentrations of the ions studied for the same component analogically arranged series are the same. In the case of humic acids, there is a relationship between the DTA energy and the ionic radius. The lower this value, the more strongly the ion is bonded to the humic acid. The results are presented in Table 3.

Table 3. The relationship between the DTA energy and the ionic radius

Ion	DTA energy [J · 100 ⁻¹ mg]	Ion	Ionic radius [nm]
Cu ²⁺	110.5	Cu ²⁺	0.069
Cr ³⁺	109.7	Cr ³⁺	0.069
Ni ²⁺	103.7	Ni ²⁺	0.072
Zn ²⁺	99.8	Zn ²⁺	0.074
Fe ²⁺	95.0	Co ²⁺	0.074
Co ²⁺	91.3	Fe ²⁺	0.076
Pb ²⁺	89.6	Hg ²⁺	0.11
Hg ²⁺	78.7	Pb ²⁺	0.12

Cu²⁺ and Cr³⁺ have the strongest complexing abilities. The way in which these values change is in agreement with the findings of other authors (Duursma *et al.*, 1984; McAlister, 1984; Rashid, 1971, 1972; Schnitzer *et al.*, 1972).

Hence, such components of bottom sediments as humic acids and bentonite are mainly responsible for the sorption of trace element ions. This is confirmed by the IR spectra, as well as the TG and DTA curves. When various ions are bonded to humic acid, IR band shortening occurs in its spectra as compared with the spectrum of the acid alone. In the case of bentonite, the greater the ion concentration, the greater the DTA energy, the loss of mass in the 600–780°C temperature range and the characteristic IR band shortening in relation to the standard samples. The presence or absence of particular minerals and functional groups occurring in humic substances can be inferred from the IR spectra of sediments.

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