

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

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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 selected ion chromatograms. The compounds are identified based on mass spectra obtained by Electron Ionisation (EI) in full scan mode.

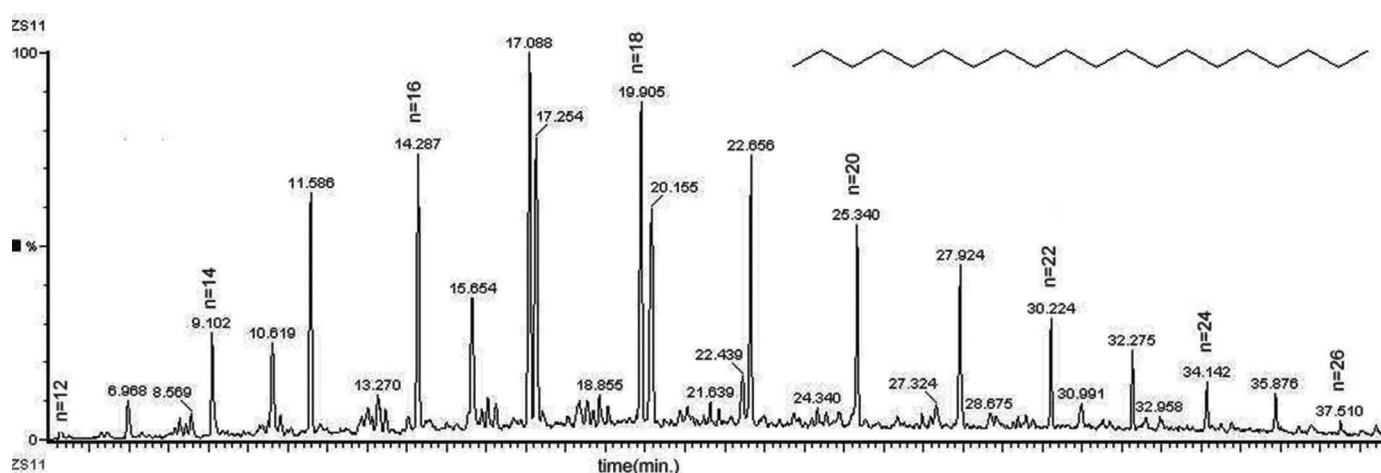


Figure 1. GC/MS chromatogram of m/z 85 for a sediment sample collected from river for visualisation of n -alkanes (n range 12-26)

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 the ecosystem.

The concentrations of organic compounds in an environmental sample reflect both the original source of organic matter, as well as the 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 the various 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 the present paper is the characterisation of organic molecular markers detected in the river sediment by GC/MS analysis 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 several 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 Someș River catchment and were analysed for a large number of organic compounds commonly used as molecular markers for sediment mater 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

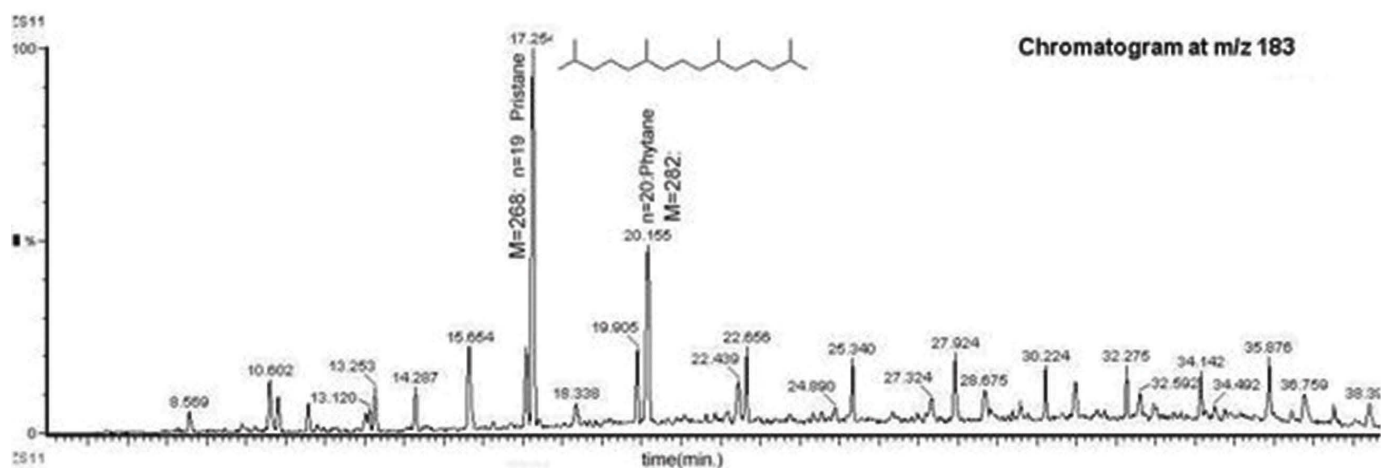


Figure 2. The detection of acyclic isoprenoids (Pristane and Phytane are main compounds) in a sediment river sample.

minutes every extraction. The sediment was centrifuged at 3000 cycles/minute for 10 minutes. To reduce molecular interference from different families of compounds, the extract was fractionated on Al_2O_3 with the following organic phases: a) n-hexane, b) n-hexane: CH_2Cl_2 (1:2), c) CH_2Cl_2 :methanol (1:1) and d) methanol, respectively. The final extract, after evaporation, was dissolved in 1ml n-hexane [11,12]. The n-Alkanes, Isoprenoids and Linear Alkyl Benzenes were analysed from fraction a, Polyaromatic Hydrocarbons and Sulphonated Polyaromatic Hydrocarbons from fraction b and Trialkylamines and 2M-Ketones from fraction c.

Instrumentation

The GC/MS analyses were performed using a Thermo Electron Ultra Trace GC coupled with a Polaris Q mass spectrometer operated in EI mode to 70 eV. The ion source temperature was 250°C and the emission current was 300 μA . The gas chromatograph was equipped with a HP-5MS (30m \times 0.25mm) capillary column

possessing a film thickness of 0.25 micron. The temperature was programmed from 90°C (1minute) to 120°C at 10°C/minute, then to 200°C at 3.5°C/min, and finally to 315°C at 5°C/min (keeping this temperature for 11 min). Helium was used as carrier gas at a flow of 2 ml/min.

3. Results and discussions

3.1. The n-Alkanes.

Alkanes are detected in high quantity and show compounds with the number of carbon atoms ranging from 12 to 26. They are represented by the characteristic ion m/z 85 on fraction a of extract (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 selected ion chromatogram on selected ion m/z 85 is unimodal with a maximum to 17 carbon atoms having a CPI (C14-C21) value of 1.3. This finding reveals that the observed n-alkanes originate from aquatic

algae [2,6]. The relative amount of odd/even carbon number n-alkanes (or CPI) is then used to obtain information on relative maturities of organic matter from sediment.

3.2. Acyclic isoprenoids

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

This group of compounds includes pristane (C19) and phytane (C20) is often used as an indicator of depositional environments [5,8]. The idea is based on the premise that pristane is formed from oxidation and decarboxylation reactions of phytol while phytane is formed by hydrogenation and dehydration of phytol. The type of reaction is mainly dependent on the oxidisation and reducing-type environments. The samples

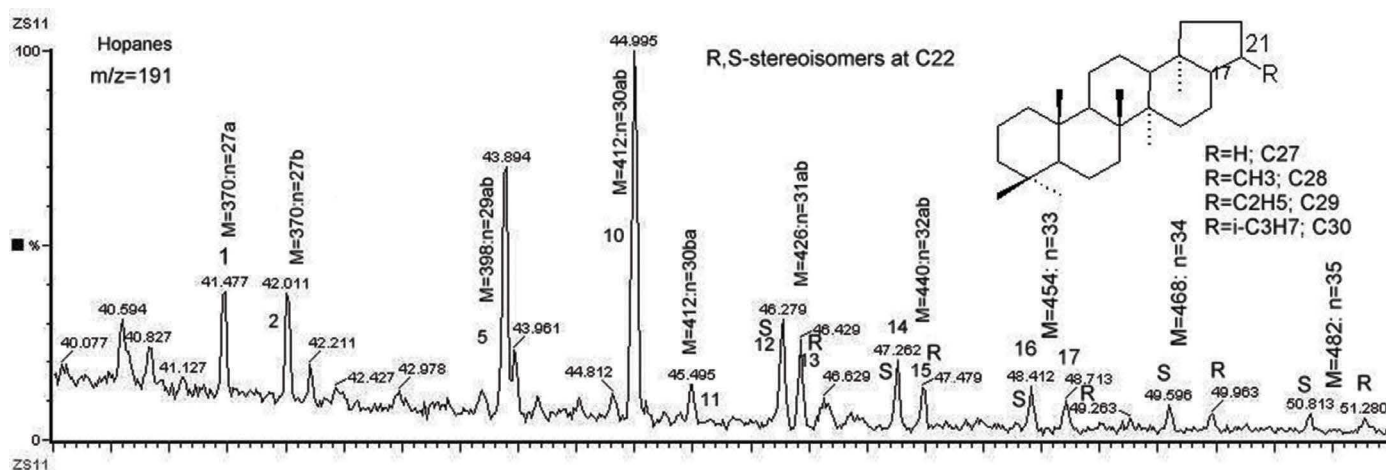


Figure 3. Detection of Hopanes in a river sediment (m/z 191) in the time range 40-51.2 min.

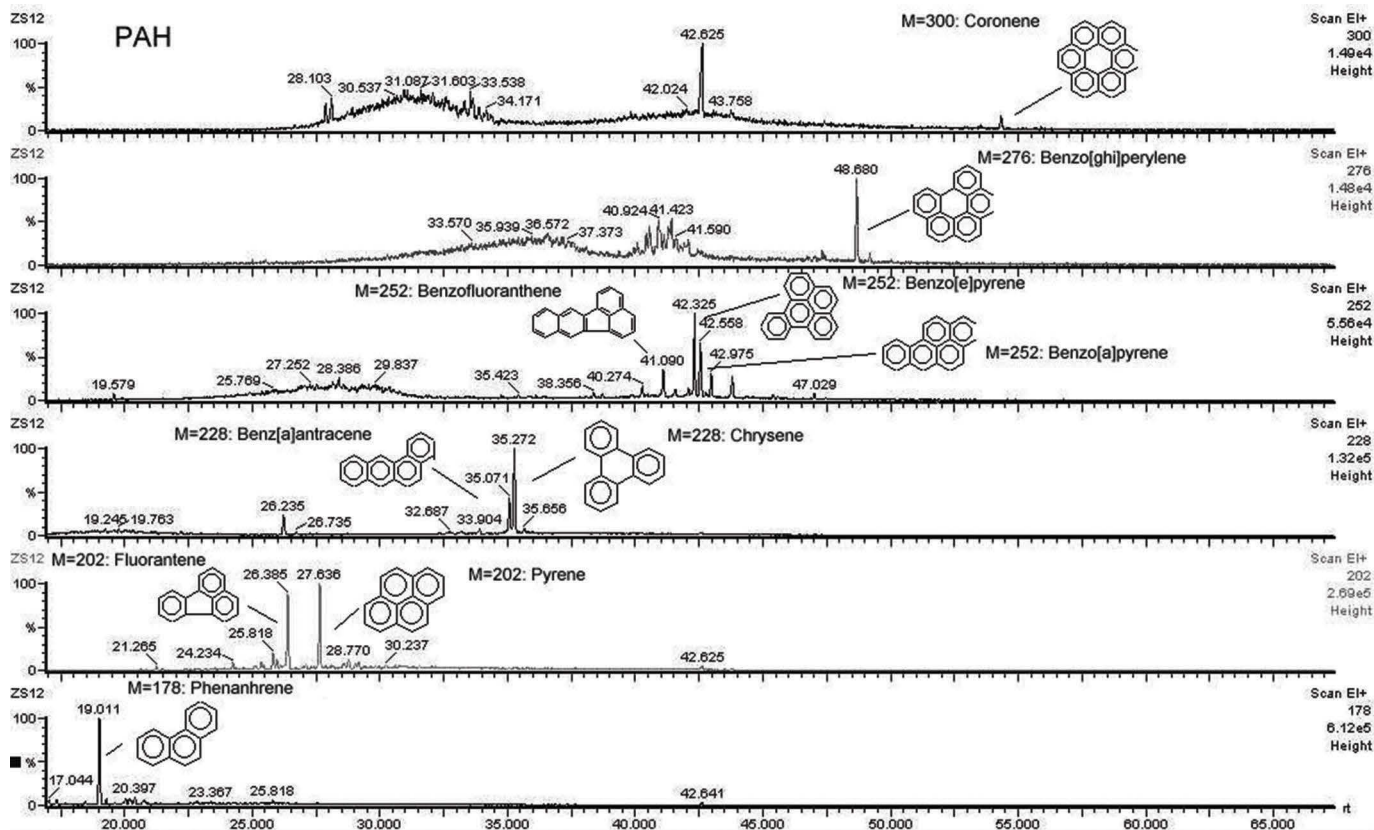


Figure 4. Polyaromatic Hydrocarbons (PAHs) detected by ion chromatograms at m/z 178, 202, 228, 252, 276 and 300 (shown above and in Table 1) respectively in the range time of 18-70 min.

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 are 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 (fraction a). In addition to providing maturity information, the detected molecular ions of the hopanes are also useful as source indicators. The hopanes detected in a sediment sample collected from Somes River are shown in the Figure 3.

The 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 $17\beta(H)$, $21\beta(H)$ and configuration R at C_{22} . As the maturity level increases $17\alpha(H)$, $21\beta(H)$ stereochemistry predominates and 22S configuration for the C_{31} 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 C_{27} : $18\alpha(H)22,29,30$ -trisorhopane and $17\alpha(H)22,29,30$ -trisorneohopane (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). These compounds show the molecular ion as the base peak in mass spectrum and therefore the molecular ion is used for selected ion chromatogram (Figure 4). The molecular ion was also used as the diagnostic ion for all PAHs in early papers [2].

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 such as 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 parent rings. The

pyrogenic markers include fluoranthene, benzofluoranthenes, 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 ratio Fluoranthene/(Fluoranthene + Pyrene) and ratio 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 similar to PAHs in the fact that they are both very persistent chemicals [15]. Because of their environmental impact, PAHs are included in the list of priority pollutants (U.S. EPA). This group of compounds can be analysed by selected ion chromatogram having also the molecular ion as selected ion (Figure 5).

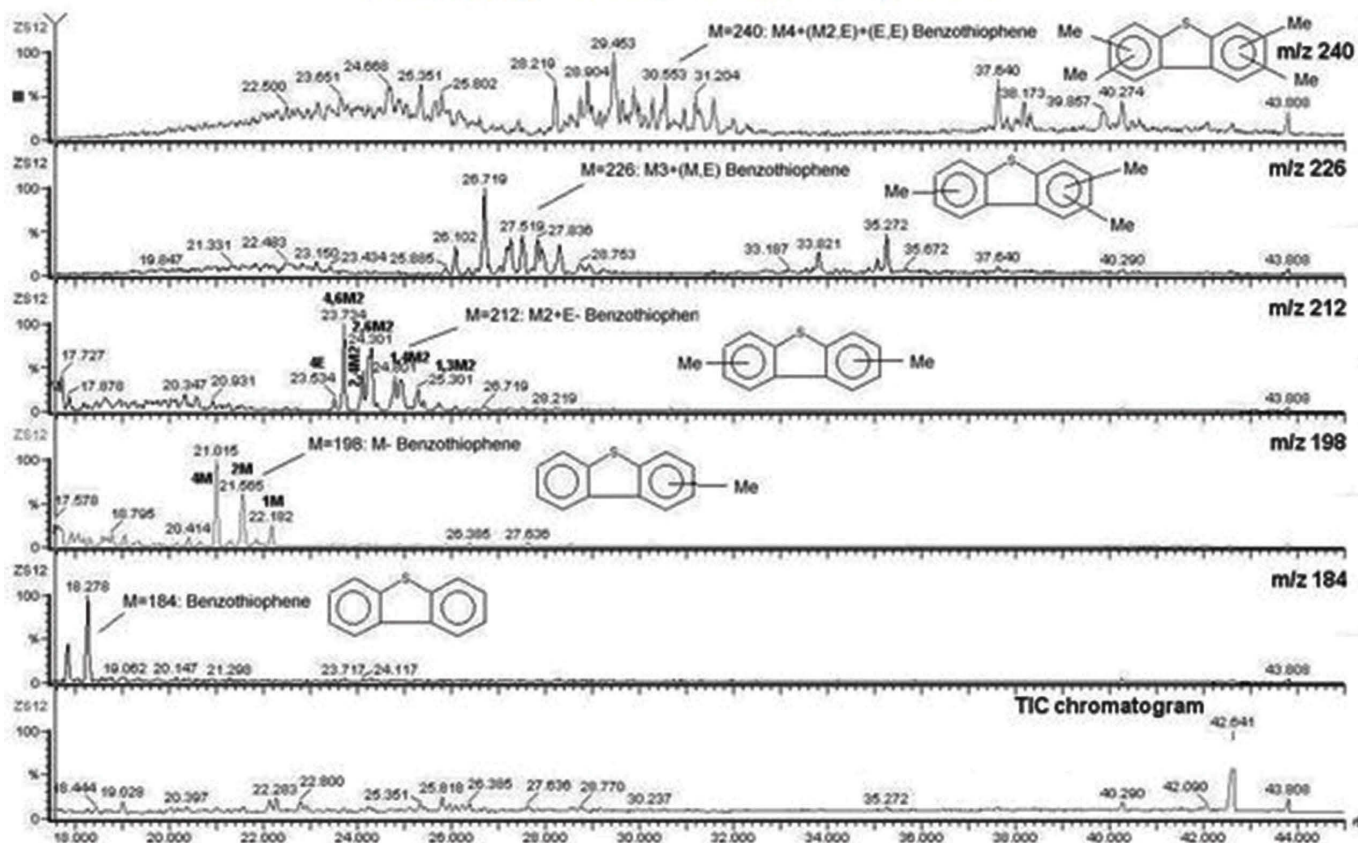


Figure 5. Benzothiophenes presented by ion chromatograms at m/z 184, 198, 212, 226 and 240 respectively in the range time of 18-45 min.

3.6. Linear Alkylbenzenes (LABs)

A very important group of pollutants found in the sediment river samples are Linear Alkylbenzenes (LABs). This group of compounds was the subject of investigation in many early papers [7, 16, 17]. They can be seen by extracting the ion chromatogram at m/z 91 on fraction a. This class of compounds originates from the biodegradation of alkyl sulfonic surfactants which are present in numerous detergents. 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.

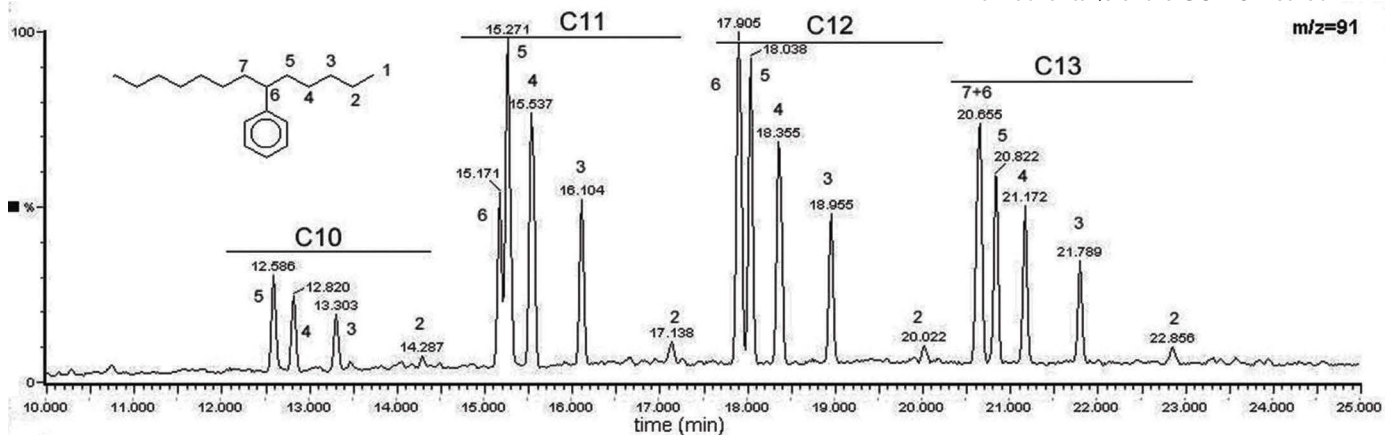


Figure 6. GC/MS Chromatogram of m/z 91 for a sediment rivers sample for visualisation of Linear Alkyl Benzenes (LABs). The alkyl n range 10-13.

3.7. Trialkylamines and 2M-Ketones

Trialkylamines (TAMs) 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 studying 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, as can be seen in the Figure 7, using fraction c. 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 the structure $CH_3-(CO^+H)=CH_2$. The ion at m/z 58 is also produced from trialkylamines by a fission reaction involving C-C bond along of the amine chain (beta-position) leading to structure $(CH_3)_2N^+=CH_2$.

4. Conclusions

In the sediment samples collected from the Somes river, several important groups of molecular markers were identified. These detected groups of markers and their main characteristic are shown in Table 1. The main advantage of the GC-MS method

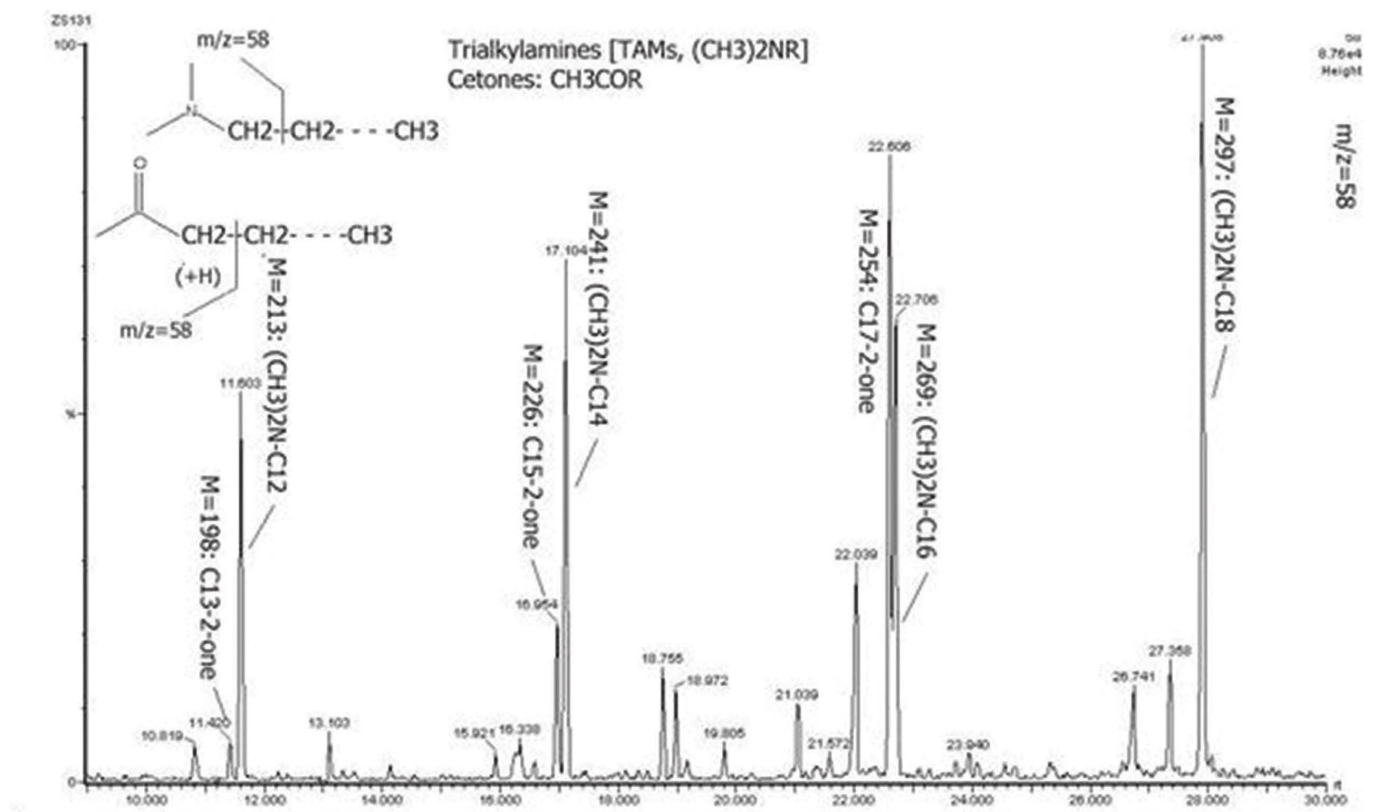


Figure 7. GC/MS chromatogram of m/z 58 for a sediment sample collected from river for visualisation of Trialkylamines and 2M-Ketones

presented is that from a single measurement multiple characteristic parameters can be determined. The method can also be applied to the study of sediment originating from any aquatic medium such as lake, sea or wastewater treatment plant (WWTP).

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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: $17\beta(H), 21\beta(H)/17\alpha(H), 21\beta(H)$
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