

Investigation of sediment samples from the Gulf of Trieste (northern Adriatic) by FTIR spectroscopy

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Abstract: The infrared spectra (FTIR) of homogenised and HCl/HF treated surficial marine sediment samples from the Gulf of Trieste (northern Adriatic) were recorded to investigate the sediment composition. The samples were collected by gravity core sampler and analysed after freeze-drying and homogenisation. The results revealed carbonates and silicates as the major inorganic components, while the content of organic matter was rather low.

Key words: sediment, northern Adriatic, FT-IR, organic matter

INTRODUCTION

Organic matter in sediments originates from organic matter synthesized by marine organisms and from terrigenous sources, mostly introduced in water body across the atmosphere and by riverine inflows. Besides from the origin, the quantity and quality of sediment organic matter depend on its composition and biochemical transformations that occur during sedimentation of organic matter. Labile organic matter such as proteins and sugars could become resistant to degradation by complex interactions with sedimentary mineral particles and/or highly refractory organic compounds (KEIL ET AL., 1994; KNICKER & HATCHER, 1997).

In the present work the compositional and chemical characteristics of three sediment samples from the Gulf of Trieste, obtained by the FT-IR spectroscopy, are presented.

MATERIALS AND METHODS

Surficial sediment samples (0-2 cm) were collected using 40mm diameter gravity core sampler (MEISCHNER AND RUMOHR, 1974) at each station. The sediment was freeze-dried, homogenized and used for X-ray diffraction and FT-IR analyses.

FTIR spectra were obtained on homogenized and HF/HCl treated samples (HF/HCl procedure; BLAIR ET AL., 2003) using a Perkin-Elmer System 2000 spectrometer and KBr pellets. Mineral constituents were eliminated by this treatment procedure.

The composition of the mineral fraction was determined by X-ray diffraction analysis (Phillips).

RESULTS AND DISCUSSION

Surficial sediment samples collected from three sampling sites were analysed in this study. The sampling site D6 is located near the *Soča* (Isonzo) River mouth, the station AA is located in the central part of the *Tržaški zaliv* (Gulf of Trieste) and the site FA at the south edge of the Gulf of Trieste (off Piran).

FTIR spectra of all homogenised sediment samples showed similar features (Fig. 1A). The band between 3600-3650 cm^{-1} we attributed to n(O-H) vibrations of hydroxyl groups in aluminosilicates (HOWE ET AL., 2002). The broad band at $\sim 3430 \text{ cm}^{-1}$ is most probably associated with n(O-H...O) vibration of water and with OH groups that might also belong to organic fraction of sediments. The

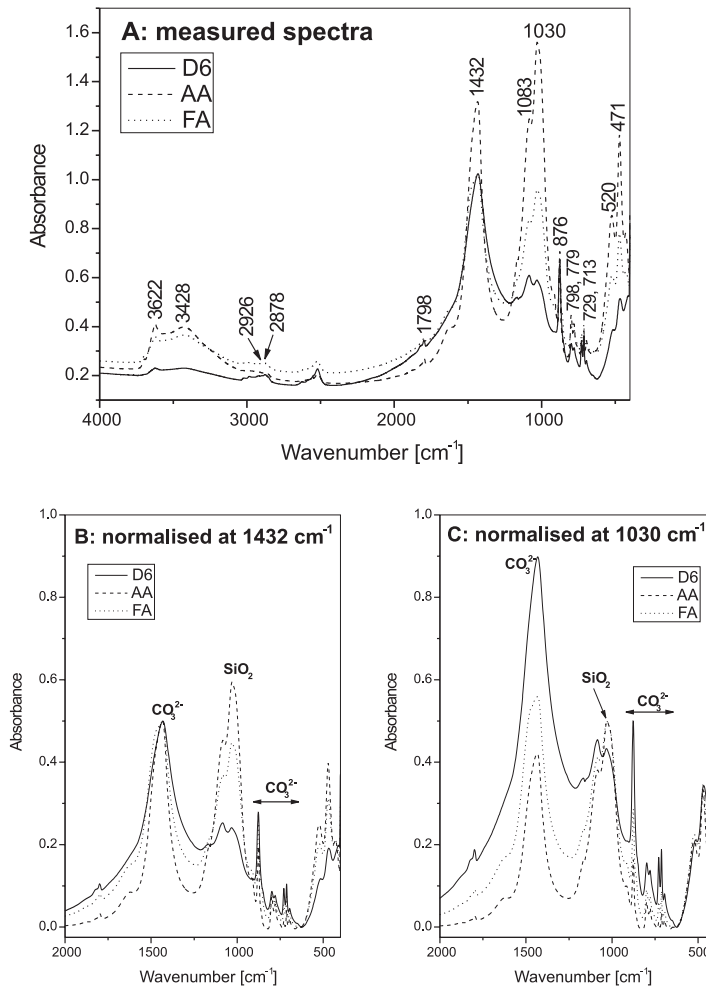


Figure 1. FT-IR spectra of homogenised sediment samples: A) measured spectra, B) spectra normalized to 1432 cm^{-1} (CO_3^{2-}) band and C) spectra normalized to 1030 cm^{-1} (SiO_2) band.

C-H stretching modes at 2800-3000 cm^{-1} are weak and indicate the presence of organic matter in investigated sediment samples.

In the region below 1700 cm^{-1} numerous minerals express their IR vibrations, therefore the assignment of bands is not a straightforward task in natural samples. In our sediment samples, for example, x-ray analyses confirmed the presence of the main mineral phases, i.e. calcite, silica (quartz) and dolomite. Calcite absorption bands were in IR spectra found at 1432, 876 and 713 cm^{-1} , while other carbonates (Li^+ , K^+ , Na^+ ,...) caused the formation of additional bands at 798, 779, 729 and 690 cm^{-1} (Fig. 1A) (FARMER ET AL., 1974). The band at 727 cm^{-1} corresponds to the bending $\text{d}(\text{CO}_3^{2-})$ vibration of dolomite. The absorption bands at 1165, 1083, 1030, 520 and 471 cm^{-1} correspond to silicates, but the other silicate bands (798, 779, 695 cm^{-1}) overlap with carbonates. Quartz bands appear at 1083, 695 and

469 and as a characteristic doublet with peaks at approximately 800 and 780 cm^{-1} (PACÁKOVÁ ET AL., 2000). The surficial sediment from D6 sampling site is mostly composed of carbonates originating from the Isonzo River (OGRINC ET AL., in press) while in the sediments from AA and FA sites the contribution of silicates is also important.

To confirm the interpretation of the directly measured spectra (Figure 1A), the spectra were normalized (Figure 1B,C) and used to rationalize more clearly the relative amount of carbonate vs. silicate components in samples. For example, with regard to the carbonates (Figure 1B), the silicates are contained in sediment samples in the following order: D6 (Isonzo river mouth) < FA (south edge of the Gulf) < AA (central part of the Gulf). The same conclusion we obtained when the spectra were normalized to the silicate band at 1030 cm^{-1} : the carbonate sediments were the most abundant in the sample

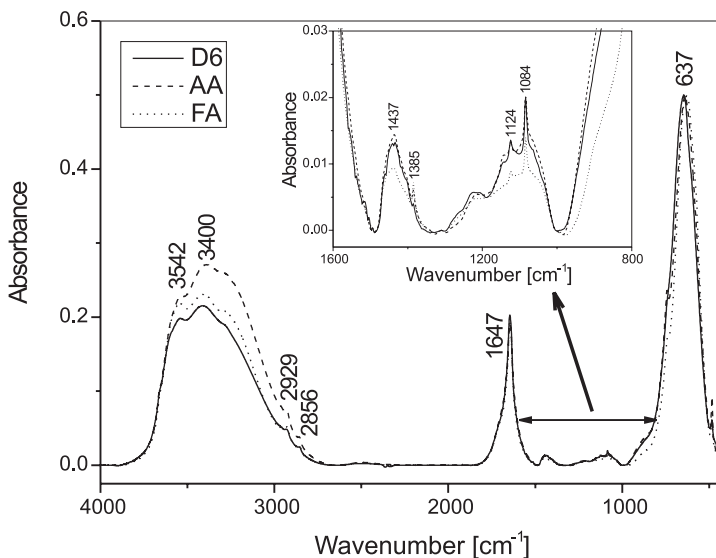


Figure 2. Spectra of HCl/HF treated sediment samples (*demineralized fraction of sediments*)

collected at the Isonzo river mouth (D6), followed by the samples taken from the south edge (FA) and the central part (AA) of the Gulf. Normalisation also confirmed that the bands at 1200-1000 cm^{-1} and 550 – 450 cm^{-1} have the same origin, since the intensities followed the same order.

The spectra of sediments that were treated with HCl and HF showed a number of absorption bands at 3542, 3400, 2900-2800, 1647, 1437, 1385, 1124, 1084, 637 cm^{-1} . The bands appearing with high intensities at 3500-3200, 1647 and 637 cm^{-1} unquestionably belong to the stretching, bending and rocking modes of water. It should be noted that the treated samples are strongly hygroscopic, thus preventing the complete desiccation of prepared KBr pellets. The only bands that could be unambiguously ascribed to the presence of organics are those at 2929 and 2856 cm^{-1} belonging to the stretching modes of $-\text{CH}_2$ and $-\text{CH}_3$ moieties. The corresponding deformational band was observed at 1385 cm^{-1} . Tentatively, we could attribute the bands at 1124 and 1084 cm^{-1} to the C-O-C modes of organic materials (polysaccharides). The broad band at ~ 1437 cm^{-1} is not characteristic of CH_2 deformational bands of organic residues and its origin remains unclear. The band at 1647 cm^{-1} is mostly attributed to free water, but C=C stretching of aromatics and alkene double bonds (PICHEVIN ET AL., 2004) and amide C=O group might also contribute to this band.

FT-IR analyses of HCl/HF treated sediment samples indicated rather low content of organic matter. This is in accordance with previous studies of elemental composition (OGRINC ET AL., 2005) of northern Adriatic

sediments. Moreover, the applied demineralization procedure could lead to hydrolysis, alteration and losses of organic matter. Dissolution of the inorganic matrix eliminates their protective role of organic carbon that can be subsequently released into solutions (GÉLINAS ET AL., 2001). These transformations are significant for more labile and immature organic matter. This could also be considered in our case since the Gulf of Trieste is affected by inputs of fresh organic material. In the future we intend to inspect the presence of organic matter using treatments of sediments with solvents having various polarities.

CONCLUSIONS

FT-IR spectroscopic analysis performed on homogenised sediment samples taken from different locations in the Gulf of Trieste allowed clear distinction of samples with regard to the amount of carbonate and silicate constituents. The relative content of carbonates was found higher close to the shore. This agrees with the large input of these types of sediments by the Isonzo river or washing of the carbonate material from the shore. However, the silicates are more abundant at the central part which could be explained by the fact that they do not agglomerate and remain due to their quasi-colloidal state in the water much longer than carbonates. Treatment of the sediment samples with the modified HCl/HF procedure revealed low organics content.

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