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C. Marfil^a; J. Albaigés^a

^a Environmental Chemistry Unit, Institute of Bio-Organic Chemistry (C.S.I.C.), Barcelona, Spain

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Analysis of Hydrocarbons in Aquatic Sediments

I. Sample Handling and Extraction

J. GRIMALT, C. MARFIL AND J. ALBAIGÉS

Environmental Chemistry Unit, Institute of Bio-Organic Chemistry (C.S.I.C.), Jordi Girona Salgado, Barcelona-34, Spain

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Sonication has been evaluated as a method of extraction of hydrocarbons in aquatic sediments. Soxhlet extraction was used as a reference technique. The higher recoveries (92% for aromatic hydrocarbons and 96% for aliphatics and PCBs) were obtained with freeze-dried samples and using methylene chloride-methanol (2:1) as solvent. Recoveries were independent from the solvent/sediment ratio provided that a sufficient number of extractions is carried out. The accuracy of the analysis was improved to 4% (s.d.) when sediments were previously sieved through a 250 μm filter.

KEY WORDS: Hydrocarbons, marine sediments, extraction, sonication.

INTRODUCTION

Contemporary sediments are considered as a "sink" for hydrocarbons in the aquatic environment and their importance in pollution monitoring has been recognized by several authors.¹⁻³ In fact, in the aquatic environment (lacustrine or marine) there is a net downward flux of hydrocarbons within the water column towards the sediment as a result of the deposition of particulate material, both organic (dead organisms, fecal pellets, etc.) and inorganic (eolian dust, eroded soils, etc.), that contains significant amounts of

natural and anthropogenic hydrocarbons. Therefore, sediments are a good source of integrated samples, exhibiting levels of hydrocarbons several orders of magnitude higher than those found in the water column. Moreover, they are relatively easy to sample and store and, studied at different depths (cores), they may provide an historical record of hydrocarbon inputs in a particular area.

Nevertheless, sediments exhibit certain characteristics, for example grain size and morphological composition, that sometimes make difficult the interpretation and the intercomparison of results. In addition, aspects concerning the sedimentary environment such as sedimentation rates, redox conditions and biological mixing velocities are determinant not only for interpreting the data but also for establishing the strategy for obtaining these data.

On the other hand, hydrocarbons represent only a small percentage of the total organic matter in sediments and their extraction, isolation and fractionation are closely dependent on the total amount and characteristics of the bulk organics as well as on the nature of the sediment matrix itself. Thus, classical sample work-up problems cannot be obviated.

Sedimentary hydrocarbons constitute also very complex mixtures and nowadays there is not a unique analytical procedure for their characterization. In each case, accordingly with the specific objectives of the study and the analytical facilities available a particular set of parameters will be selected and determined, giving rise to a diversity of data arising from different studies, whose accuracy is often difficult to assess. In this respect, interlaboratory comparison exercises generally provide a high variability of results⁴⁻⁶ pointing to the necessity for the continuous development of the state-of-the-art of trace hydrocarbon analysis.⁶

Sample handling and extraction procedures are the first steps where the validity of the analysis is decided. Although from the practical standpoint they are considered as relatively simple processes, they involve a variety of parameters which are often underestimated.

Surface sediments, particularly coastal and riverine, are frequently non-homogeneous. They are sandy and contain rests of organic and inorganic debris that may affect the reproducibility of the results. On the other hand it has been noticed that minor changes in extraction procedures may cause significant variations not only in quantitative but also in qualitative results.⁷

Our involvement in an extensive study for the assessment of natural and anthropogenic hydrocarbon inputs in several areas of interest in Spain, namely the Mediterranean Coast and the Doñana National Park using sediments and organisms as integrating systems,^{3,8} prompted us to the evaluation of sediment handling and extraction procedures for improving the accuracy of our analytical results. The conventional Soxhlet extraction has been compared for different solvent systems (*n*-hexane, chloroform and methylene chloride-methanol (2:1)) with the lower-temperature and less time-consuming sonication procedure. The influence of the pretreatment of the sample (drying and sieving) has also been taken into consideration. Recoveries have been determined for aliphatic, aromatic and chlorinated hydrocarbons.

EXPERIMENTAL

Surface sediments were collected with a previously cleaned grab sampler in a moderately polluted site of the Spanish Mediterranean Coast. Immediately after collection, samples were frozen at -20°C and stored. A large composite sample (500 g) containing 10% of sand and 90% of silt+clay was thawed and aliquots (10 g) were taken for comparative studies. The sediments were analysed as such, after freeze-drying or just after drying in an oven at 50°C for 24 h. When necessary samples were sieved through a $250\ \mu\text{m}$ filter to remove coarser detritus or fractionated in the following grain-size ranges: $> 250\ \mu\text{m}$, $250\text{--}125\ \mu\text{m}$, $125\text{--}66\ \mu\text{m}$ and $< 66\ \mu\text{m}$.

The extraction procedures used were the following:

- a) Soxhlet extraction during 76 h using 500 ml of clean solvent (*n*-hexane, chloroform or methylene chloride-methanol (2:1)) each 24 h.
- b) Sonication in glass centrifuge tubes ($9.5 \times 3\ \text{cm}$ i.d.) containing 10 g of sediment and variable amounts of the above solvents. The tubes were introduced during 10 min into the sonication bath, stirred with a glass rod and sonicated again during 10 min. Afterwards, they were centrifuged at 3000 rpm during 5 min and the solvent decanted. The operation was repeated with clean solvent 6 times.

The collected extracts were concentrated to about 20 ml in a rotary evaporator (Büchi AG) and then passed through a small column

(5 × 0.5 cm) filled with copper powder recently activated by successive washings with 6 M hydrochloric acid, water and acetone.

The eluate was vacuum-evaporated to near dryness and finally to dryness under nitrogen. The residue was dissolved in *n*-hexane (1 ml) and poured onto top of a column (25 × 0.9 cm i.d.) filled with 8 g of 5% water-deactivated silica gel (70–230 mesh, Merck) (bottom) and 8 g of 5% water-deactivated alumina (70–230 mesh, Merck) (top).^{9,10} Three fractions were collected: (a) 20 ml of *n*-hexane (alkanes + alkenes), (b) 20 ml of 10% of methylene chloride in *n*-hexane (mono- and diaromatic hydrocarbons, PCBs and DDEs) and (c) 40 ml of 20% of methylene chloride in *n*-hexane (polyaromatic hydrocarbons and DDDs).

Quantitative analysis of these fractions was carried out by gas chromatography (saturated and chlorinated hydrocarbons) and UV-fluorescence (aromatic hydrocarbons).

Gas chromatographic analyses were performed with a Carlo Erba FV 4160 GC instrument equipped with a FID detector and a 20 m × 0.25 mm i.d. open glass capillary column coated with SE-52 (surface film thickness, 0.15 μm). Glass capillary columns were prepared and tested as described previously.¹¹ The carrier gas was helium (50 cm/sec). The temperature was programmed from 60 to 310°C at 6°C/min. Injector temperature, 260°C; detector temperature, 340°C. The injection was in the splitless mode (solvent, isooctane), keeping split and sweep valves closed for 40 sec. *n*-Alkanes and isoprenoid hydrocarbons were quantitated by comparison with an external standard mixture on *n*-C₁₄, *n*-C₂₂, *n*-C₃₂ and *n*-C₃₆. The unresolved GC envelope was measured by planimetry. All these operations were carried out semi-automatically using a Hewlett-Packard 86 microprocessor equipped with a digital planimeter.

Chlorinated hydrocarbons were analyzed in a Carlo Erba FV 2200 GC instrument fitted with an ECD detector and a 2 m × 3 mm i.d. column packed with 1.5% of OV-17 and 1.95% of QF-1 on Supelcoport 100/120. The carrier gas was argon-methane (95:5) (70 cm/sec). Injector and detector temperatures, 250°C; oven temperature, 190°C. PCBs were quantitated by comparison with an external standard of Aroclor 1254. Injections of both standard and samples were repeated until low dispersion in the area of the chromatographic peaks was observed.

UV-fluorescence analyses were carried out in a Perkin Elmer MPF-3 UV spectrofluorimeter. Emission spectra from 320 to

500 nm were obtained with an excitation wavelength of 300 nm (slit 20 nm). Synchronous excitation spectra were recorded with a $\Delta\lambda(\lambda_{em} - \lambda_{exc})$ of 20 nm. Both slits were set at 5 nm. Quantitation was performed on the emission spectra at 330 nm, using a Kuwait diesel-oil reference sample (b.p., 250–350°C) (second fraction) or at 360 nm comparing with an Arabian light fuel-oil (b.p., 400–450°C) (third fraction).

RESULTS AND DISCUSSION

Extraction

Different extraction methods have been described in the literature and their performances compared. These include Soxhlet extraction,^{5,7,12–16} Soxhlet extraction with internal thimble stirring,¹⁷ direct reflux, without or with alkaline hydrolysis^{6,12–15} and steam distillation.¹⁶ Lower-temperature and shorter-time extraction procedures have also been applied in order to diminish the risk of losses for low-boiling hydrocarbons and transformations of labile compounds. Among these are ball-mill tumblers,^{6,13,14} mechanical shaking¹⁴ and sonication.^{5,16} Sonication which has been used for extraction of aromatics from hi-volt filters¹⁸ and soots,¹⁹ has not been, however, studied in detail with sediment samples.

Soxhlet extraction has been considered as the reference technique. Aliquots (10 g) of freeze-dried composite marine sediment samples, from a moderately polluted site, have been extracted with different solvents and the extracts analyzed by UV-fluorescence, GC-FID and GC-ECD for aromatic, aliphatic and chlorinated hydrocarbons, respectively. Results are presented in Tables I and II.

The best efficiencies were obtained with methylene chloride-methanol (2:1). Chlorinated hydrocarbons (PCBs) were also well recovered with hexane. These results are in agreement with the study of Brown *et al.*¹³ who found an increase in extraction efficiency when using solvent mixtures containing methanol. Monin *et al.*⁷ also obtained the best results with methylene chloride-methanol (2:1) in the extraction of oil source rocks.

Another set of subsamples was extracted by sonication using the same solvents, with a solvent/sediment ratio of 4(v/w). The cumulative recovery according to the number of extractions is

TABLE I

Efficiency of different solvents in Soxhlet extraction of a freeze-dried sediment. Concentrations in $\mu\text{g/g}$ (aromatic hydrocarbons, A.H.) and ng/g (PCBs). In parenthesis percentage of recovery relative to methylene chloride-methanol (2:1).

Solvent	24 h		24-48 h		Total	
	A.H.	PCB	A.H.	PCB	A.H.	PCB
$\text{CH}_2\text{Cl}_2/\text{MeOH}$ (2:1)	56(97)	67(81)	1.5(2.5)	10(12)	58	77
CHCl_3	49(84)	65(78)	1.2(2.1)	7.8(9.5)	50(86)	73(94)
<i>n</i> -Hexane	41(71)	73(88)	1.0(1.7)	5.8(6.9)	42(73)	79(102)

presented in Fig. 1A. As can be seen the results parallel those obtained with Soxhlet extraction. Methylene chloride-methanol (2:1) was more efficient than hexane although this provided slightly better recoveries for PCBs. In the above conditions no significant improvement was observed beyond six extractions. By sonication the final recoveries of aromatic hydrocarbons and PCBs were 92 and 96% of those obtained by Soxhlet extraction.

When the extraction was attempted changing the solvent/sediment ratio the overall recoveries were identical as it is shown in Fig. 1B. However, when using a solvent/sediment ratio of 8, the extraction can essentially be accomplished in three steps.

As far as the qualitative analysis is concerned, the comparison was based on the aliphatic fraction. The chromatographic profiles were characterized by conventional parameters such as *n*-alkane ratios, carbon preference index (CPI), pristane/phytane ratio and the unresolved complex mixture (UCM). The results obtained for two marine sediments are reported in Table II and it can be concluded that no appreciable differences are observed. The recovery of aliphatics by sonication was 95.5%, which is closer to the results for the PCBs than to those for the aromatics (see Table I). This may be attributed to the lower polarity of these compounds.

It is difficult to explain at present the slightly low recoveries of hydrocarbons obtained by sonication with respect to Soxhlet extraction. However, although hydrocarbons are mainly retained in

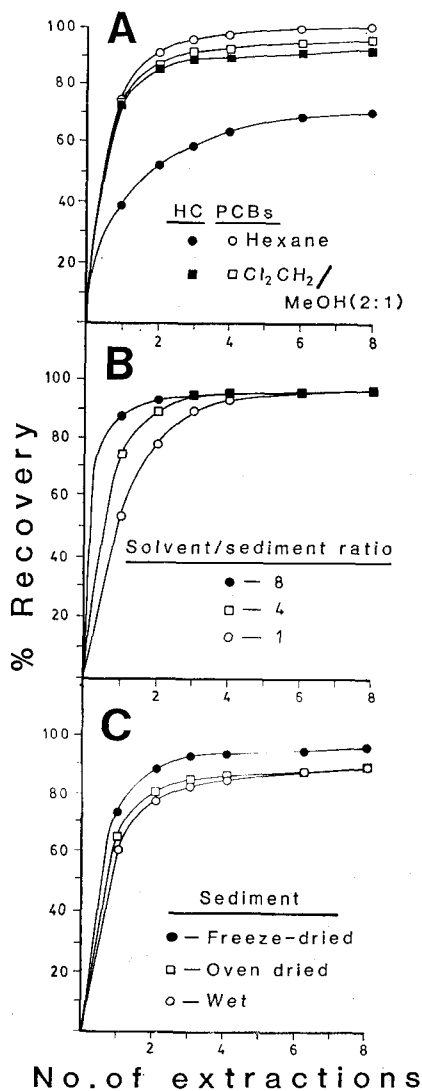


FIGURE 1 Efficiency in the extraction by ultrasonic stirring of the sediment of Table I (plotted against the number of extractions).

- A) Cumulative percentage recovery of aromatic hydrocarbons (HC) and PCBs as a function of the solvent. Solvent/sediment ratio, 4.
- B) Recovery of aromatic hydrocarbons as a function of the solvent/sediment ratio. Solvent: methylene chloride-methanol (2:1).
- C) Recovery of aromatic hydrocarbons as a function of sediment pretreatment. Solvent: methylene chloride-methanol (2:1). Solvent/sediment ratio, 4.

TABLE II

Analysis of free and bound aliphatic fractions of two marine sediments. Free hydrocarbons were obtained by sonication (1) and Soxhlet extraction (2) with methylene chloride-methanol (2:1). Bound hydrocarbons (3) were obtained with methanolic KOH after solvent extraction. Sample A corresponds to that for which the aromatic hydrocarbon concentration is reported in Table I. Concentrations are given in $\mu\text{g/g}$.

$$\text{CPI} = \frac{\sum_{n+1}^m \text{odd } n\text{-alkanes}}{\sum_{n+1}^{m+1} \text{even } n\text{-alkanes}}$$

Aliphatic hydrocarbons	Sample A			Sample B		
	(1)	(2)	(3)	(1)	(2)	(3)
<i>n</i> -Alkanes	2.7	2.8	0.22	2.0	2.2	0.15
<i>n</i> -C ₂₅ - <i>n</i> -C ₃₉ / <i>n</i> -C ₁₄ - <i>n</i> -C ₂₄	5.7	5.3	4.7	2.7	3.0	4.4
UCM	6.2	6.6	0.43	1.9	2.1	0.19
Total alkanes	8.9	9.4	0.65	3.9	4.3	0.34
CPI _{total}	4.2	3.8	2.0	2.9	3.3	1.6
CPI _{<i>n</i>-C₂₅-<i>n</i>-C₃₉}	6.3	5.8	2.2	5.0	5.7	1.5
CPI _{<i>n</i>-C₁₄-<i>n</i>-C₂₄}	1.7	1.4	1.4	1.4	1.5	2.2
Pristane/phytane	4.0	3.4	1.9	3.1	3.4	0.40

sediments by adsorption, it is known that humic and fulvic acids may also entrap hydrophobic compounds during deposition,²⁰ that will be preserved from solvent action unless those humic and fulvic materials are removed by alkaline treatment. It is indeed shown in Table II that after exhaustive Soxhlet extraction sediments release an additional quantity of hydrocarbons, the so-called bound fraction. Consequently, it may be suggested that the different binding forces acting between hydrocarbons and sediments may compete with different extraction procedures and may account for the slightly different recoveries observed.

The bound fraction, although not quantitatively significant, is of interest for the assessment of certain autochthonous inputs. In fact, it has been demonstrated that it includes preferentially biogenic hydrocarbons of bacterial origin.²¹ The virtual absence of the petrogenic unresolved alkanes (Table II) and the *n*-alkane

distribution with a low odd-even carbon number predominance (CPI, 1.4) are both indicators of such an origin.²² Therefore, although some authors have proposed the extraction of hydrocarbons by direct alkaline hydrolysis of sediment^{6, 12-15} it seems that bearing in mind the nature of bound hydrocarbons it is not absolutely necessary for pollution monitoring studies.

Sediment pretreatment

Analytical precision greatly depends on the reproducibility of the results. In the case of sediments the lack of homogeneity is the main source of inaccuracy. In fact aquatic sediments are composed of sands, silts and clays and as previously shown by several authors,²³⁻²⁵ these fractions are able to accumulate hydrocarbons differently. In this respect, coarser fractions contain mainly detritus from autochthonous organisms and sands, which exhibit a low adsorption capacity for organisms. On the other hand, silts and clays tend to concentrate most of the allochthonous, mainly pollutant, hydrocarbons.

Coastal sediments are a noticeable case. Important sources of marine pollutant hydrocarbons are continental inputs through the particulate material carried by river streams; depending on the coastal waters energy this will be fractionated, namely enriched or depleted in sands, along the shoreline. Moreover, benthic organisms that may rework sedimented material and contribute with detritus are abundant in the continental shelf. Therefore, the heterogeneity of sediments is especially noticeable in these areas.

To illustrate this Table III shows a detailed analysis of hydrocarbons corresponding to different grain-size fractions of coastal sediment. There is a striking difference in hydrocarbon concentrations between the coarser ($> 66 \mu\text{m}$) and the finer ($< 66 \mu\text{m}$) fractions. This difference parallels the range which separates sands from silts and clays and is indicative of distinct mineral-organic matter interactions corresponding to each material. Aromatic hydrocarbons are strongly concentrated in the finer fraction which indicates a selective association of allochthonous anthropogenic inputs with the silt + clays fraction. This is consistent with the higher relative concentration of aliphatic unresolved hydrocarbons in the same fraction which, as pointed out by Farrington and Tripp,¹² is indicative of petrogenic hydrocarbons. Therefore, grain-size

TABLE III

Hydrocarbon composition of different grain-size fractions of a marine sediment (in $\mu\text{g/g}$).

Parameters	> 250 μm	250–125	125–66	< 66 μm	Total
<i>n</i> -Alkanes	0.36	0.17	0.26	3.5	0.4
<i>n</i> -C ₂₅ - <i>n</i> -C ₃₉ / <i>n</i> -C ₁₄ - <i>n</i> -C ₂₄	1.8	1.5	1.5	1.3	1.7
UCM	1.6	0.57	0.82	21	1.3
UCM/ <i>n</i> -Alkanes	3.6	3.5	3.5	6.0	3.3
Total alkanes	2.0	0.74	1.1	25	1.7
CPI _{total}	1.3	1.5	1.5	1.5	1.5
CPI _{<i>n</i>-C₂₅-<i>n</i>-C₃₉}	1.7	2.1	2.3	2.1	2.2
CPI _{<i>n</i>-C₁₄-<i>n</i>-C₂₄}	1.2	1.3	1.3	1.3	1.3
Pristane/phytane	0.81	0.80	0.85	1.1	1.1
Aromatic hydrocarbons	1.0	0.32	0.86	14	1.0

distributions have to be considered in the interpretation of analytical results.

In order to improve the reproducibility of the results we have evaluated the influence of sieving the sediment before the analysis. Ten sub-samples of the reference sediment (Table I) were sonicated with methylene chloride-methanol (2:1) and the mean value was 62 $\mu\text{g/g}$ with a standard deviation of 70%. However, after sieving through 250 μm the mean value was 53 $\mu\text{g/g}$ with a standard deviation of only 4%. This clearly illustrates that sieving is an adequate step in the analysis of sediments for pollution monitoring.

The *water content of sediments* is another parameter affecting hydrocarbon recoveries. To evaluate its influence on the extraction efficiency of sonication, several analyses of aromatic and chlorinated hydrocarbons of the reference sediment were carried out. The results for the freeze-dried sub-samples were compared with those corresponding to the wet (~25% water content) and dried (in an oven during 24 h at 50°C and atmospheric pressure) sediment. All samples were extracted with methylene chloride-methanol (2:1) and analyzed by means of UV fluorescence and GC-ECD. The results are shown in Fig. 1C.

The best recoveries were observed with freeze-dried samples. Both wet and oven-dried sediments afforded lower amounts of

hydrocarbons. Wong and Williams,¹⁵ using other solvents and extraction techniques (Soxhlet) also reported lower yields of hydrocarbons from wet sediments in comparison with previously dried samples. Moreover, they observed 16% losses as a consequence of oven-drying at 45°C. Such losses could be attributed to volatilization and/or oxidation during the process. From both studies it appears that freeze-drying is the most suitable procedure for the elimination of water. Chlorinated hydrocarbons exhibit the same tendency as the aromatics, but here the differences among freeze-dried, oven-dried and wet samples are smaller.

CONCLUSIONS

The present study has shown that sonication is a suitable technique for extraction of hydrocarbons from aquatic sediments. It is less time- and solvent-consuming than the conventional Soxhlet extraction, although recoveries are slightly lower, VCZ. 92% for aromatic hydrocarbons and 96% for the less polar aliphatic hydrocarbons and PCBs. The solvent that provided these extraction efficiencies was methylene chloride-methanol (2:1). Extraction efficiency was more dependent on the solvent polarity for aromatic than for aliphatic and chlorinated hydrocarbons. When the solvent/sediment ratio (v/w) was increased from 1 to 8, the number of extractions could be reduced from 6 to 3.

Pretreatment of the sample has a definite influence in improving the recovery and the accuracy of the analysis. In this respect, freeze-drying and sieving of the sediment through a 250 μm filter before extraction are strongly recommended.

Finally, no significant qualitative differences were observed between the extracts obtained by sonication and Soxhlet extraction. However, when sediments are used in pollution monitoring studies, for an adequate interpretation of the results one should realize that hydrocarbon sources are decoupled among different grain-size fractions and free or solvent-extractable and bound fractions.

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