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PAH Determination in Environmental Samples Using GC Analysis Technique: A Case Study on Bizerte Lagoon Sediments

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Abstract
To investigate the presence of PAH in bottom sediments of Bizerte Lagoon, 50 g of assumed contaminated samples were dried in the dark and extracted with methylene chloride. First two chromatograms of this qualitative analysis have proved the presence of many non-identified organic compounds in each analysed sample.
Compared to standards' chromatogram, the near shore sample LB 51 is likely to contain anthracene. This result was confirmed by the doping test. On the other hand, the chromatogram concerning LB 44 sample showed two other peaks at RT = 7.653 min and at RT = 8.317 min corresponding certainly to both acenaphthene and fluorene. Further stringent analyses are scheduled to identify the rest of the organic compounds which could be related to hydrocarbons derivatives or pesticides residues.
Keywords
Lagoon sediment samples, Anthracene, Acenaphthene, Fluorene.

1. INTRODUCTION

Bizerte Lagoon is located in the nothern part of Tunisia, between N37 08' and N37 16' latitudes. It is a 130 km² surface area depression known for its geostrategic position since it is connected for one side to the Mediterranean sea and to the Lake "Ichkeul" through Tinja's narrow channel for the other side (Ouakad, 2000). For many decades, this lake is known, to be a fishery and aquaculture (mainly oyster-farming) park. Since many years, lagoon's banks have undergone both urbanization and industrialuzation actions. Manufacturing facilities such as Menzel Bourguiba's iron and steel complex, the SOCOMENA ; urban wastewaters and open-dumping type municipal/industrial solid waste landfills scattered around the lagoon could have led to the ecological degradation of this fragile media. In fact, Suspended particles in effluent discharges and surface runoff carry contaminants into the lagoon basin. Much of the particulate material and associated contaminants do not dissolve into the water ; instead, they settle to the bottom to become part of the sediment (WSDE, 1990). Among those contaminants, the polycyclic aromatic hydrocarbons (PAHs) are of great concern. These carcinogenic, environmentally persistent organic chemicals are ubiquitous and the industrial revolution greatly increased the rate of anthropogenic production of PAHs, as fossil fuels were extracted and burned, often in poorly combusted environments (Jhonson and Ghosh, 1998). In localized areas such as rivers, estuaries and harbors, the rate of accumulation greatly exceeded the rate of environmental degradation (Hites, 1980 cited by Jhonson and Ghosh, 1998). Because of the relatively slow rate of anaerobic biodegradation in lakes or rivers sediments, PAHs tend to accumulate and persist in anaerobic environments. This occurs because PAHs are hydrophobic and sorb tightly to soil particles in saturated aqueous environments (Jhonson and Ghosh, 1998).
Bottom-dwelling fish and shellfish can accumulate those contaminants present in sediment. One of the major concerns associated with contaminated fish and shellfish is the threat that they pose to humans who consume them. Additional exposure to contaminated sediments may occur in intertidal areas through direct contact or ingestion of contaminated sediments during recreational activities such as wading, fishing, clamming, and water sports. Inhalation of volatile contaminants released by sediments is also a potential exposure route. Although these

exposure routes are generally not expected to contribute greatly to human health risks compared to consumption of seafood, they may be important at some sites and should be considered as part of a site-specific risk assessment (WSDE, 1990).

To investigate the presence of PAH in bottom sediments, an offshore sampling survey was conducted in the Bizerte lagoon and a total of 100 bottom sediment samples were collected in the farmework of the research project entitled "Study on Environmental Pollution of Mediterranean Coastal Lagoons (RPP-SEPMCL)" (Ghrabi et al., 2002 ; Yoshida et al., 2002). This paper preliminarily report the result of PAH analysis of the sediments.

2. MATERIALS AND METHODS

2.1. Reagents

All solvents were HPLC grade. Dichloromethane used for extraction was purchased from Acros, methanol from Acros and Hexane from Prolabo. 6 PAH standards reagents: acenaphthene, anthracene, fluorene, fluorenthene, phenanthrene, pyrene provided by Acros were dissolved into hexane to prepare a 10 ppm standard solution at 98% without further purification steps. Bidistilled water was obtained from Milli-Q water purification system (Millipore). A PVDF 0.45 µm pore size filter was purchased from Millipore. An Alltech's solid phase extraction SPE end-capped cartridges C18 (50 mg – 1,5 ml) were used for cleaning steps.

2.2. Apparatus

A roller table (Bioblok Scientific 64736) was used as an agitator during the extraction phase of PAHs compounds from sediment samples. After filtration, A rotary evaporator (Büchi R-114) equipped with water bath (B-480) was used to concentrate the extracted compounds. Analyses of the concentrated solutions were performed by gas chromatography (Shimadzu GC – 17A ATF ver.3), equipped with a splitless injector, a 30 m long and 0.25 mm id capillary column, packed with DB 17 (moderately polar phase) and connected to a FID detector.

2.3. Samples extraction and preparation technique

Two assumed contaminated samples were analyzed:
LB 51 [(depth = 5.1m ; E 9° 52', N 37° 8.5') ; (Yoshida et al, 2002)]
LB44 [(depth = 9.9 m ; E 9° 52', N 37° 12') ; (Yoshida et al, 2002)]

50 g of each sediment sample representing the lower layer (sediment repository) was dried in the dark at room temperature and transferred into 250 ml glass flask to undergo a 3 times extraction phase with 100 ml of dichloromethane during 6 h under vigorous stirring (150 tr/min) at room temperature. Then, the obtained solutions were filtrated, concentrated using a rotary evaporator at 30^{o}C and 650 mm Hg vacuum pressure and solvent-exchanged to methanol. The extracts (1.5 ml in methanol) were further filterated using a PVDF 0.45 µm pore size filter (millipore filter) and cleaned by SPE C18 cartridges, previously preconditioned with 1ml methanol followed by 2 ml of bidistilled water. The sample (1.5 ml) was applied to the top of the tube and drawled through the packing bed at 1ml/min. The retained PAHs were washed with 2 ml of bidistilled water (to remove impurities) and then eluted with 1.5 ml of hexane. The eluted solution was further concentrated to ~500 µL under gentle nitrogen flow.

2.4. Gas Chromatography analysis conditions

Concentrated solutions in hexane were analysed by GC under the following conditions:

- Column temperature program: 140ºC to 180ºC at 12ºC/min [1 min of holding time], to 210ºC at 7ºC/min, to 218ºC at 2ºC/min and to 270 at 10ºC/min.
- Injector temperature : 275 ºC
- Detector temperature : 300 ºC
- Carrier gas : Helium
- Pressure program: 133 KPa (8.5 min) to 150 KPa at 7/min to 133 KPa at –7/min.
- Injected volume: 10 µL.

These conditions were optimized to obtain a higher resolution of PAHs standards chromatogram (Fig. 1) with the related retention times (Table 1).

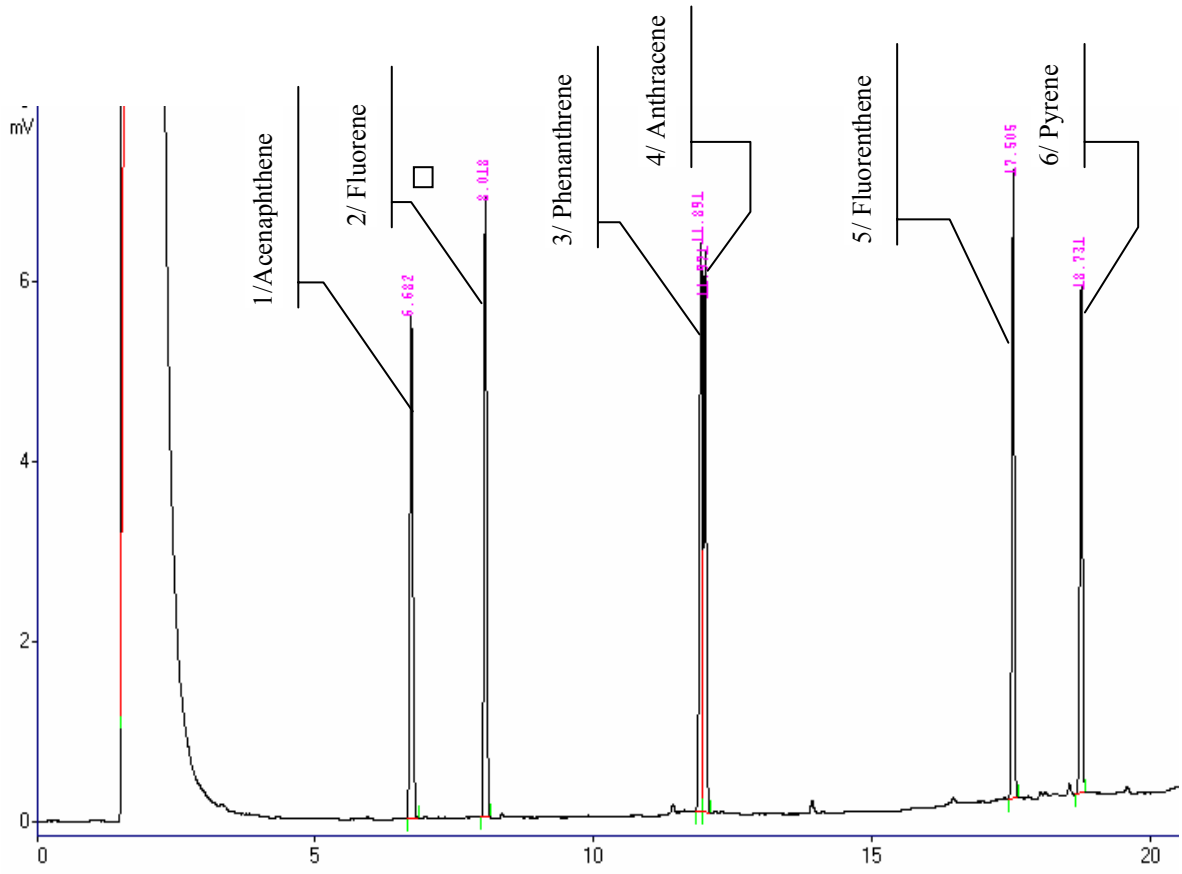

Figure 1. Chromatogram of the standard solution (6 PAHs) RT (min)

Table 1: Retention time (RT)

Compound	RT (min)
Acenaphtene	6.682
Fluorene	8.018
Phenanthrene	11.891
Anthracene	11.971
Fluorenthene	17.505
Pyrene	18.731

3. RESULTS AND DISCUSSIONS

The initial results of this qualitative analysis indicated the presence of many non-identified organic compounds in both analyzed sediment samples.

The chromatogram of LB 51 sample (Fig. 3) showed the presence of an identified PAH peak at the RT=12.812 min which could be attributed to anthracene when compared to the anthracene standard representative chromatogram (Figs. 2 & 3).

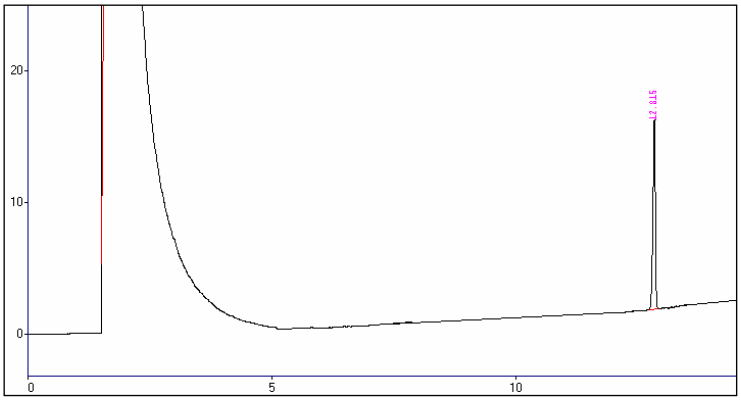

Figure 2. Chromatogram of anthracene standard solution

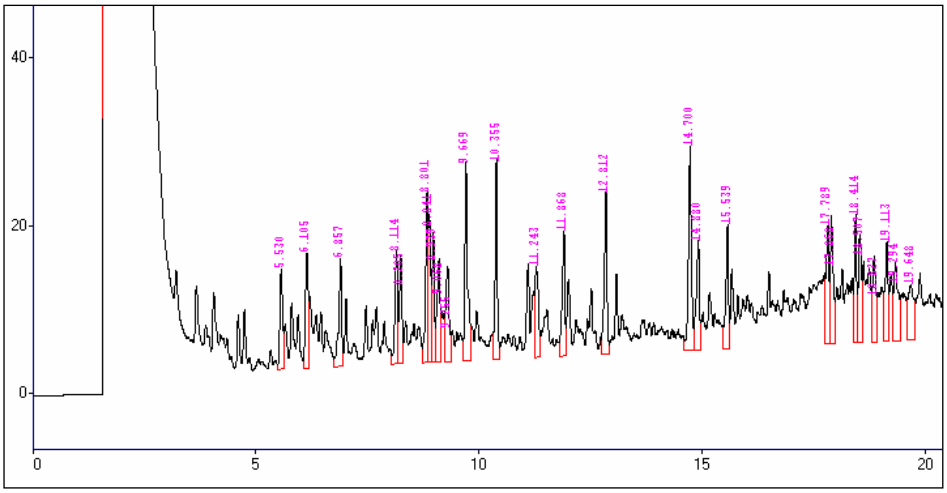

Figure 3. Chromatogram of LB51 lower layer sediment sample

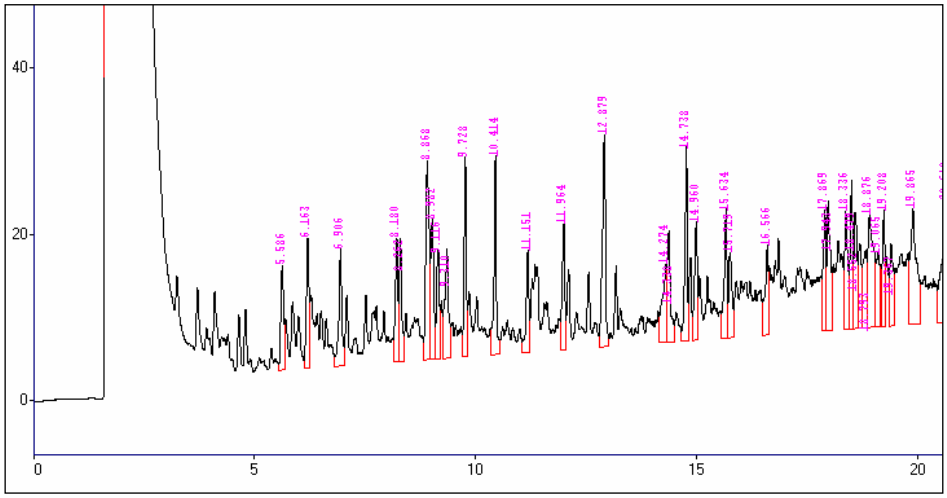

Figure 4. Chromatogram of LB 51 sample doped with Anthracene standard

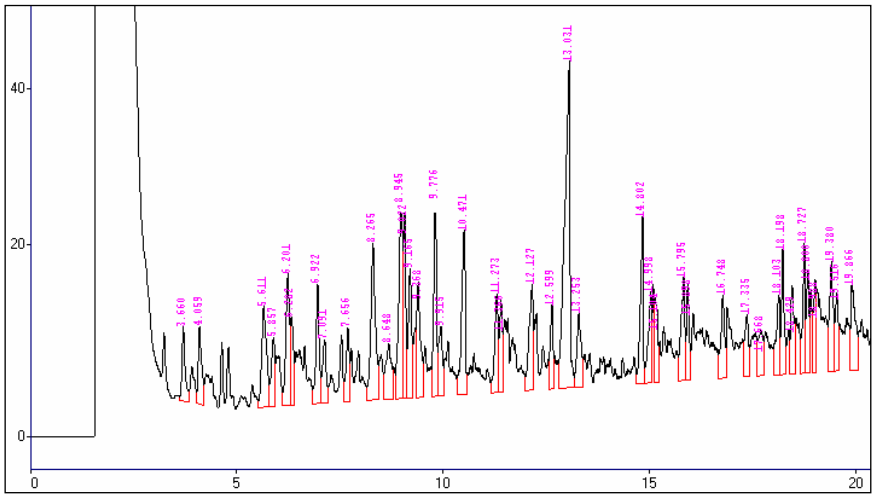

Figure 5. Chromatogram of LB 51 sample highly doped with anthracene standard

This result was confirmed through the doping test with anthracene standard solution added to LB 51 injected sample (Figs. 4 & 5).

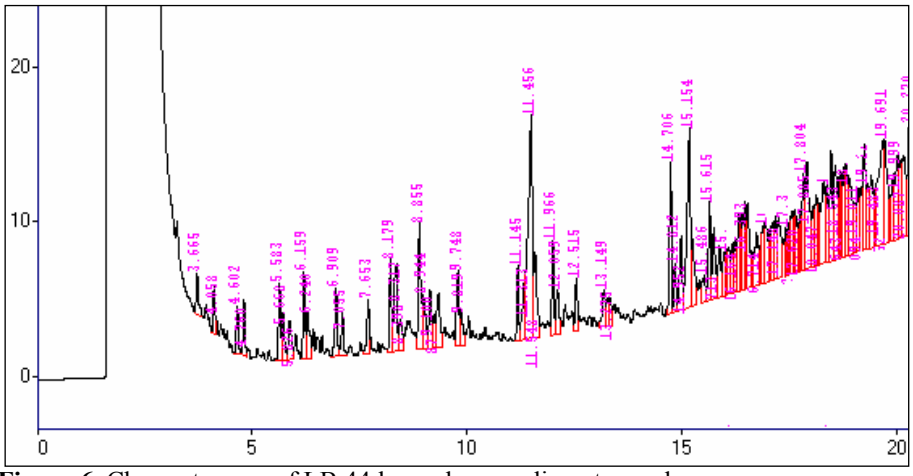

Figure 6. Chromatogram of LB 44 lower layer sediment sample

The representative chromatogram of LB 44 lower layer sediment sample showed the presence of many peaks. In addition to anthracene (RT=11.996 min), Two new compounds seem to be identified at RT = 7.653 min and at RT = 8.317 min which might correspond to acenaphthene and fluorene compounds.

4. CONCLUSIONS

Through this short and qualitative study, it has been demonstrated that the lower layer of lagoon Bizerte bottom sediments contains many organic compounds which needs stringent analysis conditions to be qualitatively and quantitavely identified. Those organic contaminants could be related to hydrocarbons derivatives or pesticides residues.

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