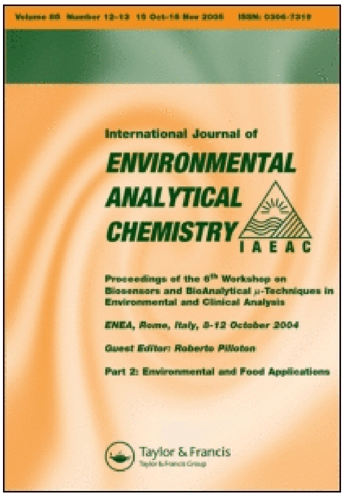

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Method Development and Quality Assurance for the Analysis of Hydrocarbons In Environmental Samples

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METHOD DEVELOPMENT AND QUALITY ASSURANCE FOR THE ANALYSIS OF HYDROCARBONS IN ENVIRONMENTAL SAMPLES

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Extraction procedures for the analysis of hydrocarbons at the trace level in marine sediment samples were compared in terms of trueness and precision. Three extraction techniques—ultrasonic bath, mechanical shaker and Soxhlet—and three solvents—hexane, 1,1,2 trichloro-trifluoroethane (Freon-113) and dichloromethane (CH_2Cl_2)—were used. Extracts were analyzed by synchronous scanning fluorescence spectrography (SSFS); high-performance liquid chromatography (HPLC) on NH_2 normal-phase columns with UV and fluorescence detectors, gas chromatography on fused-silica capillary columns (GC) with flame ionization detector (FID), and high-resolution molecular spectrofluorimetry in Shpol'skii matrix at 10 K (HRMSS). The more effective parameter for recovery efficiency proved to be the solvent selection. Hexane and freon-113 were found of very low efficiency for sediment samples. Soxhlet washing and mechanical shaking with CH_2Cl_2 on freeze-dried sediment gave the best recoveries. Precisions (repeatability and reproducibility) found for total hydrocarbon determination after both extraction methods varied from 2% up to 18%, mostly depending on the proficiency of the analyst. Mechanical extraction after acidic treatment of the freeze-dried sediment gave the more accurate GC-FID profiles. Repeatabilities of this technique as determined on the total saturated and aromatic fractions by GC-FID and HPLC-fluorescence measurements were 7% and 12% respectively. This was selected as the more convenient method. A biota sample (oysters) was extracted by mechanical extraction while using a $CH_3OH:CH_2Cl_2$ (2:3) solvent mixture; GC-FID and HPLC-fluorescence measurements showed good precision, 8% and 6% for the total saturated and aromatic fractions respectively. A standard research material (SRM-1649—urban dust/organics) was analyzed by HRMSS and HPLC after mechanical extraction, and results were in good agreement with certified values.

KEY WORDS: Extraction, marine sediments, oysters, hydrocarbons, quality assurance.

INTRODUCTION

Environmental intercomparison studies of the fate and effects of hydrocarbon compounds are subordinate to the use of accurate analytical methods. Hertz *et al.*[1] discussed the problems associated with performing such trace organic analyses. Despite the abundant literature describing developments of the distinct analytical steps, interlaboratory comparison exercises[2–4] have shown more or fewer discrepancies in results. Hilpert *et al.*[2] reported bias for recovery standards varying from 41 to 83% for two apparently similar sediment samples. They also quoted loss of hydrocarbons (up to C20) due to the drying process before extraction and high variability of results (from 9 to 500 ng/g and 49 to 6625 ng/g for the two samples) due to the GC quantification. Later, Mac Leod *et al.*[3] reported significant improvement in interlaboratory comparisons results for individual hydrocarbons, which paralleled advances in high resolution GC. However, high inconsistencies in the results provided by some laboratories were noticed and attributed to the solvent evaporation procedures for volatile compounds (below C15 and phenanthrene), to incomplete vaporization in the GC for the less volatile compounds (above C29), to the GC quantifications, and in some cases to the lack of proficiency in the handling of extraction procedures (Soxhlet, ultrasonication). In general it appears that the weak point in interlaboratory exercises stays in the fact that they focus mainly on the result as a capability of the involved laboratories without extracting from a whole procedure which step could have entailed a result. Eisenberg *et al.*[4] during their interlaboratory exercise for the determination of PAHs in extracts from diesel particulate emissions tried to solve part of this problem by focusing only on the analytical method of quantification used and found that all methods, HPLC-fluorescence, GC-FID and GC-MS when carefully applied gave similar results. Accordingly, it seems that sources of errors have to be searched in the previous steps by exercises that would avoid systematic errors originating from the mishandling of a protocol by different laboratories. Such an inconvenience in interlaboratory exercises can be solved by intralaboratory comparisons of procedures[5–14]. Availability of standard research materials[15] is an essential tool for internal adaptation of methodologies. In the last ten years high improvement has been made in the analysis of hydrocarbons and reference methods have been proposed[16,17]. Meanwhile, some papers have shown that some steps can be shortened and made easier and with less cost without entailing the result or even while improving the quality of the results. Some authors have shown the possibility to reduce time and cost of extraction[10–12], cleanup and fractionation[6,18], while others have shown the interest of the use of deuterated surrogate standards for better quantification[9,19]. The development of highly sophisticated instrumentations have proved sufficiently specific to allow the analysis of PAHs while avoiding tedious fractionation procedures[20].

The choice of an efficient extraction technique for desorbing hydrocarbons from solid matter is directly related to factors such as granulometry, organic content and chemical composition of the matrix as well as to other factors, such as boiling point range, partition factor in water and organic solvents, polarity, thermal stability, light stability of the hydrocarbons to be analyzed[21] and measurement techniques to be used[13]. A quality assurance study for the analysis of hydrocarbons in sediments[22] showed that the extraction-partition step in the IOC reference method[16] is the main source of error. Some authors have pointed out the lengthiness of the Soxhlet extraction procedure and have proposed other procedures that in some cases look more tedious than the incriminated Soxhlet one. In a previous paper[23] we described an extraction procedure for hydrocarbons from sediments and an evaluation of the extraction efficiency based on a Freundlich isotherm model. We found that the mechanical stirring extraction procedure while offering optimal operational simplicity can provide, considering some theoretical approximations, after only one two-hour-and-a-half extraction, a result that corresponds to 96% of the "true value" with a precision of 6% (relative standard deviation) as determined by infrared spectrometry (IR). This extraction time corresponds to the one resulting from six extractions by sonication as carried out by Grimalt *et al.*[8]. Other authors have compared similar methods based on spontaneous thermodynamic desorption of hydrocarbons from sediment with appropriate solvents[8,14,24,25] to dynamic extraction procedures, i.e., the Soxhlet procedure or the Supercritical Fluids Extraction (SFE) technique[12]. Results are often contradictory from one study to the other and it appears that depending on the matrix and/or the experience of the considered laboratory one method is better handled than the others. SFE technology, in most cases, gave better recovery of PAHs than sonication or Soxhlet extraction[12]. Ultrasonic extraction was either more[10,11] or less[3,8,12] efficient than Soxhlet extraction. Sporstol *et al.*[10] compared these two methods to alkaline digestion in methanol under reflux, the IOC reference method[16], and equivalent results were found concerning recoveries. However, the repeatability was better in the increasing order, ultrasonication, alkaline digestion and Soxhlet extraction. Lindhardt *et al.*[14] found that a single or a repeated shake extraction of PAHs with CH_2Cl_2 or CH_2Cl_2:CH_3OH from coal tar polluted soils gave most of the cases lower recovery than a sequential Soxhlet extraction.

Methylene chloride, which is frequently the selected solvent these last years, was shown more efficiently than acetonitrile and cyclohexane for PAHs measurements in diesel exhausts[7]; it is more[12] or less[11,12] efficient than benzene or toluene to extract PAHs depending on the matrix (sediment or ash respectively) and on the extraction technique used (Soxhlet or sonication respectively). Pyridine has been suggested to attract more attention as an extracting solvent for particulate matter[11]. These solvents are either not suitable for global IR and fluorescence measurements or because of their high boiling points not convenient for the analysis of hydrocarbons up to n-alkane C20 (BP = 343°C) and phenanthrene (BP = 340°C). The solvent used for the extraction is often related to the analytical technique operated for total quantification. CCl_4 and hexane have been extensively used for IR and UV fluorescence measurements; CH_2Cl_2, despite what has been postulated by some authors, is a suitable solvent for fluorescence measurements. These three solvents have been frequently used for the extraction of hydrocarbons from seawater. Freon-113 is a suitable solvent for both kinds of global measurements[26]. It was shown that this solvent gives reliable results for the extraction of saturated and aromatic hydrocarbons at the trace levels in seawater[27,28]. It is usable for the extraction of the saturated hydrocarbons from the sediment despite lower efficiency than CCl_4[23]. EPA method # 3450 advises its use for the Soxhlet extraction of hydrocarbons from soil. The addition of a polar solvent such as methanol to CH_2Cl_2 has been shown to improve[8,14,24] or not[3] extraction efficiencies. Saponification has been shown not to improve efficiency[8,10,29] while it is advocated by reference methods[16,17] that it can increase extraction recovery.

Treatment of the sediment matrix before or during extraction influences the accuracy of the extraction procedure. For instance, 250 or 63 μm sieving improves the reproducibility[8]. Drying of the sediment improves the trueness[5,8] but can give rise to loss of lighter hydrocarbons and to cross-contamination. Saponification can create formation of artefact compounds, such as, methyl esters of fatty acids when using methanol as a co-extractant solvent[2], and organosulphur compounds when elemental sulphur is present[30].

These last years, a new solvent extraction technology, consisting in 20 mn microwave heating using CH_2Cl_2, has been developed for PAHs and total petroleum hydrocarbons in soils and marine sediments[31]. It is worthwhile mentioning that, apart the cost of the equipment, this method is of interest for environmental analysis. Comparative studies with the SFE technology would be of concern for further proposals for reference methods.

Because of our involvement in extensive studies about the assessment of oil pollution in Kuwait environment before the war, methodologies for the analysis of petroleum-derived compounds were adapted and intercomparisons of methods were carried out[26,32,33]. Despite the loss of part of the results during the events, results about three extraction methods, i.e., Soxhlet, ultrasonic bath, and mechanical shaking with the combination of three different solvents, i.e., hexane, Freon-113 and CH_2Cl_2 are presented in this paper. Different analytical methods were used to analyze the extracts, i.e., SSFS, HPLC-UV-fluorescence on NH_2-normal-phase column, GC-FID, and HRMSS. The selected extraction technique, the mechanical extraction procedure with CH_2Cl_2 on dry matter was tested on a dust sample standard research material, SRM-1649, and on a biota sample (oysters) using a CH_3OH:CH_2Cl_2 (2:3) solvent mixture.

EXPERIMENTAL

Samples. Sediment samples were collected from offshore marine environment in Shuaïba area (SH, 48° 20'E; 29° 04'N) and Kuwait bay (KB, 47° 56'E; 29° 27'N). They were homogenized and deep frozen (-20°C) in glass bottles. The average water contents (105°C, 12 hours) of the sediments were (55.6 ± 0.4)% and (44.5 ± 0.8)% for SH and KB respectively. The average "organic contents" (550°C, 24 hours) were (8.3 ± 0.7)% and (16 ± 2)% for SH and KB respectively. The carbonate contents determined by acidimetry were (40.4 ± 0.4)% and (41.2 ± 0.5)% for SH and KB respectively. Samples were analyzed wet and freeze-dried. All concentrations are given on dry weight basis.

Biota samples were deep frozen and freeze-dried for 40–48 h. Dried samples were then ground to fine powder using an agate mortar and pestle. The powdered samples were stored in amber glass bottles until they were analyzed.

Air particulate standard reference material, SRM-1649, was obtained from the National Bureau of Standards (Washington, D.C.).

Sample preparation. The number of experiments needed to cover all the parameters corresponded to 27 combinations. This number of experiments was reduced by considering that Soxhlet extraction on wet sediment had been proved inefficient[5], and by eliminating some combinations that would not bring any additional information from similar combinations. By carrying out only one analysis for system blanks and only duplicate analysis for sediment extractions brought the number of experiments to 22. Simultaneously the possibility of cleanup procedure directly in the Soxhlet apparatus[34] was tested, which increased the number of analyses to 28. This resulted in:

- Soxhlet extraction on dry sediment by CH_2Cl_2 (SDC), and hexane (SDH); and with a florisil layer in the Soxhlet (SDFC, SDFH).
- Mechanical extraction by CH_2Cl_2 and by Freon on dry sediment (MDC, MDT), and on wet sediment (MWC, MWT).
- Ultrasonic extraction on dry sediment by CH_2Cl_2 and by Freon (UDC, UDT) and on wet sediment by Freon (UWT).

With MDCF, MWCF, UDCF, SDCF corresponding to MDC, MWC, UDC, SDC extracts, purified on silica Sep-pak cartridges.

Mechanical and ultrasonic extractions. About 25.0-g subsamples of freeze-dried sediment and 50.0-g subsamples of wet sediment were placed into 250 ml amber glass bottles with Teflon-lined screw caps. Concentrated HCl was added to the sediment samples until the end of reaction. 100 ml of solvent (hexane, CH_2Cl_2 or freon-113) were added to the extraction bottle. Samples were shaken few minutes and anhydrous sodium sulphate was added proportionally to the water content of each subsample. Subsamples were then extracted by mechanical shaking at 320 rpm on a G10 gyratory shaker (New Brunswick Scientific Co., Inc.) and by a 100-W ultrasonic bath (Bransonic 220) at room temperature during 3-h and 1-h periods respectively. Aliquotes of this only one step solvent extraction were taken for further procedures and analyses.

About 10.0-g subsamples of freeze-dried biota were extracted over 3 h, as above, by mechanicals means, but a $CH_3OH:CH_2Cl_2$ (2:3) solvent mixture was used, and three extractions were made using 100ml and twice 25 ml mixture.

Soxhlet extractions. About 30.0-g subsamples of freeze-dried sediment were transferred to pre-extracted thimbles. The possibility of cleanup procedure directly in the Soxhlet apparatus[34] was tested by avoiding the use of thimbles and by placing 30.0-g subsamples of freeze-dried sediment on the top of 20-g precleaned and activated florisil. 160 ml of solvent (hexane or CH_2Cl_2) were added in the round bottom boiling flasks and heating was adjusted to one refluxing solvent drop per second for 8-h.

Clean-up, concentration and fractionation. Extracts were filtered through glass wool plugs in funnels. A global quantitation was made on all sediment extracts by SSFS. The more concentrated extracts were selected for further analyses. Surrogate standards (RS: n-tetradecene, n-hexadecene, n-eicosene, anthanthrene, benzothiazole and deuterated PAH standards) were added to aliquotes of the extracts for chromatographic quantifications. The addition of the RS in the first part of the study concerning the "extraction techniques comparison," was done purposely after the extraction procedure only to avoid any deviation in the results that could have arisen by their potential degradation by light and/or heating processes. Different aliquotes of the extracts were purified by eluting them through precleaned silica Sep-Pack cartridges and global quantifications were done after clean-up on aliquotes of the extracts without RS. Purified aliquotes that contained the RS were concentrated gently to one drop by rotary evaporation under reduced pressure at room temperature and brought to dryness at room pressure and temperature. Residues were redissolved in 1-mL of hexane and fractionation was made by HPLC on a normal amino-silane phase (LC-NH_2, Supelcosil) column using a CH_2Cl_2:hexane mobile phase program from 0% to 100% in 25 mn. Two fractions were collected; the first one, F1, contained the saturated and ethylenic compounds, and the second one the aromatic hydrocarbons.

Biota samples were purified and fractionated according to Risebrough *et al.*[35] on 40 ml of florisil (deactivated by 0.5 % of water) topped by 5 ml of anhydrous Na_2SO_4.

Sample preparation for the analysis of SRM 1649. The air particulate sample (1.0 g) was extracted by mechanical shaking with 20 ml of CH_2Cl_2 during 3 h. An aliquote of the extract was purified by elution through a Sep-Pak silica cartridge with 3 additional ml of CH_2Cl_2. The resulting eluate was gently reduced in volume by rotary evaporation to approximately 1 ml and brought to dryness at room pressure and temperature. The residue was redissolved in 1-mL of hexane and fractionation was made by HPLC as above. Fraction F2 was then analyzed by HPLC and HRMSS.

Reagents and analytical methods. A full description of reagents, instruments and analytical methods has already been given in Morel *et al.*[13]. The difference in this study, stays in the fact that tentative corrections based on recovery of surrogate standards, as measured by GC-FID, were done for HPLC and HRMSS measurements.

RESULTS AND DISCUSSION

Extraction techniques comparison

Global measurements of the extracts before and after clean-up on Shuaïba (SH) sediment sample are given in Table 1. These measurements made at fixed wavelengths (317/367 nm) reflect the ability of the extraction procedures to recover PAHs fluorescing at these settings.

Table 1 Total hydrocarbon concentrations, determined by SSFS, in Shuaïba Sediment Extracts as a function of extraction procedures.

Extracts[a]	*Concentration before clean-up*[b] *(μg/g dry weight)*		*Concentration after clean-up (μg/g dry weight)*	
	Chrysene equivalents	*KCO equivalents*	*Chrysene equivalents*	*KCO equivalents*
SDC	2.6 ± 0.5 (5)	37 ± 7	2.3	33
SDFC			2.4	35
SDH	1.0–1.1	15–16	–	–
SDFH			0.7–0.5	11–7
MDT	0.3–0.4	4–6	–	–
UDT	0.4–0.5	6–7	–	–
MWT	0.6–0.7	9–11	–	–
UWT	0.3–0.3	4–4	–	–
UDC	3.1–4.0	45 –58	2.4	35
MDC	2.8 ± 0.3 (4)	40 ± 5	3.1	45
MWC	2.2–2.4	32–35	2.4	35

a—Letters in acronyms stand for extraction solvents and procedures; M, U and S for mechanical, ultrasonic and Soxhlet extractions; D and W for dried and wet sediment; C, H and T for $MeCl_2$, hexane and Freon 113 respectively; F for purified extract and KCO for Kuwait Crude Oil. All blank system determinations were below two digits after the decimal point of the corresponding measurement, except for the Soxhlet blanks, which corresponded to 0.05 μg/g chrysene equivalent concentration, assuming extraction of 30 g of sediment.

b—Measurements were made at 317/367 nm and expressed in terms of chrysene equivalents and of Kuwait Crude Oil (KCO) equivalents. Number in brackets stands for number of extractions. In other cases, number of results is number of extractions.

It appears from the data that Freon 113 and hexane were inefficient for extracting PAHs. The efficiency of Freon by either method, mechanical shaking or ultrasonic extraction on dry or wet sediment, was unexpectively very low when compared to our previous data[23]. This controversial result may be due to the different types of petroleum compounds present in the sediment and to the global quantification method used. In our previous work the sediment was recently heavily contaminated by Arabian light crude oil originating from the Amoco Cadiz oil spill while in this study the hydrocarbons extracted consisted of the remanent residue of heavily biodegraded and photo-oxydized chronic oil pollution. The IR measurements made in our previous study are more sensitive to saturated hydrocarbons than to aromatics, while fluorescent measurements are of course totally insensitive to aliphatics.

With the use of CH_2Cl_2 the average results and the standard deviations found, for all samples before clean-up (39 ± 7) and for the more concentrated samples after clean-up (37 ± 5) show precisions of 18% and 13% respectively. Based on three experiments, the repeatability of extractions carried out the same day was better by the Soxhlet procedure (5%) than by the mechanical shaking (12%). However the reproducibility of the Soxhlet can be more affected if the setting conditions are not perfectly reproduced; Table 1 shows a relative standard deviation of 18% for Soxhlet extractions carried out on different days. The repeatability of the mechanical extraction was found better during our previous study (6%); the lower levels analyzed during this study or the different analytical methods used for the quantification may be the reasons of these variations in the precision. Previous interlaboratory exercises have shown total IR measurements to give more precise results than total UV fluorescence measurements, i.e., 44% vs. 54% at the 290 μg/g level and 25% vs. 75% at the 1700 μg/g level[36], and vice versa, i.e., 61% vs.

24% at the lower 41 µg/g level[37]. In fact, we did a further checking of the repeatability of the Soxhlet and mechanical extractions by CH_2Cl_2 on freeze-dried sediment, by analyzing a sample from Kuwait environment with similar sedimentological characteristics for which the concentration of oil was expected to be lower. SSFS results without purification of the extracts were 24 µg/g and 22 µg/g by Soxhlet and mechanical extraction, respectively, with a relative standard deviation of 2% for both of them after three analyses. This shows that the repeatability of both types of extractions can be excellent. Mishandling and potential nonhomogeneous samples are the major factors affecting the precision.

The freeze-drying procedure did not show a clear trend in recovery efficiency when using Freon, but improved it when using CH_2Cl_2. The clean-up procedures by silica Sep-Pak and by direct introduction of florisil in the Soxhlet gave equivalent results.

Similarly to Wakeham[38] while he was using a 25-nm offset, we can roughly delimit on the synchronous scan spectra, zones of maximum fluorescence of the different PAH groups according to the number of cycles[26]. Linear PAHs over two cycles do not follow this rule, but as they are minor PAHs in the marine environment they should not interfere in the interpretation of the spectra. It could be observed on the spectra that the CH_2Cl_2 and Freon extracts after mechanical shaking or ultrasonication on wet sediment presented a deficiency of light PAHs emitting fluorescence below 350 nm, which are one and two cycles aromatic hydrocarbons. This can be attributed to the dissolution of these PAHs having an unfavorable partition coefficient in the interstitial water of the wet sediment. On the other hand, mechanic and ultrasonic extractions by Freon on dry sediment produced a low recovery of PAHs emitting fluorescence above 365 nm, which are hydrocarbons over three cycles, which could be explained as an ineffective desorption and dissolution by Freon of heavy hydrocarbons trapped in sediment pores not occupied by water molecules that would deactivate these sites in case of wet sediment. This phenomenon was not observed when CH_2Cl_2 was used to extract hydrocarbons from dry sediment because of a good solvatation of the heavy PAHs in this solvent. Hexane was also inefficient to extract heavier PAHs from dry sediment by the Soxhlet procedure. The fluorescence spectra showed that Soxhlet extraction with CH_2Cl_2 on dry sediment gave the best recovery for the heavier PAHs.

Comparison of extraction techniques with the use of CH_2Cl_2

Based on these findings, we selected four of the dichloromethane extracts (MDC, SDC, UDC, MWC) to study by different analytical methods the effect of the extraction procedure on the recovery of individual compounds. Figure 1 shows the synchronous scan fluorescence spectra obtained on the extracts. Similarly to Hawari *et al.* (1995) we observed the deficient recovery on wet sediment. A better recovery of heavy PAHs was obtained by Soxhlet extraction.

Extracts were fractionated by HPLC. Fraction 1 was analyzed by GC-FID while fraction 2 was analyzed by GC-FID, HPLC-NH_2-UV and HRMSS techniques. Tables 2 and 3 give concentrations measured by GC-FID. From a qualitative point of view the GC-FID chromatograms (originals lost) obtained on the saturated (F1) and aromatic fractions (F2) after MDC were more informative. Indeed, they revealed the existence of a bimodal unresolved complex mixture, which was less evident by SDC and UDC and nonexistent at all by MWC.

Corrections of results according to percentage recovery of surrogate standards (RS) added after the extraction procedures improve slightly the precision of the saturated

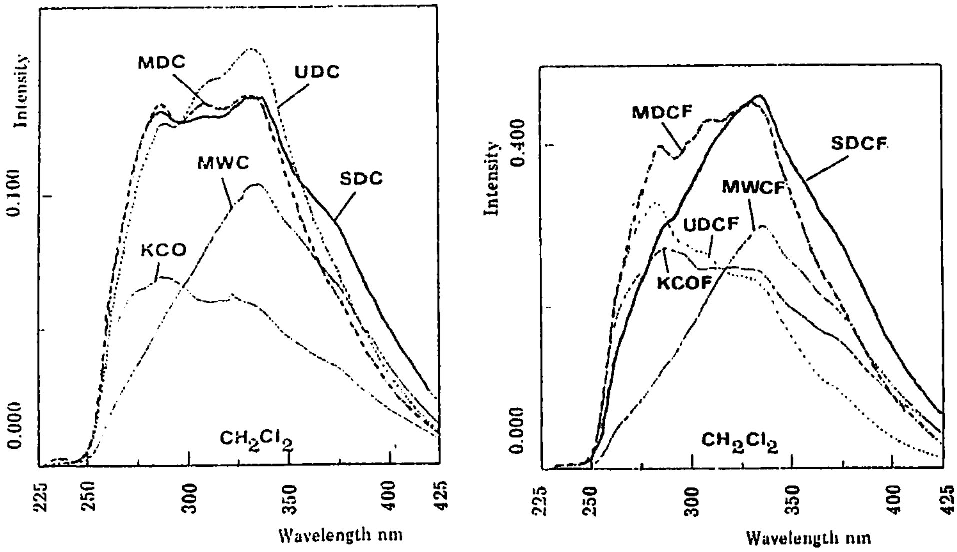

Figure 1 Synchronous scan fluorescence spectra (50 nm offset) of sediment extracts as a function of extraction procedures.

Legend: Letters in acronyms stand for extraction solvents and procedures; M, U and S for mechanical, ultrasonic and Soxhlet extractions; D and W for dried and wet sediment; C, H and T for $MeCl_2$, hexane and Freon 113 respectively; F for purified extract and KCO for Kuwait Crude Oil.

hydrocarbon measurements; but due to the very low recovery of anthanthrene and benzothiazol we obtained after Soxhlet extraction, corrections worsen the precision of total aromatic hydrocarbon quantifications. The important four-techniques-variation-coefficients obtained (42% VC pooled average after recovery correction for individual n-alkanes) show that extraction efficiencies vary greatly from one technique to the other. The use of RS improved slightly the precision. It did not correct, in this study, the bias due to extraction procedure because the RS were added on purpose after the extraction procedures.

Table 4 shows the results obtained by HRMSS on the four extracts. Results confirm what was found by fluorescence spectrometry at room temperature concerning a better efficiency by Soxhlet (SDC) for heavier polyaromatics, e.g., perylene and benzo(ghi)perylene. However HRMSS shows a more efficient recovery for pyrene by mechanical MDC technique, fluorescence spectrometry at room temperature did not show stronger fluorescence for MDC extract in the range—375-400 nm—4-cycle PAHs maximum fluorescence emission.

Figure 2 shows the HPLC analyses on the NH_2 column. It shows a more accurate chromatogram for MDC. UDC shows the same kind of chromatogram as MDC, but SDC is less effective for the 14-aromatic carbon compounds (family of phenanthrene), whereas MWC again shows a bad recovery for the aromatic compounds. Table 5 reports semi-quantitative HPLC-UV evaluations of total KCO equivalent contents for the four aromatic fractions. It can be noticed that due to the bad recovery of the RS added after the Soxhlet extraction, the recovery correction based on GC measurements worsens the VC%. Again here, this can be explained by the non addition of the surrogate standards before the extraction (and by potential bad spiking of the Soxhlet extract).

Table 2 Aliphatic hydrocarbon concentrations, determined by GC-FID, in Shuaïba Sediment Extracts as a function of extraction procedures.

Compounds	*Extraction methods*[a]											
	Mechanic Dry (MDC)		*Soxhlet Dry (SDC)*		*Mechanic Wet (MWC)*		*Ultrason Dry (UDC)*		*X*		*VC(%)*	
Surrogate standards (ng/g)[b]:												
n-C14:1	130 (62)		150 (74)		140 (54)		100 (49)		150		17	
n-C16:1	170 (81)		185 (92)		175 (69)		145 (70)		169		10	
n-C20:1	200 (95)		180 (89)		180 (71)		205 (100)		191		7	
Resolved hydrocarbons (ng/g)[c]:												
	BR	AR	BR	AR	BR	AR	BR	AR	BR	AR	BR	AR
n-C14	50	81	80	108	60	111	50	102	60	101	23	13
n-C15	29	42	35	42	20	33	15	25	25	36	37	23
n-C16	50	62	80	87	60	87	55	79	61	79	21	15
n-C17	38	46	43	47	25	35	20	23	32	38	35	30
Pristane	19	23	18	20	7	10	8	9	13	16	51	45
n-C18	54	63	65	72	40	57	37	44	49	59	27	20
Phytane	18	21	14	15	6	9	7	8	11	13	51	45
n-C19	76	84	71	78	30	43	26	30	50	59	51	45
n-C20	55	58	39	44	15	21	30	30	35	38	48	42
n-C21	95	100	79	89	35	49	30	30	60	67	54	49
n-C22	60	63	29	33	15	21	40	40	36	39	53	45
n-C23	70	74	39	44	15	21	25	25	37	41	64	59
n-C24	35	37	20	22	25	35	25	25	26	30	24	25
n-C25	60	63	50	56	45	63	50	50	51	58	12	11
n-C26	20	21	35	39	25	35	10	10	23	27	46	51
n-C27	40	42	69	78	25	35	35	35	42	48	45	43
n-C28	10	11	29	33	65	92	25	25	32	40	72	89
n-C29	55	58	104	117	15	21	25	25	50	55	80	80
n-C30	140	147	149	167	75	106	50	50	104	118	47	44
n-C31	45	47	54	61	25	35	30	30	39	44	35	31
n-C32	35	37	35	39	15	21	10	10	23	27	56	51
n-C33	30	32	29	33	15	21	15	15	22	25	38	35
n-C34	15	16	11	12	10	14	5	5	10	12	40	41
Total resolved hydrocarbons (μg/g)[d]:	2.9	3.1	2.9	3.3	1.8	2.6	1.3	1.3	2.3	2.6	36	35
Total unresolved hydrocarbons (μg/g)[d]:	29.5	31.2	23.9	26.8	13.9	19.6	10.9	10.9	19.6	23.2	44	40

a—MDC, SDC, MWC, UDC refer to extraction techniques described in the text; BR and AR are the concentrations calculated before and after recovery corrections; X and VC are the averages and the variation coefficients (standard deviation/average) of the measurements.

b—Percentage recovery of surrogate standards are in brackets.

c—Concentrations corrected for percentage recovery of surrogate standards (see text).

d—Concentrations corrected for percentage recoveries of n-C20:1. Concentrations of total resolved hydrocarbons also corrected to subtract concentrations of internal and surrogate standards added to the samples.

Table 3 Aromatic hydrocarbon concentrations, determined by GC-FID, in Shuaïba Sediment Extracts as a function of extraction procedures.

Compounds	Extraction methods[a]											
	Mechanic Dry (MDC)		*Soxhlet Dry (SDC)*		*Mechanic Wet (MWC)*		*Ultrason Dry (UDC)*		*X*		*VC(%)*	
Surrogate standards (ng/g)[b]:												
Bzth	190 (60)		100 (34)		165 (53)		150 (48)		151		25	
Anth	125 (53)		90 (38)		133 (57)		150 (66)		125		20	
Total Resolved hydrocarbons (μg/g)[c]:												
	BR	AR	BR	AR	BR	AR	BR	AR	BR	AR	BR	AR
	3.1	5.4	2.6[d]	7.2	2.1	3.8	1.5	2.6	2.3	4.8	30	42
Total Unresolved Hydrocarbons (μg/g)[c]:												
	19.3	33.9	15.8	43.9	12.4	22.5	8.1	14.2	13.9	28.6	35	45

a—MDC, SDC, MWC, UDC refer to extraction techniques described in the text; BR and AR are the concentrations calculated before and after recovery corrections; X and VC are the averages and the variation coefficients (standard deviation/average) of the measurements.

b—Percentage recovery of surrogate standards, Anthanthrene (Anth) and Benzothiazol (Bzth) are in brackets.

c—Concentrations corrected by considering an average recovery of 57, 36, 55 and 57% for MDC, SDC, MWC and UDC, respectively.

d—Value obtained after deducting the concentration of two large contaminant peaks that appeared in the chromatogram.

Table 4 Individual aromatic hydrocarbon concentrations, determined by HRMSS, in Shuaïba Sediment Extracts as a function of extraction procedures.

Compounds	Extraction methods[a]											
	Mechanic Dry (MDC)		*Soxhlet Dry (SDC)*		*Mechanic Wet (MWC)*		*Ultrason Dry (UDC)*		*X*		*VC(%)*	
	BR	AR[b]	BR	AR	BR	AR	BR	AR	BR	AR	BR	AR
Py	1.6	3.1	0.7	1.7	0.6	1.1	1.8	2.7	1.2	2.2	53	43
B(a)Py	0.12	0.24	0.10	0.27	0.18	0.32	0.20	0.31	0.15	0.29	32	13
B(k)Ft	0.14	0.26	0.16	0.42	0.15	0.26	0.13	0.20	0.15	0.29	9	33
Per	0.2	0.3	0.2	0.5	0.2	0.4	0.1	0.2	0.2	0.4	24	37
B(ghi)Per	0.4	0.8	0.7	1.7	0.6	1.0	0.4	0.6	0.5	1.0	24	47
Total PAH	2.4	4.7	1.8	4.6	1.8	3.1	2.7	4.0	2.2	4.1	21	18

a—MDC, SDC, MWC, UDC refer to extraction techniques described in the text; BR and AR are the concentrations calculated before and after recovery corrections; X and VC are the averages and the variation coefficients (standard deviation/average) of the measurements.

b—Based on Anthanthrene recovery as determined by GC-FID, concentrations (ng/g) were calculated by estimating an average recovery for all PAHs of 53, 38, 57 and 66% for MDC, SDC, MWC and UDC, respectively.

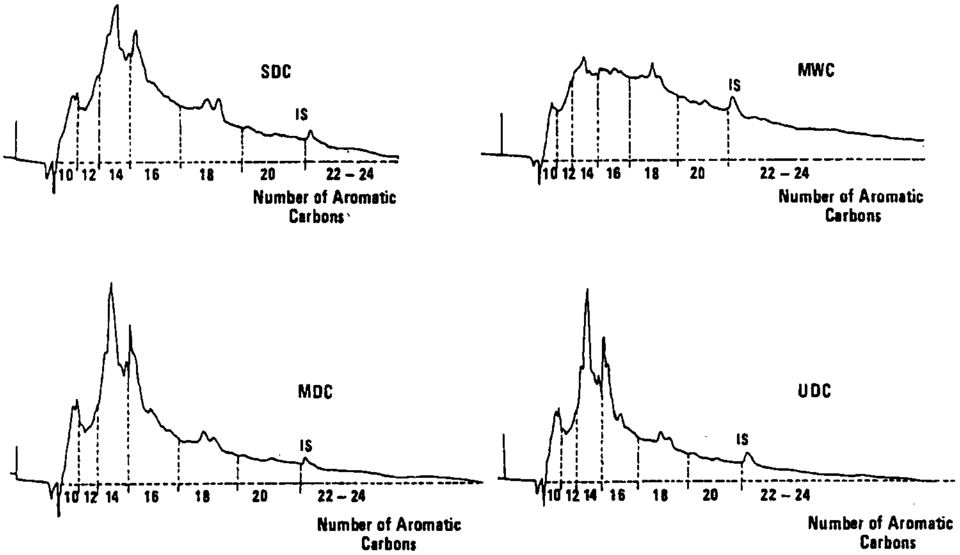

Figure 2 High pressure liquid chromatographic analyses of the aromatic fractions of sediment extracts.

Legend: Letters in acronyms stand for extraction solvents and procedures; M, U and S for mechanical, ultrasonic and Soxhlet extractions; D and W for dried and wet sediment; C for $MeCl_2$. IS stand for internal standard (anthanthrene).

Table 5 Total hydrocarbon concentrations, determined by HPLC-UV, in Shuaïba Sediment Extracts as a function of extraction procedures.

Extraction method	*Concentrations as (μg/g dry weight)*			
	Anthanthrene equivalents[a]		*KCO equivalents*[b]	
	BR	AR	BR	AR
MDC	4.2	7.4	46	81
SDC	3.6	10.0	40	111
MWC	2.0	3.6	22	40
UDC	1.8	3.2	20	35
X	2.9	6.0	32	67
VC(%)	41	53	41	53

a—Anthanthrene was used as internal standard.

b—Relative response factor of Kuwait Crude Oil toward anthanthrene was determined by co-injection of known quantities of both of them and electronic integration of signals.

c—MDC, SDC, MWC, UDC refer to extraction techniques described in the text; X and VC are the averages and the variation coefficients (standard deviation/average) of the measurements. BR and AR are the concentrations calculated before and after recovery corrections; based on GC-FID results, average recovery correction of 57, 36, 55 and 57% were tentatively used for MDC, SDC, MWC and UDC.

Total hydrocarbon contents of the different extracts as found by the different analytical methods are summarized in Table 6. It can be observed that the lower VC% are obtained for the SSFS method (13%) and for the MDC technique (9%). Both present minimum of handling and are easier to control. Comparison of variation coefficients shows that extraction step is a source of higher errors than analytical techniques operated for measurements.

All the results show that for total quantification of aromatic and saturated compounds, mechanical extraction (MDC) and Soxhlet extraction (SDC) on dried sediment are 1.5 to 3 times more efficient than mechanical extraction on wet sediment (MWC) and than ultrasonication on dried sediment (UDC) which provided in this study the less accurate and reproducible results. A one-hour-extraction by this procedure at this energy level (100 W) may be not sufficient.

In summary, Soxhlet extraction on dried sediment (SDC) was more efficient than mechanical extraction (MDC, MWC) and ultrasonic extraction (UDC) for the heavier polyaromatic hydrocarbons (over 5 aromatic cycles) and mechanical extraction on dried sediment after acidic treatment was found as the more convenient and accurate method for a wide scope of analyses. The addition of appropriate surrogate standards before extraction should allow better precision of the results for individual aromatic compounds.

Study of the mechanical extraction by CH_2Cl_2 on dry matter

Precision of the MDC method. The results concerning the precision of the analytical protocol for sediment, determined on triplicate analyses of a sediment sample, are shown in Table 7. The lower recovery (53% average bias) obtained for the surrogate standard RS1 than for the two others RS2 and RS3 (68% average bias) is due to a greater loss by volatilization during the concentration procedures. This emphasizes the need to correct the concentrations of hydrocarbons by the % of loss of the surrogate standards in the same boiling point range. The n-C14 and n-C16 are corrected considering the % loss of n-C14:1 and n-C16:1 respectively, the n-C15 is corrected by interpolation between n-C14:1 and n-C16:1 % losses, and the higher molecular weight hydrocarbons are corrected considering an average % loss for n-C16:1 and n-C20:1. Considering total

Table 6 Total hydrocarbon concentrations, in µg/g without recovery correction, in Sediment Extracts as a function of extraction techniques and analytical methods.

Extraction method[a]			*Analytical methods*			
	SSFS	*GC-FID*	*HPLC-UV*	X_1	S_1	$VC_1\%$
MDC	45	55	46	48.6	4.4	9
SDC	33	45	40	39.4	5.0	13
MWC	35	30	22	29.1	5.4	18
UDC	35	22	20	25.6	6.7	26
X_2	37.0	38.0	32.0	35.7		
S_2	4.7	12.8	11.2	9.0		
$VC_2\%$	13	34	35	25		

a—MDC, SDC, MWC, UDC refer to extraction techniques described in the text; X, S and VC are the averages, the standard deviations and the variation coefficients (standard deviation/average) of the measurements.

alkanes, total fraction F1 resolved compounds and total F1 unresolved compounds, the results show estimated repeatability of 12, 5 and 7% after recovery corrections, respectively.

Total hydrocarbon content was determined by HPLC by external calibration as equivalent KCO. Internal standard calibration procedure would have improved the precision (see below the precision on a biota sample with internal standard calibration). VC % found for the HPLC-fluorescence estimate of total hydrocarbon content is 12% only. Due to the fact the results concerning the individual recovery of deuterated PAHs standards used to spike the sediment before extraction were lost, planned corrections for HPLC-fluorescence measurements based on the GC-FID measured average recoveries on each sample are not done. An average result is however given considering the global average recovery, 58% (17% VC) that was obtained by GC-FID for the sum of all the deuterated PAHs considered in the three samples. Benzo(a)anthracene D12 added after the extraction procedure did not show better recovery than other surrogate standards added before extraction procedure, suggesting that loss of PAHs be mainly occurring during the steps after the extraction.

The estimate of the precision based on the variation coefficient (VC%) for each alkane varies from 6 to 53%. The recovery correction improves sensibly the precision for all the results except n-C28. The poor precision found for n-C28 is due to unreproducible contaminations by a coeluting phthalate artefact. The highest coefficients of variation correspond to the lowest concentrations of alkanes and vice-versa in the range 1–100 ng/g. Results show that a 12% minimum target for precision, as recommended for heavy metals in sediment and PCBs in biota[40], looks ambitious when considering individual hydrocarbons in sediment at these concentration levels.

The linear equation obtained to describe the relationships between the coefficient of variation (S/X) and the concentration (X) after recovery correction of an alkane,

$$S/X\ (\%) = 28.34 - 0.18\ X\ (\mathrm{ng/g})$$

can be used at a first approximation, to estimate the precision of an alkane measurement. From this equation, measurement precision of 12% is obtained for alkanes concentrations above 90 ng/g. At concentrations at the 10 ng/g level, coefficient of variation of 27% only can be reasonably expected considering results of this work.

An important consideration in environmental impact assessment is the real significance of the analytical results reported. Albaiges and Grimalt[22] pointed out that the t test for comparison of mean values of different populations allows an estimate of the level of differentiation between samples. The test statistic can be used, considering some approximations, to calculate the minimum value of $p = x_1/x_2$ (x_i is the mean of population i) for observing a significant difference between the means of two populations. The p value depends on the number of replicates per sample and on the standard deviation of the analytical method. In Table 8 several p values are shown, for different precisions and at two confidence levels, 90 and 95% when only one measurement is made. Thus, if the precisions for different observations are 22, 14, 12, 7 and 5%, two samples will be significantly differentiated for p values higher than 3.08, 1.87, 1.69, 1.35 and 1.24 at the 90% level of confidence. The figures obtained in this table reveal that in environmental studies, considering the levels of precision reached, it cannot be expected to get data interpretation at confidence levels better than 90%. However, the results concerning total quantifications allow to expect sufficient interlaboratory precision when using equivalent extraction methods, for significant environmental intercomparison studies.

The results (Table 9) concerning triplicate analyses of an oyster tissue sample show estimated precisions of 3 and 11% for total F1 resolved and total F1 unresolved,

Table 7 Results and statistics for the characterization of the precision of the analytical procedure (MDC) by analysing a sediment sample (Kuwait bay) in triplicate (A, B and C).

Compounds	*Samples*				X_m^a		*S*		*VC(%)*		*St/V3*		X_m *+/– St/V3*		$CI/2X_m$*(%)*	
	A	*B*	*C*	*Blank*	*BR*	*AR*	*BR*	*AR*	*BR*	*AR*	*BR*	*AR*	*BR*	*AR*	*BR*	*AR*
Resolved alkanes (ng/g):																
nC14	55[b]	59	71	–	62	117	8	7	13	6	14	11	48 – 75	106 – 128	22	09
nC15	44	46	60	–	50	83	8	5	17	6	14	8	36 – 64	75 – 91	28	10
nC16	60	68	87	–	72	105	14	9	19	9	23	15	49 – 94	90 – 120	32	14
nC17	50	55	74	–	60	88	13	12	21	13	21	19	39 – 80	69 – 107	35	22
Pr	33	42	45	–	40	59	6	2	16	3	11	3	30 – 51	56 – 62	26	05
nC18	50	60	83	–	64	94	17	16	27	16	28	26	36 – 93	69 – 120	44	27
Ph	29	33	24	–	29	43	5	10	16	23	8	16	21 – 36	27 – 59	27	38
nC19	42	45	66	–	51	75	13	13	25	17	21	21	30 – 72	54 – 96	41	28
nC20	44	48	63	–	52	76	10	9	20	12	17	15	35 – 69	61 – 91	33	20
nC21	36	45	70	–	50	73	18	18	35	24	29	30	21 – 80	44 – 103	58	40
nC22	32	44	55	–	44	64	12	9	27	15	19	15	24 – 63	48 – 79	44	24
nC23	23	28	38	–	30	43	8	7	26	15	13	11	17 – 42	32 – 54	43	25
nC24	22	23	32	–	26	38	5	6	21	15	9	9	17 – 35	29 – 47	35	24
nC25	18	30	35	–	28	40	9	8	31	19	14	13	14 – 42	28 – 53	51	31
nC26	13	17	20	–	17	25	4	2	21	8	6	3	11 – 23	21 – 28	35	14
nC27	13	15	22	–	17	25	5	5	29	19	8	8	9 – 25	17 – 32	48	32
nC28	37	18	24	–	26	41	10	21	37	53	16	35	10 – 42	5 – 76	61	87
nC29	18	20	36	–	25	36	10	11	39	29	16	18	9 – 41	18 – 54	64	49
nC30	31	31	45	–	36	53	8	9	24	17	14	15	22 – 50	38 – 68	39	29
nC31	17	20	27	–	21	31	5	4	23	13	8	7	13 – 30	24 – 38	39	22
nC32	5	4	5	–	5	7	0.5	2	10	21	1	3	4 – 16	5 – 10	17	34
nC33	12	12	20	–	14	21	5	6	37	27	9	9	6 – 23	12 – 30	61	44
nC34	6	5	12	–	8	11	4	5	47	40	6	7	2 – 14	4 – 19	78	66
Total alkanes (ng/g):																
	638[b]	734	966	–	780	1146	169	140	22	12	279	232	501 –1059	914 –1378	36	20

Continued

Table 7 Continued

Compounds	Samples				X_m[a]		S		VC(%)		St/V3		X_m +/- St/V3		CI/2X_m(%)	
	A	B	C	Blank	BR	AR	BR	AR	BR	AR	BR	AR	BR	AR	BR	AR
Fraction 1:																
Resolved[c]	1881[b]	2232	2533	-	2215	3267	326	153	15	5	540	253	1675 -2755	3014 -3519	24	08
Unresolved[d]	12.0	13.5	16.0	-	13.9	20.5	2.0	1.5	15	7	3.3	2.4	10.5- 17.2	18.1- 22.9	24	12
Total[d]	13.9	15.8	18.6	-	16.1	23.7	2.3	1.6	15	7	3.9	2.7	12.2- 19.9	21.1- 26.4	24	11
Total hydroc. (μg/g):	24.8[e]	19.9	21.1	-	21.9	37.8[f]	2.5	4.4	12	12	4.2	7.2	17.7-26.1	30.6- 45.0	19	19
F1 surrogate standards (%)[g]:																
RS-1	50	48	60	(41)	52.7		6.4		12		10.8		42–63		20	
RS-2	57	71	76	(63)	68.0		9.9		14		16.7		52–84		24	
RS-3	57	73	73	(66)	67.7		9.2		14		15.5		52–83		23	

a—X_m, S, VC (%), X+/-St/V3 and CI/2X_m (%) are the averages, the standard deviations, the variation coefficients (standard deviation/average), the confidence limits (at the 90 % level) and the % confidence interval around the average value for each observation. BR and AR stand for calculations made without and after recovery corrections respectively.

b—GC-FID results not corrected to the recoveries of RS1, RS2 and RS3 standards.

c—GC-FID results in ng/g.

d—GC-FID results in μg/g.

e—HPLC-fluorescence (Ex/Em = 280/389) equivalent KCO results not corrected for recovery.

f—Result corrected to the average recovery (58%) of deuterated PAHs (acenaphthene-D10, chrysene-D12, naphthalene D8, perylene-D12, phenanthrene-D10) used as surrogate standards for F2 and measured by GC-FID. Individual results for each sample and each PAH lost.

g—GC-FID results for the recovery of n-tetradecene (RS1), *n*-hexadecene (RS2), *n*-eicosene (RS3) in fractions F1 for samples and blank. Spiking amount was equivalent to 180 ng/g dry weight sediment.

Table 8 Estimation of the minimum ratios ($p = x_1/x_2$) between values of observations needed for the differentiation of samples from their content in petroleum hydrocarbons (in the case of one analysis per sample).

Confidence	*p Values at precision percentage*						
	5	*7*	*10*	*12*	*14*	*21*	*22*
90% level	1.23	1.34	1.53	1.69	1.87	2.85	3.08
95% level	1.36	1.56	1.94	2.29	2.78	10.7	18.9

Table 9 Results and statistics for the characterization of the precision of the analytical procedures by analysing a biota (oyster) sample in triplicate (A, B and C).

Compounds	*Samples*							
	A	*B*	*C*	*X*	*S*	*VC%*	*St/V3*[a]	*X+/-St/V3)*
Resolved Alkanes (ng/g)[b]								
nC14	190	170	-	180	10	6	17	197 -163
nC15	320	300	190	270	70	26	118	388 -152
nC16	250	210	340	267	66	25	111	378 -156
nC17	410	430	780	540	208	38	351	891 -189
Pr	94	81	120	98	20	20	34	132 - 64
nC18	100	96	140	112	24	21	40	152 - 72
Ph	60	60	70	63	6	9	10	73 - 53
nC19	120	130	110	120	10	8	17	137 -103
nC20	60	66	68	65	4	6	7	72 - 58
nC21	c	c	c	c	c	c		
nC22	75	110	100	95	18	19	30	125 - 65
nC23	85	80	97	87	9	10	15	102 - 72
nC24	23	51	58	44	18	41	30	74 - 14
nC25	40	60	65	55	13	24	22	77 - 33
nC26	39	66	65	57	15	26	25	82 - 32
nC27	23	40	42	35	10	28	17	52 - 18
nC28	26	48	65	46	19	41	32	78 - 14
nC29	30	110	120	87	49	56	83	170 - 4
nC30	13	41	45	33	17	51	29	62 - 4
nC31	51	108	120	93	37	40	62	155 - 31
nC32	21	31	39	30	9	30	15	45 - 15
nC33	c	c	c	c	c	c		
nC34	c	c	c	c	c	c		
Total Alkanes (μg/g)[b]								
	1.9	2.1	1.6	1.9	0.25	13	0.4	2.3- 1.5
Fraction 1 (μg/g)[b]								
Resolved	18	17	18	17.7	0.6	3	1.0	18.7- 16.7
Unresolved	28	26	32	28.7	3.1	11	5.2	33.9- 23.5
Total	46	43	50	46.3	3.5	8	5.9	52.2- 40.4
Total Hydrocarbons (μg/g)[d]								
	20	20	22	20.7	1.2	6	2.0	22.7- 18.7
Surrogate Standards (%):[e]								
RS-1	78	72	0	50	43	87	72	122 - 0
RS-2	87	84	22	64	37	57	62	126 - 2
RS-3	84	83	77	81	4	5	6	86 - 77

a—X, S, VC and X+/-St/V3 are the averages, the standard deviations, the variation coefficients (standard deviation/average) and confidence limits (at the 90 % level) for each observation.

b—GC-FID results corrected to the recovery of RS1, RS2 and RS3 standards.

c—Not quantified because of coeluting peak.

d—HPLC-fluorescence (Ex/Em = 280/389 nm) results without surrogate standards correction.

e—GC-FID results for the recovery of *n*-tetradecene (RS1), *n*-hexadecene (RS2), n-eicosene (RS3) in samples.

Table 10 Analysis of PAHs in SRM-1649 (urban dust/organics) by HRMSS and HPLC on normal phase NH$_2$ column.

Concentrations: (µg/g) Compounds	*This Study*		*Certified Value*[b]	
	HRMSS	*HPLC*[a]	*GC*	*LC*
An		2.2	0.49	0.4 ± 0.04
Phe		7.6	4.5 ± 0.3	4.7 ± 0.1
Py	6.5	8.1	7.2 ± 0.2	6.0 ± 0.2
Ft		9.2		7.7 ± 0.5
B(a)An	1.6	5.9[c]	2.4 ± 0.1	2.4 ± 0.1
Chy	8.3		4.6 ± 0.2	3.5 ± 0.1
B(a)Py	2.3	8.2[d]	3.0 ± 0.3	2.4 ± 0.2
B(b)Ft	8.8			6.0 ± 0.3
B(k)Ft	2.5	2.1		2.0 ± 0.1
Per	0.8		0.84 ± 0.09	0.74 ± 0.05
B(ghi)Per	4.9	6.3	4.7 ± 0.2	4.1 ± 0.1
I(1,2,3-cd)Py		3.4	3.3 ± 0.3	3.4 ± 0.1

a—Concentrations were calculated directly by calibration with the recovery standard (anthanthrene).

b—From Wise *et al.* (1986).

c—Determination includes benzo(a)anthracene and chrysene which coelute on aminosilane column.

d—Determination includes benzo(a)pyrene and benzo(b)fluoranthene which coelute on aminosilane column.

respectively. HPLC-fluorescence measurements by internal standard (anthanthrene) calibration of the F2 total fraction are given without recovery standard corrections. However, a precision of 6% is found. Besides the oyster sample, fish liver samples were also extracted with the same procedure. Results and chromatograms showed good reproducibility.

Trueness of the MDC method. Results found for SRM 1649 by HRMSS and HPLC reported in Table 10 are generally consistent with the certified values. When using HRMSS, chrysene is the PAH that deviates more toward the certified value. HPLC measurements were made while using the NH$_2$ normal-phase column, which is not as appropriate as the C18 reversed-phase column normally used for this kind of analyses[41]. It must be mentioned that the normal-phase column is not suitable for separating the different alkylated PAHs. This property is used in oil pollution studies to quantify PAHs according to the number of aromatic carbons. Quantifications of individual non substituted PAH parents are overestimated as the alkylated PAHs are coeluting. Nevertheless, due to the low levels of alkylated PAHs in pyrolytic products, i. e. in the urban dust, results found with this type of column are in good agreement with certified values.

CONCLUSION

The more effective parameter for recovery efficiency proved to be the solvent selection. Hexane and Freon-113 were found of very low efficiency for hydrocarbon extraction from sediment samples. Hexane was also inefficient to extract heavier PAHs from dry sediment by the Soxhlet procedure. Dichloromethane was the selected solvent, it gave the best recovery with either extraction techniques used.

Freeze-drying procedure did not show a clear trend in recovery efficiency when using Freon 113 as the extraction solvent but improved it when using dichloromethane. A bad recovery of the aromatic compounds was observed when extracting wet sediment.

Soxhlet and mechanical extractions could provide, based on total hydrocarbon quantifications, precisions better than 12%, but showed variations from 2% for repeatability up to 18% for Soxhlet reproducibility. Clean-up of the extracts improved the precisions of results. The clean-up procedures by silica Sep-Pak and by direct introduction of florisil in the Soxhlet gave equivalent results. Mishandling and potential nonhomogeneous samples were incriminated as the major factors affecting the precision.

Results showed that, for total quantification of aromatic and saturated compounds, mechanical extraction (MDC) and Soxhlet extraction (SDC) on dried sediment are 1.5 to 3 times more efficient than mechanical extraction on wet sediment (MWC) and than ultrasonication on dried sediment (UDC) which provided in this study the less accurate and reproducible results. A one-hour-extraction by this procedure at this energy level (100 W) may not be sufficient.

Soxhlet extraction with dichloromethane on dry sediment gave the best recovery for the heavier PAHs (over 5 aromatic cycles) but was less effective than mechanical and ultrasonic extractions for the recovery of the 14-aromatic-carbon compounds (family of phenanthrene) and of pyrene.

GC-FID showed in the dichloromethane mechanical extract of dried sediment the existence of a bimodal unresolved complex mixture, which was less evident in the dichloromethane Soxhlet and ultrasonic extracts of dried sediment and nonexistent in the dichloromethane mechanical extract of wet sediment.

Comparison of extraction techniques with dichloromethane and of total quantification methods showed that the lowest variation coefficients were obtained for the mechanical extraction (9%) and for the Synchronous Scanning Fluorescence Spectroscopy (13%). Both present minimum of handling and are easier to control.

From a qualitative and quantitative point of view, mechanical extraction on dried sediment after acidic treatment was found as the more convenient and accurate method for a wide scope of analyses.

The estimation of the precision of the measurements of alkanes based on the variation coefficient, while using this technique, varied from 6 to 53%. The recovery correction improved sensibly the precision for all the results except n-C28 due to a phthalate coeluting artefact. However loss of PAHs was assumed to occur mainly during the steps after the extraction, the addition of appropriate surrogate standards before extraction, e.g., deuterated PAHs, should improve significantly the accuracy of the PAHs measurements.

Results of this work enlighten the fact that the extraction step is a source of a higher variability in results than analytical techniques operated for measurements.

The linear equation obtained to describe the relationships between the coefficient of variation (S/X) and the concentration (X) after recovery correction, of an alkane (S/X (%) = 28.34–0.18 X (ng/g)) can be used, at a first approximation, to estimate the precision of an alkane measurement. From this equation, measurement precisions of 27% and 12% are obtained for alkane concentrations at the 10 ng/g and 90 ng/g levels respectively.

The degrees of precision obtained for individual hydrocarbons at the 10 ng/g level reveal that in environmental studies, when single analyses are carried out, correct data interpretation cannot be expected at confidence levels better than 90%.

In conclusion, sufficient interlaboratory precision for significant environmental intercomparison studies can be expected only by using equivalent extraction techniques. Dichloromethane mechanical extractions on dry sediment followed by Synchronous Scanning Fluorescence Spectroscopy for total quantification of hydrocarbons is a method presenting the less potential interferences for which can be expected the 12% Quasimeme target precision. Go behind HPLC fractionation on normal phase and analyses of saturated hydrocarbons by GC-FID and of PAHs by HRMSS is a procedure for which 12% precision can be expected at the 100 ng/g level, keeping in mind than 20 to 30% precision range is a more likely realistic range that can be reached through monitoring programs.

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