

Detection of molecular markers in aquatic sediments by ion profiles obtained by GC/MS system

Zaharie Moldovan

National Institute of Research and Development for Isotopic and Molecular Technology, 400293 Cluj-Napoca, Str. Donath 72-103, Email: zaha@itim-cj.ro

An analytical method has been developed that permits the determination of molecular markers in aquatic sediments. The procedure consists of ultrasonic solvent extraction followed by a clean-up operation and then analysis by a GC-MS method. The molecular markers are visualised by ion profile chromatography. The compounds were identified based on mass spectra obtained by Electron Impact (EI) in full scan mode.

1. Introduction

The sedimentary organic matter results from a complex combination of both natural and anthropogenic sources [1-7]. The activities of present day civilisation have released into the aquatic environment a wide variety of natural and synthetic compounds not found previously. Many of these compounds when found provide a means of identification of sources of input and pathways of movement of chemicals through ecosystem.

The concentrations of organic compounds in an environmental sample reflect both the original source of organic matter and alteration processes, which have occurred in the environment. The anthropogenic and naturally occurring compounds are found mixed together in recent environmental samples and several of these compounds may be used as tracers to study natural processes affecting the fate and effects of chemical contaminants in aquatic sediments.

The sediments constitute archives of environmental processes. In order to differentiate between inputs of organic matter, molecular marker approaches have been developed on the potential of molecules to be source specific [2-4,8,9].

The purpose of this present paper is the characterisation by GC/MS analysis of organic molecular markers detected in the river sediment to evaluate the degree of contamination and identify the sediment sources in a surface water catchment in Romania. The GC/MS method has the advantage of generating a number of parameters from a single analysis. The study presents data for several families of organic compounds used as molecular markers [8-10] in sediment organic matter investigation: n-Alkanes, Acyclic isoprenoid, Pentacyclic triterpanes (Hopanes), Polyaromatic Hydrocarbons (PAHs), Benzothiophenes, Linear Alkylbenzenes (LABs), Trialkylamines (TAMs) and 2M-Ketones.

2. Experimental section

Sample sites

The samples were collected from places along a 60 km section (between Cluj-Napoca and Dej, Romania) of the Somes River catchment and were analysed for a large number of organic compounds considering as molecular marker for sediment matter composition.

Ultrasonic solvent extraction

An aliquot (2g) of freeze-dried sediment was extracted successively with 10 ml CH_2Cl_2 +methanol (2:1) 3 times for 15 minutes every extraction. The sediment was centrifuged at 3,000 cycles/minute for 10 minute. The extract was fractioned on Al_2O_3 with following organic phases: n-hexane, n-hexane+ CH_2Cl_2 (1:2), CH_2Cl_2 +methanol (1:1) and methanol respectively. The final extracted was dissolved in 1ml in n-hexane [11,12].

Instrumentation

The GC/MS analyses were performed using a Thermo Electron Ultra Trace GC and a Polaris Q mass spectrometer operated in EI mode to 70 eV. The source temperature was 250°C and emission current 300 μA . The gas chromatograph was equipped with a capillary column HP-5MS (30x0.25mm) with 0.25 micron film thickness. The temperature was programmed from 90°C (1minute) to 120°C at 10°C/minute and then to 200°C at 3.5°C/min and then to 315°C at 5°C/min (keeping this temperature for 11 min). Helium was used at a flow of 2 ml/minute as carrier gas.

3. Results and discussions

3.1. The n-Alkanes.

The alkanes are detected in high quantity and show compounds with the number of carbon atoms ranging from 12 to 26. They are presented by the characteristic ion m/z 85 (Figure 1). To investigate the origin of n-alkanes the results and information from ion chromatogram data analyses as carbon number range and Carbon Preference Index (CPI) [2,5,8] are used. This number can be used also as an indicator of the product origin.

The ion chromatogram is unimodal with a maximum to 17 carbon atoms having a CPI (C14-C21) value of 1.3 leading to the conclusion that n-alkanes originate from aquatic algae [2,6]. The relative amount of odd/even carbon number n-alkanes (or CPI) is used to obtain information on relative maturities of organic matter from sediment.

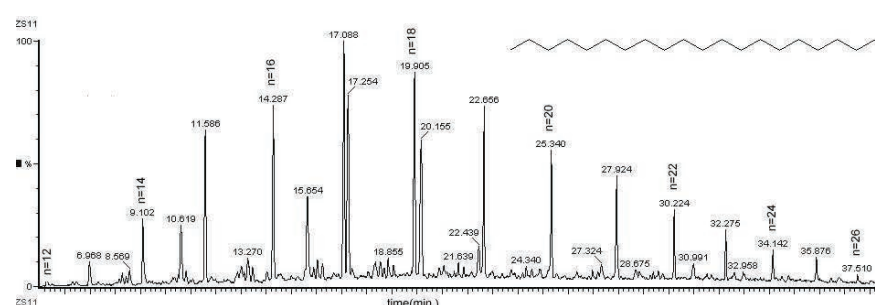


Figure 1. GC/MS chromatogram on m/z 85 for a sediment sample collected from river for visualisation of n-alkanes (n range 12-26)

3.2. Acyclic isoprenoid

The acyclic isoprenoid compounds have a large number of methyl branching points in their structure leading to the production of information rich spectral content enabling, in most cases, the branching points in the molecules to be determined. They are presented with the fragment m/z 183 containing 13 carbon atoms. The profiles of acyclic isoprenoids based on drawing the signal to m/z 183 is shown in Figure 2.

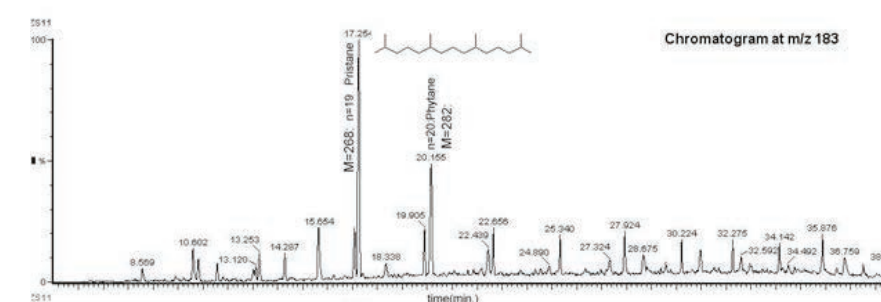


Figure 2. The detection of acyclic isoprenoids (Pristane and Phytane are main compounds) in a sediment river sample.

This group of compounds includes pristane (C19) and phytane (C20) often used as an indicator of depositional environments [5,8]. The idea is based on the premise that pristane is formed from phytol by oxidation and decarboxylation reactions and on other hand phytane is formed by hydrogenation and dehydration of phytol. The type of reaction is mainly dependant on the oxidation and reducing-type environments. The samples derived from terrestrial sources have higher concentration of the long chain isoprenoids than samples derived from marine sources [8].

3.3. Pentacyclic triterpanes (Hopanes)

Hopanes is a class of compounds that has a great impact on petroleum geochemistry. They are very resistant to biodegradation and can serve therefore as conserved internal standards for assessing the biodegradation of more degradable compounds [13]. They have carbon atom numbers ranging from 27 to 35. The hopanes are detected by drawing the profile using the ion m/z 191. Additional detailed information can also be made for based on the detected molecular ions. In addition to providing maturity information, hopanes are also useful as source indicators. The hopanes detected in a sediment sample collected sample from Somes River is showed in the *Figure 3*.

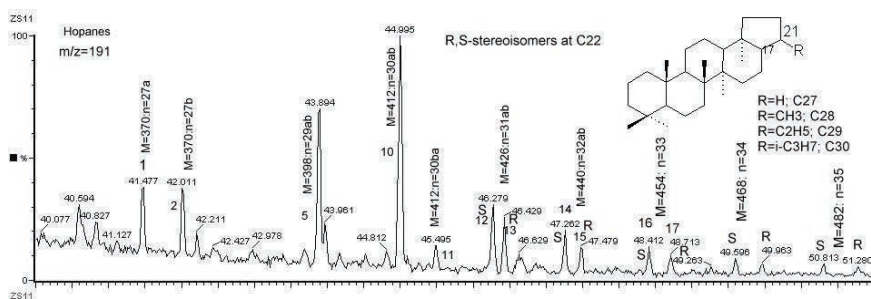


Figure 3. Detection of Hopanes in a river sediment (m/z 191 in the time range 40-51.2 min).

Hopanes are molecular markers used currently for estimation of the mineral maturity [2,5]. In low maturity materials the group of hopanes are dominated by stereochemistry 17β (H), 21β (H) and configuration R at C22. As the maturity level increases increases 17α (H), 21β (H) stereochemistry predominates and 22S configuration for the C31 and higher homologues [5,8].

The chromatogram obtained to $m/z=191$ can be used directly for estimation of the maturity minerals by comparison of the two compounds at C27: 18β (H)22,29,30-trisnorhopane and 17β (H)22,29,30-trisnorneohopane (the peaks 1 and 2 respectively).

3.4. Polyaromatic Hydrocarbons (PAHs)

An abundant class of compounds detected in the river sediment samples are Polyaromatic Hydrocarbons (PAHs). This type of compound presents a mass spectra of the molecular ion as base peak and therefore can be shown by selective chromatograms (*Figure 4*). The molecular ion is also used as the diagnostic ion for all PAHs in early papers [2].

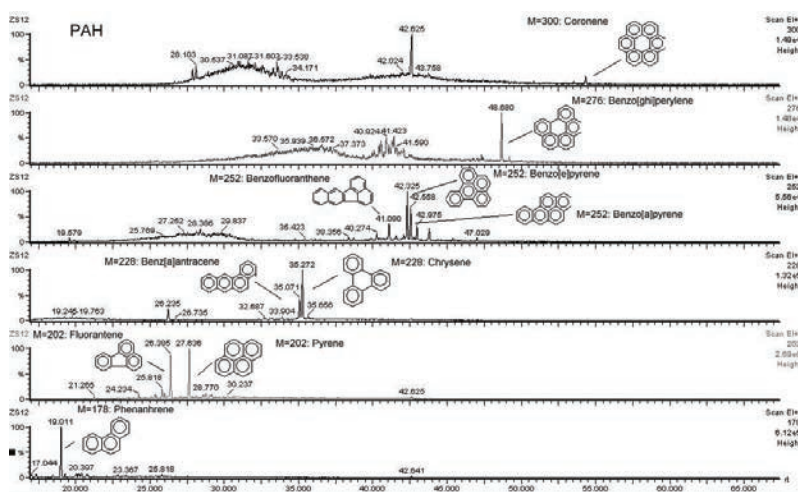


Figure 4. Polyaromatic Hydrocarbons (PAHs) detected by ion chromatograms at m/z 178, 202, 228, 252, 276 and 300 respectively in the range time of 18-70 min.

The presence of polycyclic aromatic hydrocarbons (PAHs) in sediment samples reflects the anthropogenic impact on sediment organic matter [2,7]. The input of PAHs into the environment are due to anthropogenic activities such as combustion of fossil fuel as well as natural processes (forest fires). The PAHs source can be of petrogenic, pyrogenic or biogenic origin [2,7]. Combustion of fossil fuels and plant materials leads to pyrogenic PAHs with four to eight parental rings. The pyrogenic markers include fluoranthene, benzo[fluoranthene], benzoanthracenes, benzo[e]pyrene, benzo[a]pyrene and benzo[ghi]perylene, with low abundances of alkylated surrogates. The petrogenic sources (ancient plant material) are characterised by alkylated structures. The values of characteristic source parameters [2] defined as Fluoranthene/(Fluoranthene + Pyrene) and Benz[a]anthracene/(Benz[a]anthracene + Chrysene) for investigated samples have the average values 0.47 and 0.40 respectively. These values show a pyrogenic origin of the detected PAHs.

3.5. Sulphonated Polyaromatic Hydrocarbons (SPAHS). Benzothiophenes

Benzothiophenes is another important group of pollutants used very often as biomarkers by the source information. The organosulfur compounds can be formed by the reaction of aromatic hydrocarbons with elemental sulphur [14]. They are, as are PAHs, very persistent chemicals [15]. Because of their environmental impact they are included in the list of priority pollutants. This group of compounds can be seen by ion chromatograms at molecular ion (*Figure 5*).

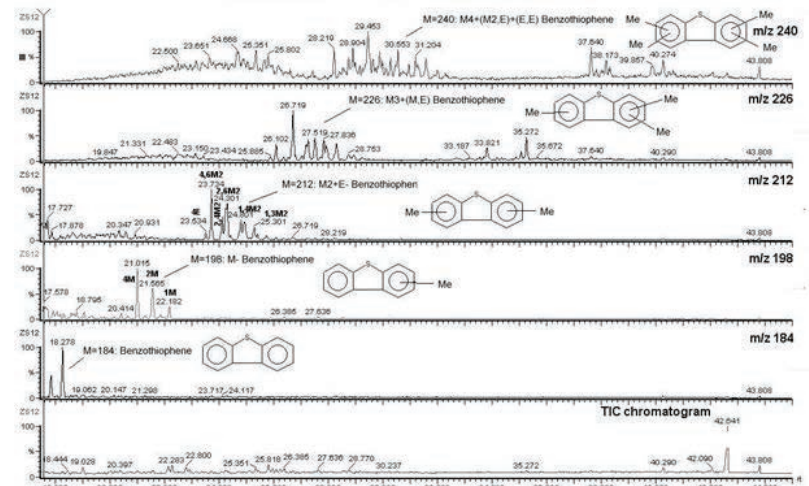


Figure 5. Benzothiophenes presented by ion chromatograms at m/z 184, 198, 212, 226 and 240 respectively in the range time of 18-45 min.

3.6. Linear Alkylbenzenes (LABs)

A very important group of pollutants found in the sediment river samples is the Linear Alkylbenzenes (LABs). This group of compounds was the subject of investigation in many early papers [7,16,17]. They can be seen by drawing the ion chromatogram at m/z 91. This class of compounds originate from alkyl sulphonic surfactants (present in a lot of detergents) by biodegradation. They comprise isomers of LABs with a number of carbons from 10 to 13 (*Figure 6*). The investigation of linear alkyl benzenes is performed in order to study the impact of sewage water on aquatic sediments.

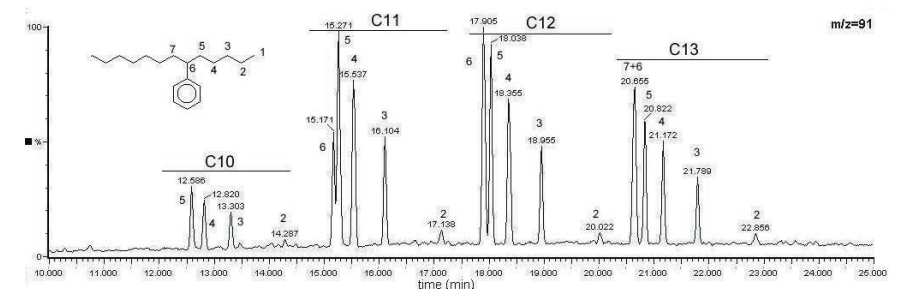


Figure 6. GC/MS Chromatogram on $m/z=91$ for a sediment rivers sample for visualisation of Linear Alkyl Benzenes (LABs). The alkyl n range 10-13.

3.7. Trialkylamines and 2M-Ketones

Trialkylamines are cationic surfactants that originate from detergents, methyl-ketones are photo-oxidation products of TAMs produced in sedimental conditions.

The detection of these families of compounds is very important in knowing the impact of sewage water on the sediment organic matter composition [18,19].

Based on chromatogram at m/z 58 two families of organic compounds can consecutively be detected: methyl-ketones and trialkylamines (TAMs) as can be seen in the *Figure 7*. The general structure of TAMs used as cationic surfactants is $(CH_3)_2N-C_nH_{2n+1}$ ($n=12, 14, 16, 18$). The ion to m/z 58 originating from methyl-ketones is produced by a rearrangement process, leading to structure $CH_3-(C-O^+H)=CH_2$, and also the ion at m/z 58 is produced from Trialkylamines by a fission reaction involving C-C bond along of the amine chain (beta-position) leading to structure $(CH_3)_2N^+=CH_2$.

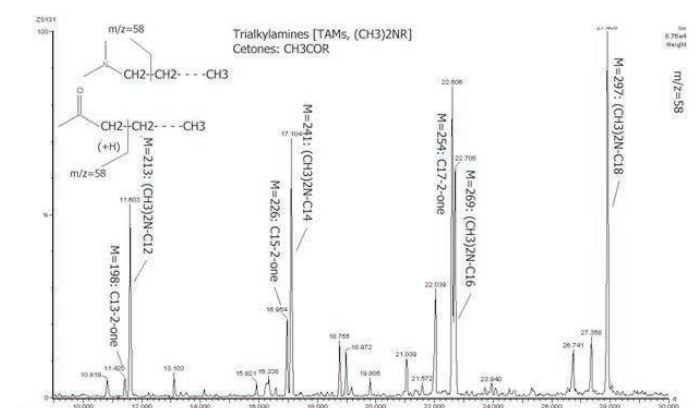


Figure 7. GC/MS chromatogram on m/z 58 for a sediment sample collected from river for visualisation of Trialkylamines and 2M-Ketones

4. Conclusions:

In the sediment samples collected from the Somes river some important groups of molecular markers were identified. The detected groups of markers and their main characteristic are shown in *Table 1*. The main advantage of the method is that from a single measurement multiple characteristic parameters can be determined. Also, the method can be applied to the study of sediment originating from any aquatic medium such as lake, sea or wastewater treatment plant (WWTP).

Table 1. Molecular markers, characteristic ion (m/z) used in GC/MS profile and parameter used for characterisation of sediment organic mater.

No	Molecular marker	m/z	Parameter
1	n-Alkanes	85	n of carbon, CPI
2	Acyclic Isoprenoids	183	n of carbon, ratio Pristine/Phytane
3	Hopanes	191	Ratio: $17\beta(H), 21\beta(H) / 17\beta(H), 21\beta(H)$
4	PAHs	178,202,228, 252,276,300	Ratio: Fluorantene/ (Fluorantene + Pyrene) and Benz[a]anthracene/(Benz[a]anthracene + Chrysene)
5	Benzothiophenes	184,198,212,226,240	Relative intensity
6	LABs	91	n of carbon, relative intensity
7	TAMs and 2M-Ketones	58	n of carbon, relative intensity

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