DETERMINATION OF ORGANIC POLLUTANTS STRUCTURE DETECTED IN RIVER SEDIMENT BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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Abstract

The extraction and analytical methods have been developed that allow determination of pharmaceuticals, antioxidants, polyaromatic hydrocarbons sulphonated polyaromatic hydrocarbons and multimolecular biomarkers in rivers sediment. The procedures consist from ultrasonic solvent extraction followed of clean-up operation and than analysis by GC-MS method.

The compounds were identified based on mass spectra obtained in full scan mode.

Introduction

The activities of modern civilization have released to the aquatic environment a wide variety of natural and synthetic compounds not found prior to modern times. Many of these compounds provide a means of identification sources of inputs and pathways of movement of chemicals through ecosystem.

The absolute and relative concentrations of organic compounds in an environmental sample reflect both the origin source of organic matter and alteration processes, which have occurred in the environment.

Human activity continues to add an increasing variety of organic compounds into the environment or has changed the ratios and amounts of naturally compounds. Both 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 water. Often used as tracers are the following compounds: Coprostanol, Linear alkyl benzenes (LABs), Trialkylamines (TAMs), Nonyl phenols (NPs), Polychlorinated biphenyls (PCBs), Polycyclic aromatic hydrocarbons (PAHs)[1]

The present paper purpose is the Mass Spectrometric (MS) characterization of organic pollutants detected in river sediment to evaluate the degree of contamination of the surface waters from Romania. The samples were

collected from Somes River places situated along of river on a segment of 100 Km near of Cluj-Napoca city.

Experimental section

Ultrasonic solvent extraction

An aliquot (PMF: 2g) of freeze-dried sediment was extracted successively with 10 ml CH_2Cl_2+methanol (2:1) 3 times for 15 min. every. The sediment was centrifuged at 3 000/min for 10 min. 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 dried to 1ml en n-hexane[2,3]

Instrumentation

The GC/MS analyses were performed using a Fisons MD 800 mass spectrometer operated in EI mode to 70 eV. The source temperature was 230^0C and emission current 300 µA. The gas chromatograph was equipped with a capillary column HP-5MS (30x0.25mm) with 0.25film thickness. The temperature was programmed from 90^0C(1min.) to 120^0C at 10^0C/min and than to 200^0C at 3.5^0C/min and than to 315^0C at 5^0C/min (keeping this temperature for 11 min.)

Results and discussions

The Somes River is one of major rivers in Easter Europe. From its source to the mouth at the Tisa (tributary of Danubium) it flows over a distance of 400 km (with 350 km located in Romania). On its catchment lives more than 1 000 000 inhabitants.

The samples were collected from places along of 60 km distance (between Cluj-Napoca and Dej) and were analysed for a large number of organic compounds.

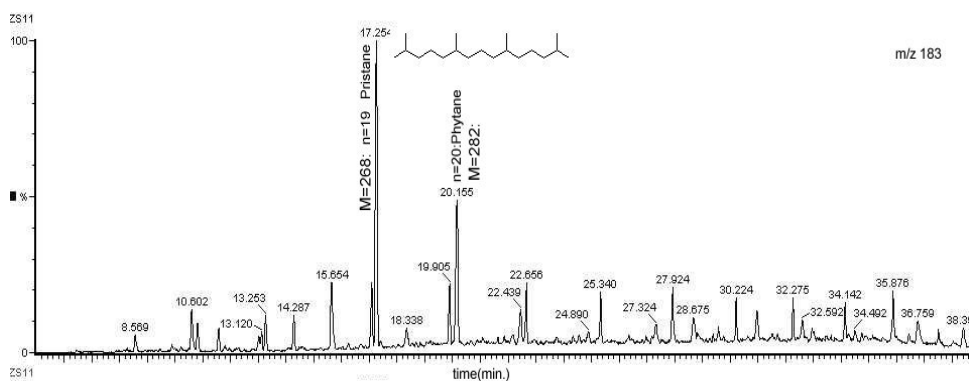The main groups of detected compounds are:

Fig. 1. The detection of acyclic isoprenoids (Pristane and Phytane are main compounds) using the ion signal to m/z 183 on a sample collected to 15 km after Cluj-Napoca.

1) The *n-Alkanes*. Its are, detected in high quantity and show compounds whit the number of carbon atom ranging from 12 to 30. They are presented by the characteristic ion *m/z 99*. The pollutants of alkane type are originating from petroleum products. The relative amount of odd/even carbon number n-alkanes (or CPI) is used to obtain information on relative maturities of oils and extracts. This number can be used also as an indicator of the product origin[4].

2) The *acyclic isoprenoids* compounds. Its have a large number of methyl branching points in their structure leading to the production of spectra with large information 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 the Fig.1

This group of compounds includes pristane (C19) and phytane (C20) often used as an indicator of depositional environments[4]. The idea is based on the premise that pristine is formed from phytol by oxidation and decarboxylation reaction and on other hand phytane is formed by hydrogenation and dehydration of phytol. The type of reaction is depending in main of oxidization and reducing-type environments.

3) *Bicyclic sequiterpenoids* and *tricyclic terpanes* are presented by chromatogram to ion m/z 123 and 191 respectively. Based on observation that one part from that occurs only from plants where the other parts occur only from bacteria its profile is very useful in the source correlation (terrestrial or marine source).

5) *Pentacyclic triterpanes (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[5]. The have carbon atom number ranging from 27 to 32. Its are detected by drawing the profile using the detected ion to m/z 191
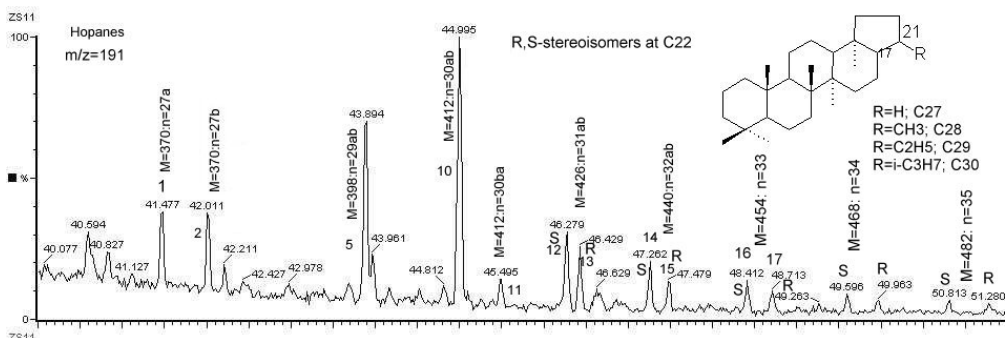

Fig. 2. Detection of Hopanes in a sediment sample from Somes river near Cluj-Napoca (m/z 191 in the time range 40-51.2 min)

The additional detection also can be made for detailed information based on molecular ions. In addition to providing maturity information, hopanes are also useful as source indicators. In many applications, and with sufficient experience, it is only necessary to routinely use the ion m/z 191 to determine the hopane distribution and not include other fragment or molecular ion. The hopanes detected in a sample from Somes near Cluj-Napoca is showed in the Fig. 2.

Hopanes (pentacyclic compounds) are molecular markers used currently for estimation of the minerals maturity. In low maturity materials the group of hopanes are dominated by stereochemistry 17 (H),21 (H) and configuration R at C_{22}. As the maturity level increases 17 (H), 21 (H) stereochemistry predominates and 22S configuration for the C_{31} and higher homologues.
The chromatogram obtained to m/z=191 can be used directly for estimation of the maturity minerals by comparition of the two compounds at C_{27}: 18 (H)-22,29,30-trisnorhopane and 17 (H)22,29,30-trisnorneohopane (the peaks 1 and 2 respectively).

6) A abundant class of compounds are Polyaromatic Hydrocarbons (PAHs). This type of compounds presents in mass spectra the molecular ion as base peak and therefore can be shows by selective chromatograms (Fig. 3)
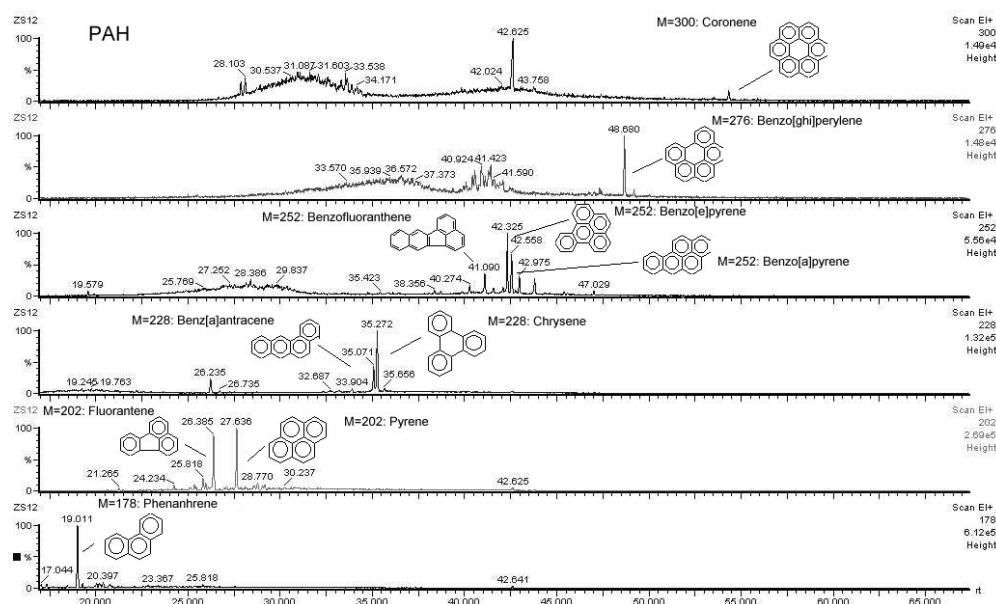

Fig. 3. Groups of compounds from Polyaromatic Hydrocarbons (PAHs) family obtained by ion chromatograms at m/z 178, 202, 228, 252, 276 and 300 respectively in the range time of 18-70 min.

7) *Sulphonated Polyaromatic Hydrocarbons (SPAHs), Benzothiophenes* is other important group of pollutants used very often as biomarkers by the source information. They are as PAHs very persistent chemicals[6]. By their environmental impact are situated in the list of priority pollutants. This group of compounds can be seen by ion chromatograms at molecular ion (Fig 4).

8) A very important group of pollutants found in the sediment samples is the *Linear Alkylbenzens (LABs).* They can by seen bay drawing the ion chromatogram m/z 91. This class of compounds originate from alkyl sulfonic surfactants (present in a lot of detergents) by biodegradation. They comprise isomers of LABs with number of carbon from 10 to 13 (Fig. 5).

9) *Sterols (Tetracyclic compounds) as markers of sewage pollution: (5ß-Stanols C27/C29).*

The us of Sterols as markers for sewage pollution is based on the observation that chemical compounds of type *5ß-Stanols* are produced from Δ^5-stenols by microbial reduction. Important information can be obtained by measurement of the ratio of compounds: 5 - Cholestan (Coprostanol, M=388) to 5 - Stigmastanol (M=416). The Coprostanol is produced from Cholesterol and predominate in sewage of omnivore animal origin but Stigmastanol is produced from Sitosterol and predominate in sewage originate from herbivore animals. The ratio of these compounds can be seen from ion chromatograms at *m/z 215* and their precursor at *m/z 213* (Fig 5)
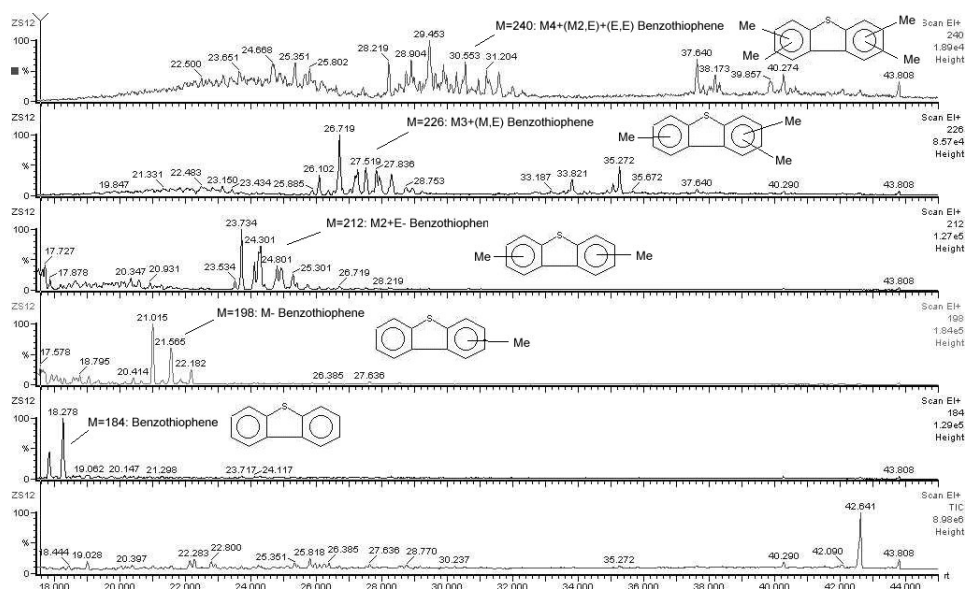

Fig. 4. Groups of compounds from Sulfonated Polyaromatic Hydrocarbons (SPAHs) family obtained by ion chromatograms at m/z 184, 198, 212, 226 and 240 respectively in the range time of 18-45 min.
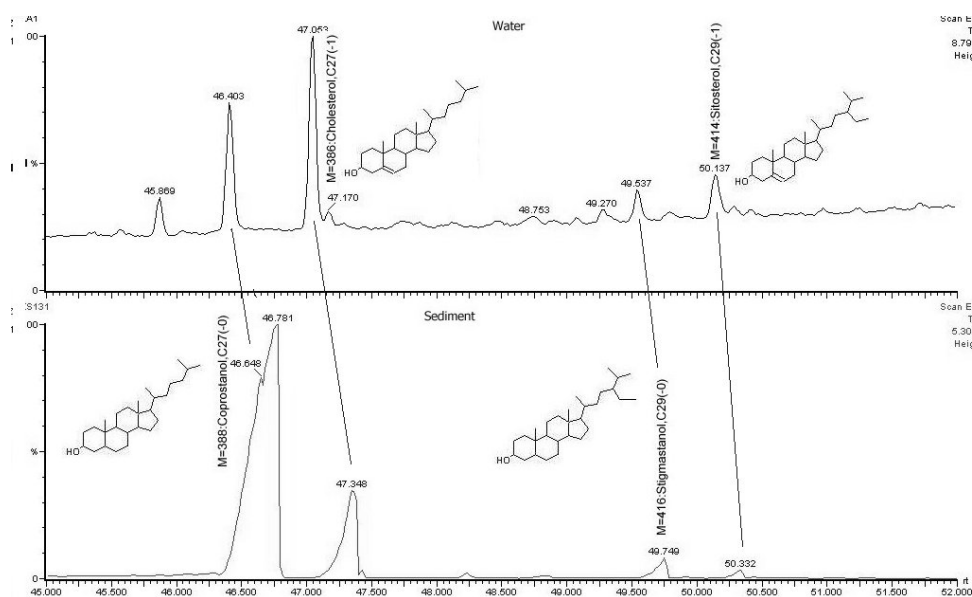
Fig. 5. TIC chromatogram in the range of time 40-52 min on two samples from the same place (Somes river): up water sample and down sediment sample. In the sediment predominate reduced compounds (Coprostanol and Stigmasterol relative to precursors Cholesterol and Sitosterol)

10) *Metilated Fatty Acids group*. This group originate from Fatty acids having as source animal fat and vegetal oils detected in high quantity in river waters. The number of carbon atoms for detected mutilated compounds are: 14(M=242), 15 (M=256), 16(M=270), 17(M=284), 18(M=296:1 and M=298:0).

11) *Synthetic detergents: Nonylphenol polyetoxylates (NPnEO, n=1)*. In the sediment sample was detected a family of NpnEO with n=1. The compounds have molecular mass M=294 and base peak *m/z 193* and *m/z 169* corresponding to different structure for alkyl chain. In water samples, from the same places, were detected family of nonionic surfactants with n from 1 to 10.

12) *Pharmaceutical products*. Pharmaceutics are extensively used for medical practices. Their annual consummation ranges between a few kilograms and several hundred tons per individual compounds. Due to an incomplete elimination in wastewater treatment plant (WWTP) residue of pharmaceutical and personal care products (PPCPs) are found both in waste and surface waters[7-10]

The detected pharmaceuticals in the sediment samples are: caffeine and triclosane. Triclosan is an ant microbial agent found in many hand soups (0.1 to 0.3%)[11] (Thomas and Foster 2005). It is used also as a preservative and disinfectant in many consumer products as acne creams and recently as a slow-release product, which is incorporated in a wide variety of plastic products.

13) *Polycyclic Musk Fragrances.*Were detected Galaxolide and Tonalide compounds used extensively in cosmetic industries (perfumes, detergents). Due to the environmental stability *Galaxolide and Tonalide* were selected as suitable tracers for musk fragrance[12].

Galaxolide and Tonalide is synthetic musk with applications as fragrances in soaps, perfumes, air fresheners, detergents, fabric softener and other cleaning products.

Conclusions:

In the sediment samples collected from Somes river were identified following groups of compounds: Sterols (predilection to saturated), Phthalates (high molecular mass), Surfactants (high branched); Pharmaceuticals (neutral), Polyaromatic Hydrocarbons (PAHs), Polyaromatic Sulphonated Hydrocarbons (PASHs); Linear Alkyl Benzenes (LABs). The molecular distribution of the detected compounds is different of those detected in the water samples

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