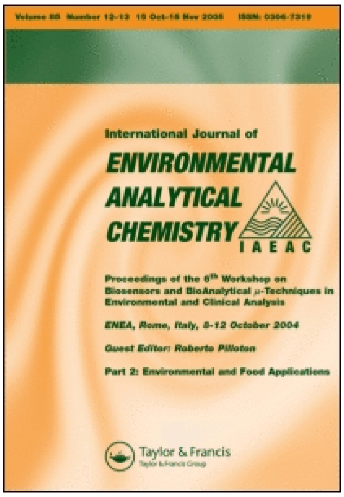

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A Study of an Extraction Procedure for Organic Trace Levels: Some Results Concerning Hydrocarbons in Marine Sediments

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A Study of an Extraction Procedure for Organic Trace Levels: Some Results Concerning Hydrocarbons in Marine Sediments

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The integration of hydrocarbons into marine sediments is the basis for numerous paleontological, bacteriological and ecological studies. It permits the explanation of the decontamination process of polluted areas over long periods of time.

A procedure for analysis of hydrocarbons in sediments is described in this paper, offering optimal operational simplicity. The yield (92%) of the extraction technique by mechanical stirring determined from the isotherm method of Freundlich, the accuracy of these results (94%), the sensitivity at the ppm level from IR spectroscopy, at the hundred ppt level from GC^2 and also the universal application of this method tested by comparison with other laboratories, make this an interesting technique for trace analysis. Results concerning the adsorption of hydrocarbons according to sediment characteristics are presented and the influence of the organic matter originally present is discussed.

KEY WORDS: Extraction procedure, trace, hydrocarbons, sediments, adsorption, organic matter.

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INTRODUCTION

Understanding the role played by organic matter in a marine environment is to a large extent dependent on knowledge of its physical state. Determining its concentration in any given phase: vapour, liquid or solid, is no easy problem for the chemical analyst in so far as its presence in this phase does not necessarily correspond to its proper physical state. The adsorption of hydrocarbons on solid matter is often believed to be an intermediate stage in numerous natural processes. The study of these adsorbed molecules is of interest in many fields: paleontology,[1-3] bacteriology,[4,5] ecology,[6,7] pollution.[8,9]

As regards this study, the oil slick caused by the running aground of the *Amoco Cadiz* posed the problem of the study on a large space-time scale of the hydrocarbons adsorbed on sediments and suspended matter in estuarine zones on the north coast of Brittany.[10,11] The analytical problem was therefore, that parallel to a qualitative study of individual hydrocarbon weathering, it was interesting to carry out a quantitative survey of global hydrocarbon contamination. Thus a simple analytical procedure had to be found, offering simultaneously optimal operational efficiency and all the characteristics—accuracy, precision, sensitivity, and universality—necessary to both extensive IR spectroscopy and intensive GC^2 analysis. The main difficulties consisted in defining an extraction procedure presenting all the aspects stated above and adaptable to both types of measurements.

The aim of this paper is to show that optimal operational simplicity can be compatible with the best trace analysis. A Freundlich isotherm model is proposed to evaluate extraction efficiency, some results concerning the adsorption of hydrocarbons according to granulometric characteristics of sediments are presented, and the influence of the organic matter orignally present is discussed.

GENERALIZATIONS

For an outline of the various techniques for extracting lipids from solid matter, exhaustive literature on the subject can be consulted.[12,13]

Two techniques are generally used:

— mechanical tumbling or ultrasonic stirring with a solvent,
— continuous washing with solvent recycled in Soxhlet apparatus.

Various combinations of solvents are used in both cases. Binary azeotropic mixtures are often used, such as methanol-benzene,[14] methanol-carbon tetrachloride,[15] methanol-methylene chloride,[16] isopropanol-heptane,[17] methanol-toluene.[18] The last three of the mixtures listed above offer the advantage of using such solvents as toluene, methylene chloride and heptane, less toxic than benzene and carbon tetrachloride.[19] In the case of extraction in view of an infrared spectroscopy analysis, carbon tetrachloride is used alone. In some cases, saponification of lipids is carried out using NaOH or KOH in methanol-water either simultaneously or after an extraction with another solvent. For a stronger treatment of the mineral matter, crushing or fluorhydric acid attack[20] are methods which can be considered.

According to the combinations of solvents and techniques chosen and the subject of the study, optimal extraction times of wet or dry sediment vary: they may be of several minutes by ultrasonication, several hours by mechanical tumbling, or several days by the Soxhlet procedure.

Freeze-drying of sediment improves extraction yield, but gives rise to a loss of light products up to C20 hydrocarbon and may cause artefact contamination.

The choice of a solvent extraction method, in opposition to a high temperature extraction method, assumes the existence of successive equilibria

$$(\mathrm{Hydrocarbons})_{\mathrm{adsorbed}} \overset{\Delta G}{\rightleftarrows} (\mathrm{Hydrocarbons})_{\mathrm{solvated}}$$

The thermodynamic condition for spontaneous desorption is a negative value for the free enthalpy variation: $\Delta G < 0$

$$\Delta G = \Delta H - T\Delta S = (\Delta H_{\mathrm{solvation}} - \Delta H_{\mathrm{adsorption}}) - T\Delta S$$

All adsorption phenomena are exergonic, so:

$$\Delta H_{\mathrm{adsorption}} < 0$$

Mixing of most liquids having similar physical properties only produces low calorific effects. In the case of this study, where hydrocarbons are only present as low concentration solutes, enthalpy variation during solvation can be neglected.

The entropy of the orderly layer is always less than that of a disorderly state in solution. We therefore have:

$$T\Delta S > 0$$

The condition of spontaneity requires that the values of $T\Delta S$ be greater than that of ΔH. Moreover, in order that this equilibrium be completely displaced towards the right, ΔG must have a highly negative value. To achieve this it is necessary to operate:

—either at high temperature, which corresponds to conditions of thermal power extraction, giving as a final state a vapour (high ΔS) or a liquid (low ΔS);

—or at ambient temperature, and fulfill the conditions which result in a high value of ΔS; that is a high value of the final entropy of hydrocarbons, corresponding to the most disorderly state possible. The obvious solution is to choose a very good solvent of hydrocarbons.

With regard to infra-red analysis, this solvent must present no absorption in the range 2800–3000 cm^{-1}. Carbon tetrachloride and trichloro-1,1,2 trifluoro-ethane (Freon 113) present the best characteristics corresponding to both conditions.

Carbon tetrachloride, a high density solvent (1,44) insoluble in water with a good distribution coefficient for hydrocarbons, has the disadvantage of a high boiling point (76.8°C) which causes loss of low boiling point hydrocarbons during the process of concentration by evaporation.

Freon 113 presents all the qualities required for the purpose. Although less transparent than CCl_4 in the range 2800–3000 cm^{-1}, measurement of ν (C–H) vibrational stretches in this field is possible. Its low solubility in water (1 ml/l of sea water), high density (1,57), and low boiling point (48°C), and low toxicity[21] (100 times less than for CCl_4) make it a useful solvent for sediment hydrocarbon extraction.

The choice of an extraction procedure is dependent on the knowledge of the state of the compounds under study; are they chemically or physically sorbed? Are they trapped in macromolecular clathrate type organic structures, or in pores of the mineral matter? It would seem, with reference to Meyers and Quinn's studies,[22] that the hydrocarbon-sediment associations are either of the type defined by Van der Waal's force, or intermolecular: that is to say that the heats of sorption involved, of less than 40 KJ mol^{-1}, in the range of vaporization heats, indicate reversible physical adsorption in normal temperature and pressure conditions, for which no appreciable activation energy is required.

According to these theoretical conditions and various practical considerations, it would seem interesting to adopt the mechanical tumbling extraction of wet sediment with CCl_4 or Freon 113. This method does not present the major inconvenients of the more efficient Soxhlet or ultrasonic method.

Continuous washing with recycling of the solvent in Soxhlet apparatus:

— causes loss of solvent which entails loss of light hydrocarbons,

— may cause formation of artefact compounds through heating,

— calls for relatively large volumes of solvent, which is troublesome in trace analysis,

— causes wastage of solvent during tedious cleaning operations.

Ultrasonic extraction, although a very efficient method, can produce artefact degradation compounds.

When a solute is in contact with a substrate, the amount of adsorbed substrate depends on two parameters: the temperature of the system and the concentration of the solute in the solution at the equilibrium. Plotting $x/m = f(c)$ at different temperatures allows the comparison with a Freundlich type variation ($x/m = kc^{1/a}$) where x/m is the weight of adsorbed solute per gram of substrate, c the solute concentration in solution and $\underset{\sim}{k}$ and $\underset{\sim}{a}$ are empirical constants depending on solute, substrate and solvent.

SOLVENTS AND APPARATUS

A great care must be taken with both solvents and apparatus, which must be regularly checked. All glassware is washed for about 12 hours in the sulfo-chromic mixture, rinsed in distilled water, rerinsed in acetone then dried at 120°C for one whole night. All glass vessels are then dried at 120°C for one whole night. All glass vessels are then rinsed with the appropriate purified solvent prior to use. The Teflon of the watertight washers is attacked by the sulfochromic mixture, rinsed in CCl_4 and dried with a hair dryer.

Two sediment extraction techniques were used for this study:

- mechanical tumbling, in glass vessels (trade mark SOVIREL or PROLABO) with screw plugs with watertight Teflon washers using an oscillating shaking machine,
- continuous washing with solvent recycled in Soxhlet apparatus.

All solvents (MERCK): carbon tetrachloride CCl_4 "For spectroscopy", Freon 113 "For trace analysis", are purified by means of an aluminum oxide column and bi-distillation. The "Suprapur" hydrochloric acid is redistilled. The sodium sulfate "For analysis", Florisil (MERCK products), and glass wool are heated in an oven at 500°C for 48 hours. Soxhlet thimbles are pre-extracted with purified CCl_4 for 24 hours.

The IR analyzer is an SP 2000—PYE UNICAM model; 2 cm, 3 cm and 5 cm quartz cells are used.

METHOD

The IR/$(GC)^2$ method using a mechanical tumbling extraction procedure at ambient temperature, developed for hydrocarbon trace analysis has been described in detail previously[23] (Figure 1).

In this study, only the part referring to IR analysis will be described. About 100 g of the sediment collected with a glass coring device are homogenized by agitation. An aliquot of about 10 g is taken to determine the dry weight/wet weight average after being dried at 100°C for one night. The organic content of the sediment is determined using gravimetric analysis: it is represented by loss in weight after oven calcination at 500°C for 48 hours. In order to evaluate the loss of carbonates by calcination at 500°C,[24] the carbonate content of the sediment is determined using the acidimetric method, and then necessary corrections regarding the organic matter content are effected.

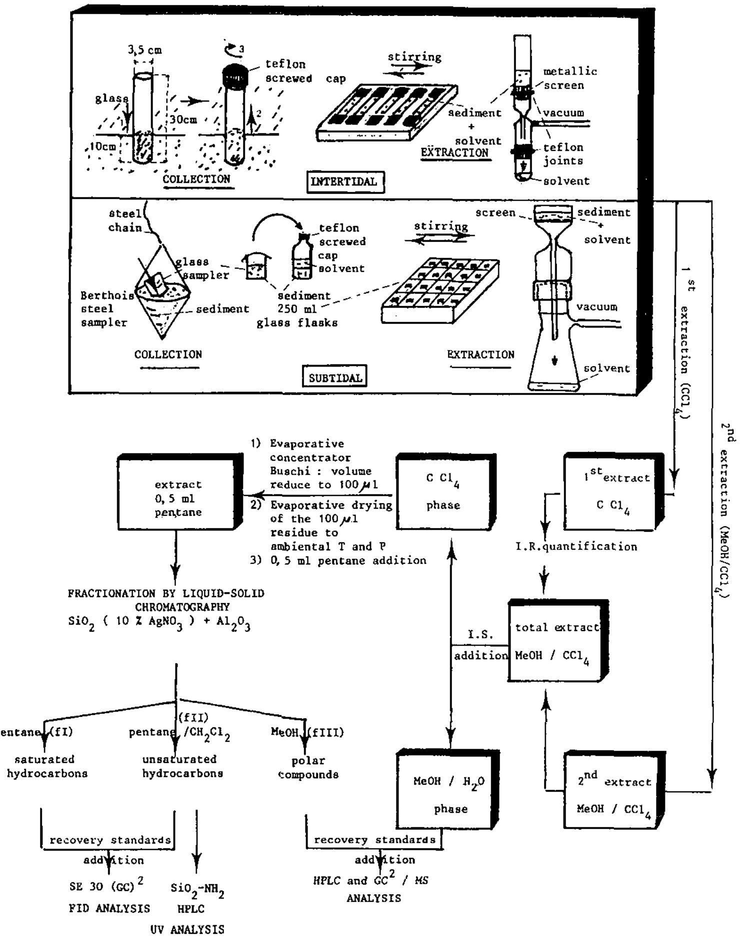

Figure 1 Analytical flow diagram.

Extraction by mechanical tumbling is carried out in HCl medium by means of an organic solvent (Freon 113 or CCl_4) in the proportion volume of solvent (ml)/wet weight (g) of sediment = 2†. After tumbling, the solvent is separated from the sediment by filtration at 20 torr and the extract is frozen in order to separate out the

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†N.B. This quantity of solvent may be reduced for analysing sands where the hydrocarbons generally exist as traces.

supernatant water. An IR measurement is carried out on this first extract.

In order to study the kinetics of hydrocarbon desorption by the solvent CCl_4 (or Freon), several measurements were carried out on this first extract at regular intervals.

In order to establish the Feundlich isotherms, successive equilibria were simulated by carrying out two further extractions on the same sample.

The extraction technique using a Soxhlet apparatus which is frequently used by many laboratories and recommended by the I.F.P. (Institut Français du Pétrole), consists in[25] taking about 300 g of sediment which are dried at 60°C. If the sediment contains much water, it is centrifuged before being oven dried. The dried sediment is reduced to a fine powder and homogenized in a crushing machine. About 100 g of the powder, thus obtained are mixed with 20 g of sodium sulfate, and the resulting mixture put in a Soxhlet apparatus and extracted for 8 hours by carbon tetrachloride, the volume of tetrachloride being fixed by that of the Soxhlet apparatus. Then the volume V of extract collected is measured and filtered with sodium sulfate in order to eliminate any water which may have been dissolved.

Liquid chromatography on Florisil is carried out in order to remove polar compounds from the extract.

The concentrations are measured using IR spectroscopy. (Figure 2).

The calibration curve equation, corresponding to absorbances at 2863, 2924 and 2959 cm^{-1} is established by linear adjustment using dilutions in CCl_4 (or Freon 113) of three standard solutions isooctane, hexadecane, benzene (7.5/7.5/5 by volume). In so far as the pollutant is known, calibrations are based on dilutions of the pollutant in CCl_4 or Freon.

The concentration X of hydrocarbons extracted from a sediment is calculated by the following equation:

$$X(\text{ppm}) = \frac{y(\text{mm}) - b}{a} \times \frac{V(\text{ml})}{P(\text{g})} \times F$$

$V(\text{ml})$ = volume of sediment (in millilitres) used in mechanical tumbling extraction process; or volume of solvent recuperated using Soxhlet extraction method.

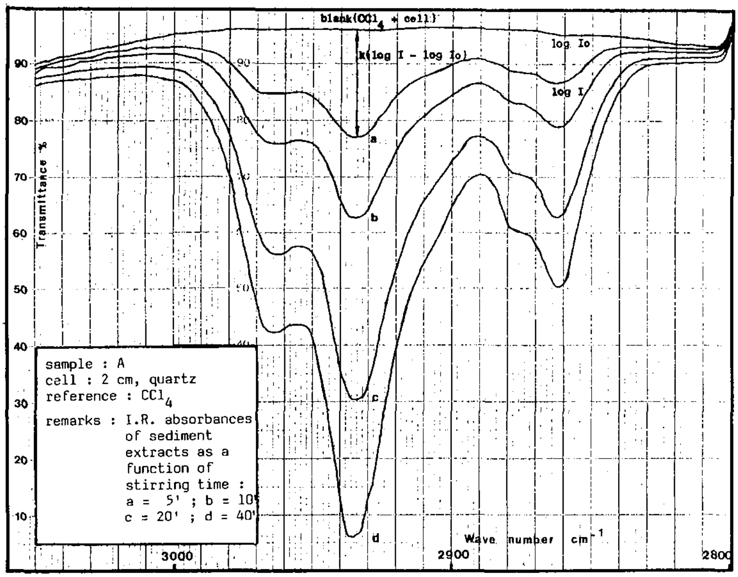

Figure 2 Determination of total hydrocarbons by I.R.

P(g) = dry sediment weight (in grammes).

F = dilution factor (this may arise from the dilution of an over-concentrated extract, and purification on Florisil).

SOURCES OF SAMPLES

The samples of sediment studied (Table I) were mainly collected from the Aber Benoît, an estuarine zone on the north coast of Finistere, France (Figure 3), which is 10 km long, and 1 km wide at its widest point. The estuary is made up in its furthest part, of sand coming partly from modified preglacial formations, and partly from shell fragments, and its inner area is alluvial mud of preglacial origin coming from the banks.[26] This area proved to be favorable ground for the accumulation and retention of hydrocarbons arising from the running aground of the *Amoco Cadiz*.

Table I Characteristics of sediment samples and extraction procedures

Sample	Sediment type	Wet weight (g)	Dry weight/ wet weight ratio %	Organic matter content/dry weight %	Pre-treatment of sample	Extraction procedure H. hours M.E. mechanical Ext. S.E. soxhlet Ext.	
A	Sandy clay mud	87.6	64	13	None	2 ml HCl	30 H
	Organic detritus					100 ml CCl_4	M.E.
B	Clay mud	79.4	52	7	None	2 ml HCl	5 H.
						100 ml freon	M.E.
C	a) Sandy clay mud	118.3					
	b) Sandy clay mud	128.1	61	9	None	2 ml HCl	3 H.
	c) Sandy clay mud	165.5				100 ml CCl_4	M.E.
D	a) Mud	30.0	—	—	freeze-drying (16 H)	101 ml CCl_4	8 H.S.E.
	b) Mud	50.6	—	—	pestle pulverization	94 ml CCl_4	25 H.S.E.
	c) Mud	26.3	—	—	manual screening (1 mm)	50 ml CCl_4	3 H.M.E.
	d) Mud	24.9	—	—	homogenization	50 ml freon	3 H.M.E.
E	d) Mud	25.7	—	—	freeze-drying (16 H)	50 ml freon	3 H.M.E.
	c) Mud	26.4	—	—	pestle pulverization	50 ml CCl_4	3 H.M.E.
	a) Mud	50	—	—	manual screening (1 mm)	183 ml CCl_4	8 H.S.E.
					homogenization		
F	Silty clay mud	31.1	42	15	None	See Table IV	
	Organic detritus						

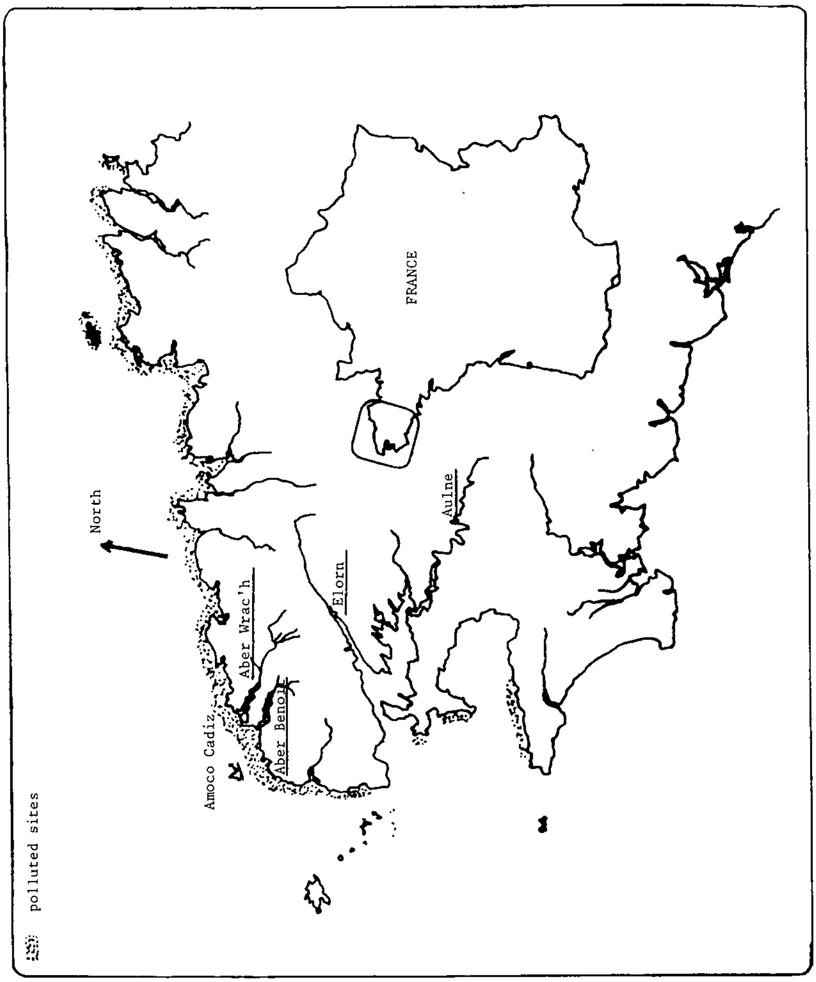

Figure 3 Coast of Brittany showing locations of sampling sites.

EXPERIMENTAL RESULTS

Description of hydrocarbon fixation on the sediment using Freundlich's isotherm method supposed that adsorption—desorption equilibrium processes take place at the solvent—sediment interface.

A study of the kinetics of hydrocarbon desorption by mechanical tumbling with a solvent makes it possible to determine an optimal duration of the tumbling process, which corresponds to the setting up of the equilibrium:

$$\text{hydrocarbons}_{(\text{adsorbed})} \rightleftarrows \text{hydrocarbons}_{(\text{solvated})}$$

The curves in Figure 4 show variation of concentrations of hydrocarbons extracted by carbon tetrachloride of Freon 113 with tumbling time. In fact, purification operations on Florisil showed that hydrocarbons constitute the essential IR response in the extracts studied. The curves level off after about two and a half hours.

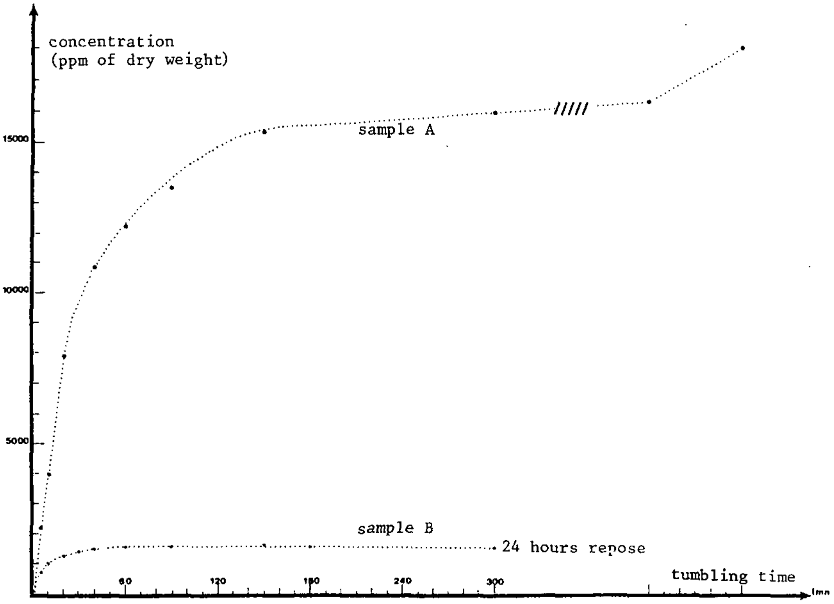

Figure 4 Extraction yield of sediment as a function of stirring time.

Twenty-four hours later, concentrations have changed only very slightly, whereas the extract has taken on a greenish tinge, showing that pigments have been extracted. Therefore, tumbling process time of three hours for each extraction was retained. (Figure 4).

Repeated extraction operations on three different fractions of the same mud (Table II) show good analysis reproducibility (variation coefficient = 6%).

Table II Precision of the analysis—3 hours of tumbling extraction by 100 ml of CCl_4 and 2 ml of HCl

	I	II	III	$\bar{X} \pm \sigma/\bar{X}$
Wet weight (g)	118.30	128.06	165.49	
$\% \frac{\text{Dry weight}}{\text{Wet weight}}$	60.3	62.4	61.3	61.3 ± 2%
Dry Weight (g)	71.3	79.9	101.5	
x (ppm of CCl_4)	80.1	96.7	109.5	
X (ppm of dry weight of sediment)	5613	6053	5394	5687 ± 6%

The unversality of the method was established by comparison of the results (samples D and E) of the "Hydrocarbon Intercomparison Exercise 1981".[27] Table III shows good quantitative correlation between the two extraction methods—Soxhlet and mechanical tumbling—whereas Figure 5 and 6 show respectively the relative distributions of saturated hydrocarbons and aromatic hydrocarbons extracted from sediment by mechanical tumbling. (Figures 5, 6).

Simulation of equilibria showing variation of relative quantities of adsorbate and solute in both phases when the global quantity of adsorbate varies, was done according to the procedure described in Table IV.

The choice of this operative procedure supposes the existence of physico-sorption forces at the hydrocarbon—sediment interface of about the same importance and such that the law of speed governing desorption be the same for all hydrocarbons analysed.

The constants of Freundlich's equation are then determined by varying the global adsorbate concentration.

The application of Freundlich's law to our study gives the quantity of product adsorbed per mass unit of dry sediment at the

Table III Intercomparison of hydrocarbon extraction procedures efficiencies. (μg hydrocarbons/g dry sediment)

Procedure	Soxhlet extraction		Mechanical extraction		Average value[a] ± Standard deviation (19 laboratories 32 values)
Extract treatment	8 H CCl_4	24 H CCl_4	3 H CCl_4	3 H freon 113	
Sediment D					
without purification of the extract	440	400	360	260	—
after Florisil purification of the extract	250	230	230	—	290 ± 130
Sediment E					
without purification of the extract	2080	—	1920	1440	—
after Florisil purification of the extract	1530	—	1810	—	1700 ± 420

[a] Results of the "interlaboratory comparison of hydrocarbon analyses"[26].

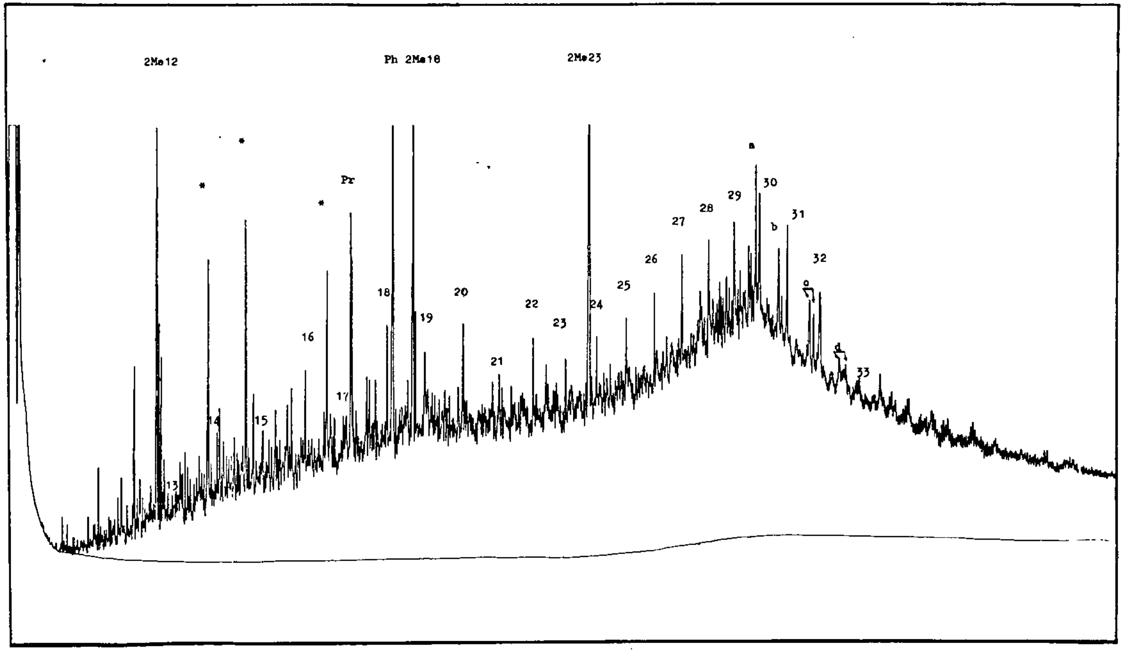

Figure 5 (GC)^2 chromatogram of the saturated fraction of sediment A extract. (SE 30 Phase, FID Detection)
2 Me 12, 3 Me 23: internal standards
2 Me 18: recovery standard
Pr: Pristane
Ph: Phytane
a, b, c, d: C29, C30, C31, C32 pentacyclic triterpanes.

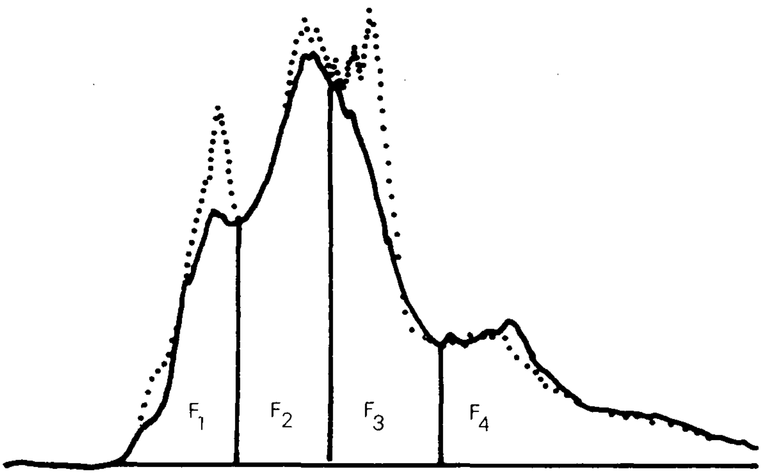

Figure 6 (HPLC) chromatogram of the aromatic fraction of sediment A extract. (SiO_2-NH_2 Phase, UV Detection $\lambda = 254$ nm)
——Aromatic fraction of sediment A extract
----Aromatic fraction of Amoco Cadiz reference mousse
F_1: Two ring compounds
F_2: Three ring compounds including a five membered ring
F_3: Three ring compounds
F_4: Four ring compounds.

equilibrium:

$$q_1 = x_1''/\mathrm{m} = k(C_1)^{1/a} \quad (1)$$

$$q_2 = x_2''/\mathrm{m} = k(C_2)^{1/a} \quad (2)$$

$$q_3 = x_3''/\mathrm{m} = k(C_3)^{1/a} \quad (3)$$

C_i = concentration in mg of hydrocarbons/litre of solvent measured in the solvent (volume V_i) extracted from the sediment at the equilibrium.

$C_1 = 792.3$ mg/l; $C_2 = 370.3$ mg/l; $C_3 = 154.8$ mg/l.

$x_1 = C_1 V_1 = 54.7$ mg; $x_2 = C_2 V_2 = 6.4$ mg; $x_3 = C_3 V_3 = 2.8$ mg.

x_1'' = quantity of hydrocarbons adsorbed at equilibrium on mass m of sediment.

m = 12,980 mg, calculated from $PS = (PH) \times \%(PS/PH) = 31.11 \times 41.73\% = 12.98$ g.

Table IV Extraction procedure for the evaluation of the accuracy of the method

Volume of solvent introduced before each extraction of sample *F* Dry weight = 13 g	Volume of total extraction solvent (V_0^i) and of residual solvent (V_i') Time of extraction	Volume of solvent extracted from sediment (V_i)	Concentration (C_i) of hydrocarbons in mg/l in the extract	Amount of hydrocarbons extracted in the volume V_i of solvent $x_i(\text{mg}) = C_i V_i$	Percentages of extracted hydrocarbons in each of the three extracted fractions $100(x_i/\Sigma x_i)\%$
80 ml CCl_4 2 ml HCl	1st extraction $V_0^1 = 80$ ml 3 hours $V_1' = 11$ ml	$V_1 = 69$ ml	$C_1 = 792.3$	$x_1 = 54.7$	85.5%
20 ml CCl_4	2nd extraction $V_0^2 = 31$ ml 1 hour $V_2' = 13.5$ ml	$V_2 = 17.5$ ml	$C_2 = 370.3$	$x_2 = 6.4$	10.1%
20 ml CCl_4	3rd extraction $V_0^3 = 33.5$ ml 1 hour $V_3' = 15.5$ ml	$V_3 = 18$ ml	$C_3 = 154.8$	$x_3 = 2.8$	4.4%

The mass balance sheet gives us 2 equations with 6 unknown quantities:

$$x''_1 + (C'_1 V'_1) = x_2 + x''_2 + (C'_2 V'_2) \qquad (4)$$

$$x''_2 + (C'_2 V'_2) = x_3 + x''_3 + (C'_3 V'_3) \qquad (5)$$

C'_i = concentration in mg of hydrocarbons/litre of solvent measurable in the solvent (volume v'_i) not extracted from the sediment.
$V'_1 = 11\,\text{ml}$; $V'_2 = 13.5\,\text{ml}$; $V'_3 = 15.5\,\text{ml}$.

This system of 5 equations with 8 unknown quantities (x''_1; x''_2; x''_3; C'_1; C'_2; C'_3; a; k) can only be solved by introducing hypotheses to simplify it. These hypotheses concern the concentration of hydrocarbons in the solvent not extracted from the sediment.

These concentrations may be estimated at the equilibrium as being in a range such as $0 \leqq C'_i \leqq C_i$. Indeed, we can suppose that the solvent CCl_4, being of polarity intermediate to that of aliphatic and aromatic hydrocarbons will cause a displacement phenomenon, and compete for the occupation of sediment adsorption sites ($C'_i = 0$) and, at the same time being capable of dissolving them, will desorb them and be found as an interstitial solvent ($C'_i = C_i$). As the boundary between these two phenomena is not very clear, both extreme hypotheses must be considered, while knowing that the real situation is intermediate between the two.

HYPOTHESIS 1 $C'_i = C_i$

$$C'_1 = C_1 = 792.3\,\text{mg/l};\; C'_2 = C_2 = 370.3\,\text{mg/l};$$

$$C'_3 = C_3 = 154.8\,\text{mg/l}$$

HYPOTHESIS 2 $C'_i = 0$

$$C'_1 = C'_2 = C'_3 = 0$$

The solution of the five-equation system can be written as follows:

$$x''_2 = x''_1 + C'_1 V'_1 - x_2 - C'_2 V'_2 \quad x''_1 = \text{km}\,(C_1)^{1/a}$$

$$x_3'' = x_2'' + C_2'V_2' - x_3 - C_3'V_3' \qquad x_1'' = \mathrm{km}\,(C_2)^{1/a} + x_2 + C_2'V_2' - C_1'V_1'$$

$$x_1'' = \mathrm{km}\,(C_3)^{1/a} + x_3 + C_3'V_3' - C_1'V_1' + x_2$$

$$x_2'' = \mathrm{km}\,(C_2)^{1/a}$$

$$x_3'' = \mathrm{km}\,(C_3)^{1/a}$$

$$k((C_1)^{1/a} - (C_2)^{1/a}) = \frac{x_2 + C_2'V_2' - C_1'V_1'}{m}$$

$$k((C_1)^{1/a} - (C_3)^{1/a}) = \frac{x_2 + x_3 + C_3'V_3' - C_1'V_1'}{m}$$

$$\frac{(C_1)^{1/a} - (C_2)^{1/a}}{(C_1)^{1/a} - (C_3)^{1/a}} = \frac{x_2 + C_2'V_2' - C_1'V_1'}{x_2 + x_3 + C_3'V_3' - C_1'V_1'} \quad I$$

A graphic solution of $Y = f(1/a)$ (Figure 7) gives the different values of:

$$\frac{(C_1)^{1/a} - (C_2)^{1/a}}{(C_1)^{1/a} - (C_3)^{1/a}}$$

for variations of $(1/a)$.

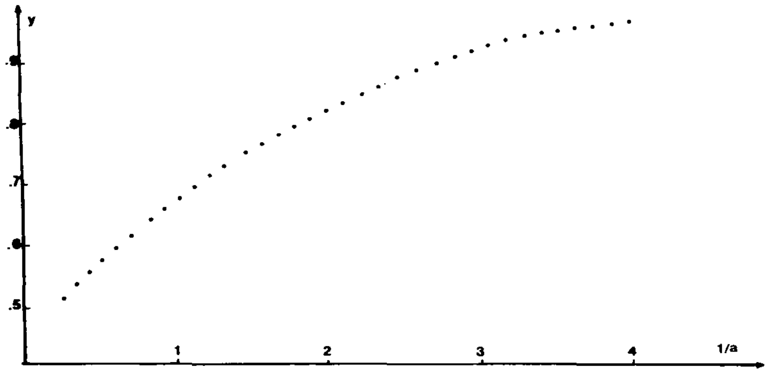

Figure 7 Graphical solution—$y = f(1/a)$

The right-hand side of the equation *I* gives values which vary according to the hypothesis chosen:

Case 1 $C'_1 = C_i$

$$\frac{x_2 + C'_2 V'_2 - C'_1 V'_1}{x_2 + x_3 + C'_3 V'_3 - C'_1 V'_1}$$

$$= \frac{6.4 + (370.3 \times 13.5 \cdot 10^{-3}) - (792.3 \times 11 \cdot 10^{-3})}{6.4 + 2.8 + (154.8 \times 15.5 \cdot 10^{-3})(792.3 \times 11 \cdot 10^{-3})} = 0.931$$

Curve $y = f(1/a)$ gives $1/a = 3.45$

Therefore

$$k = 2.22 \cdot 10^{-14} \quad x''_1 = 2.9\,\text{mg} \quad x''_2 = 0.2\,\text{mg} \quad x''_3 = 0\,\text{mg}$$

Case 2 $C'_i = 0$

$$\frac{x_2 + C'_2 V'_2 - C'_1 V'_1}{x_2 + x_3 + C'_3 V'_3 - C'_1 V'_1} = \frac{x_2}{x_2 + x_3} = 0.696$$

Curve $y = f(1/a)$ gives $1/a = 1.18$

Therefore

$$k = 3.16 \cdot 10^{-7} \quad x''_1 = 10.8\,\text{mg} \quad x''_2 = 4.4\,\text{mg} \quad x''_3 = 1.6\,\text{mg}$$

The results obtained make it possible to draw up a mass balance sheet (Table V) and give the shape of curves obtained (Figure 8).

This table shows that minimum massic efficiency (hypothesis $C'_i = C_i$) obtained is:

—82.5% after first extraction
—92.2% after second extraction
—96.4% after third extraction

The IR analysis method described previously and which consists in giving a result after the first extraction, taking into account the total volume of solvent used, gives a concentration of:

$$\frac{792.3 \times 80}{12.98} = 4883\,\text{ppm } (\mu\text{g hydrocarbons/g. of dry sediment})$$

Table V Mass balance sheet

Hypothesis	$C'_i = C_i$			$C'_i = 0$		
Quantities (mg) of hydrocarbons	In the solvent not extracted ($C'_iV'_i$)	Adsorbed on the sediment (x''_i)	Extracted (x_i)	In the solvent not extracted ($C'_iV'_i$)	Adsorbed on the sediment (x''_i)	Extracted (x_i)
1st extraction	8.7	2.9	54.7	0	10.8	54.7
2nd extraction	5.0	0.2	6.4	0	4.4	6.4
3rd extraction	2.4	0	2.8	0	1.6	2.8
Balance sheet		2.4	63.9		1.6	63.9

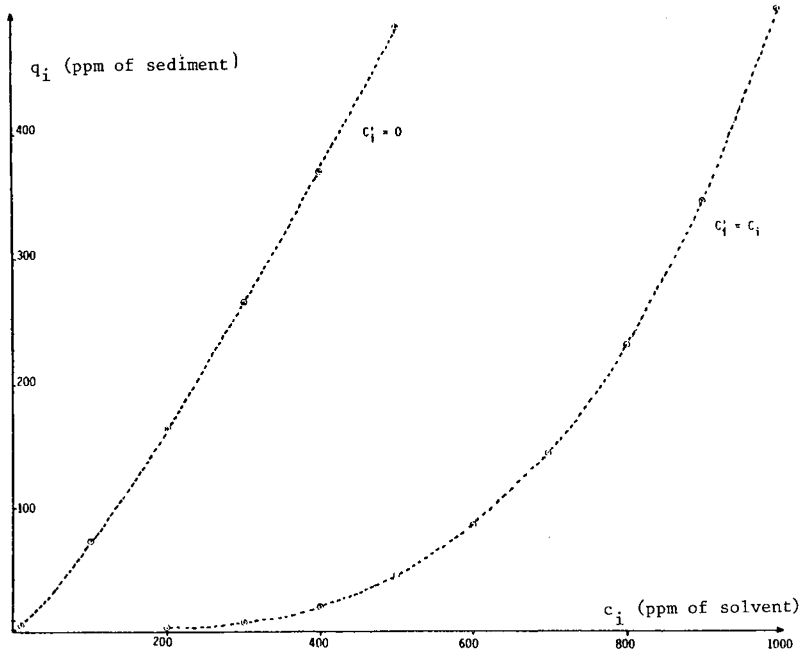

Figure 8 Freundlich isothersms—$q = kc^{1/a}$.
Curves show that for the same proportion of hydrocarbons not desorbed from sediment, it is necessary to use more solvent for high concentrations.

If the quantity of hydrocarbons not extracted after the third extraction is considered negligible, the mass balance sheet makes it possible to give the following result:

$$66.3/12.98 \cdot 10^{-3} = 5108\,\text{ppm (hypothesis } C'_i = C_i)$$

$$65.5/12.98 \cdot 10^{-3} = 5046\,\text{ppm (hypothesis } C'_i = 0)$$

The result which is obtained after the first extraction therefore corresponds to a minimum rounded-down estimation equal to:

$$\frac{4883}{5108} = 96\% \text{ of the “true” result.}$$

We consider this error as negligible (accuracy of the method shown in Table II = 94%) and see no point in correcting it.

For the purpose of a more efficient analysis of the sediment an analytical procedure would involve two extractions, the first using CCl_4 (or Freon), and the second methanol-CCl_4 (or methanol-Freon), assuming that the second extraction is as efficient as the first, an estimation based on Table VI would give a minimum massic efficiency of 92%. It would, therefore, again seem unnecessary to carry out a correction.

DISCUSSION

This analytical technique presents no general characteristics, and must be tested according to the molecules being studied. Moreover, the shapes of the adsorption isotherms may vary greatly with the chemical characteristics of the adsorbate and substrate. The parameters of Freundlich's equation are not transposable, and must be recalculated for each individual study.

Knowledge of the chemical characteristics of the adsorbate therefore takes on its full importance here. Molecules presenting high adsorption heat values can give rise to real superficial compounds, which poses the problem of the reversibility of chemisorption, or, at the very least, the non-degradation of such desorbed adsorbates. Thus some authors have shown the formation of artefact hydrocarbons from biogenic non-hydrocarbons: examples from elution chromatography are formation of phytadiene from phytol,[28] and isomerisation of olefins,[29] and by thermal desorption the formation of cyclo and iso-alkanes from alcohols.[30]

The chemical and granulometric characteristics of the substrate will determine the number of potentially active sites for hydrocarbon adsorption. It has been shown that bentonite adsorbs almost twice as much oil as kaolinite. In fact, in the *in situ* conditions of the estuarine zones studied, there would not appear in a first approximation to be any notable differences between adsorption capacities related to the chemical characteristics of the sediments as a whole. Their general characteristics in the existence of a more or less abundant fine fraction, which is sometimes predominant, and hardens the sediment when dry. They correspond to a percentage of fine clay and slit particles ($<50\,\mu$) of more than 30%. The clay fraction is essentially made up of kaolinite and illite coming from local periglaciary sediments eroded from the banks. These sediments which are generally poor in calcium carbonate, are rich in organic matter. This homogeneous property can also be found for matter in suspension within the estuary.

$(GC)^2$ measurements have shown similar hydrocarbon concentrations both upstream and downstream of the estuary.[31] This result stems from the fact that matter in suspension in the water of the Aber Benoît ria, a "homogeneous estuary" in Pritchard's classification,[32] is essentially re-suspended mud, and not matter drifted by the river, which has very low turbidity. The results are concordant with those reported by Dussauze,[33] who has shown that sediments coming from two different estuaries, those of the Aulne and Elorn rivers which are both in the Finistere region, have the same behaviour with regard to the adsorption of petroleum, similar to that of kaolinite. It can therefore be said that if the chemical characteristics of the substrate constitute the most important factor in determing adsorption in *in vitro* conditions, in *in situ* conditions the heterogeneity of the substrate at one point bestows on it a property tied to the hydrodynamic homogenization of the substrate within the estuary. The parameters of Freundlich's equation can therefore be calculated for an entire estuarine zone, and the differences in hydrocarbon concentration must be associated with granulometric differences tied to hydrodynamic conditions within the estuary.

We therefore believe it possible to say that there does not appear to be any discontinuity in the adsorption capacities of the various zones in a confined estuary site such as the one we have studied.

We have been able to show a correlation between the proportion of petroleum and the porosity of the sediment, which is a characteristic indicative of the percentage of volume of lattices existing in the sediment with regard to the total volume. As these lattices are *in situ* filled with water, an approximation of the degree of porosity can be obtained by determining the weight of water contained in a given quantity of sediment. In Figure 9, total hydrocarbon concentrations according to % porosity can be seen, (% porosity$=1-$% PS/PH). The ln(conc), by its derivative, indicates the variations in ratio d(conc)/(conc) according to porosity, in other words, the differences relative to average concentration calculated for a given degree of porosity. The upward slope of the curve (concavity towards low values), shows the more fluctuating behaviour of low porosity zones, i.e. of sediments for which the impregnation of petroleum was less homogenous.

It is interesting to note that the more organic matter a sediment contains, the more polluted it is (Figure 10). This is all the more surprising given that in an estuarine zone rich in organic matter, we expect the sediments which are churned up by tidal currents to have their surface saturated with organic matter, therefore blocking the hydrocarbon adsorption sites. Thus, the adsorption of hydrocarbons on/in the organic matter originally present must be considered. Moreover, the shape of the Freundlich isotherm obtained is indicative of multilayer adsorption and/or a condensation of hydrocarbons trapped in organic structures. (Figures 9 and 10).

The procedure considered in the aim of determining extraction efficiency may be open to criticism: indeed, it might be more realistic to carry out this operation on sediments which are identical (mineralogically, organically, structurally,...), but with different hydrocarbon concentrations. The obvious problem would be finding samples of such sediment. In that case, they absolutely must not undergo any previous treatment, whether thermal, mechanical, or chemical. Adsorption could therefore be determined as being mono or multilayer, according to the shape of isotherms obtained. Thus our knowledge, all work so far carried out on hydrocarbon adsorption dealt with treated mineral matter, without its original organic matter. Meyers and Quinn[22] studied hydrocarbon adsorption on sediment *in vitro* with heptadecanoic acid, and on sediment saturated *in vitro* with organic matter previously extracted from a marine sediment by methanolic saponification, and they obtained rather contradictory results which are interesting but not really convincing.

The extract used for "coating" a previously cleaned sediment in no case shows the same clotted structures of organic matter as those which are found as a result of bacterial modelling.

Under perfect experimental conditions, close study of a desorption curve such as those we have described would imply that hydrocarbons are not mainly adsorbed on mineral matter, because in that case, adsorption would be mono-layer, as has been demonstrated on many occasions, but are probably trapped in macromolecular clathrate-type structures.

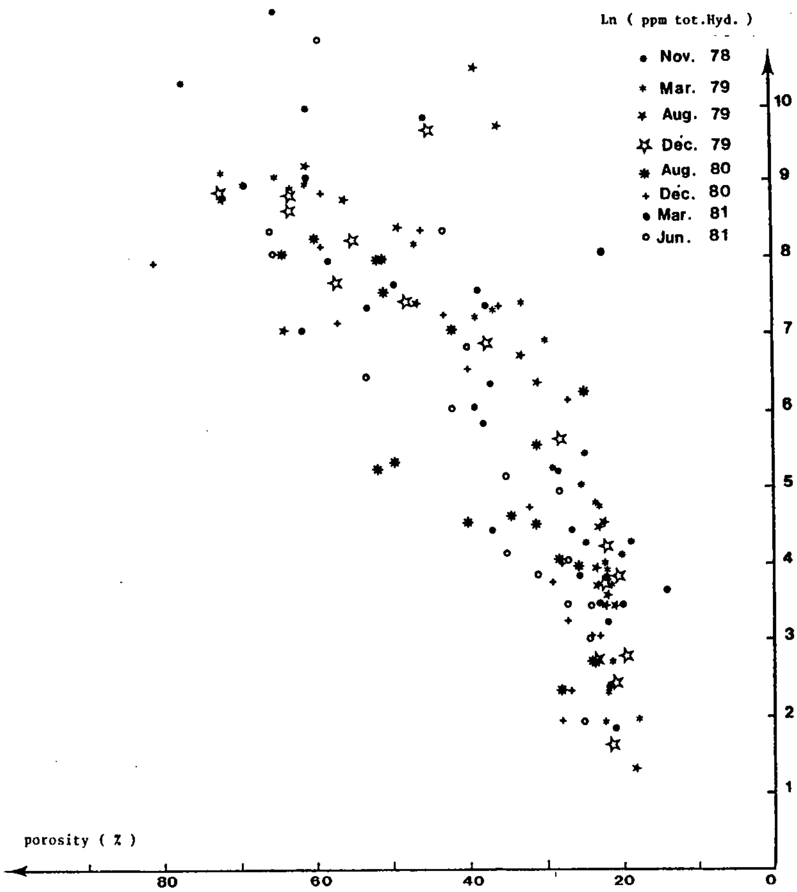

Figure 9 Correlation hydrocarbons—porosity.

CONCLUSION

The mechanical stirring extraction procedure we have studied has the analytical advantages of accuracy, precision and universality which means it can be used to analyse hydrocarbons in sediment. It is simple and fast to set up, involves a minimum manipulation of the sample, requires a bare minimum of precautions for use, and uses very small quantities of solvent—all these conditions being most

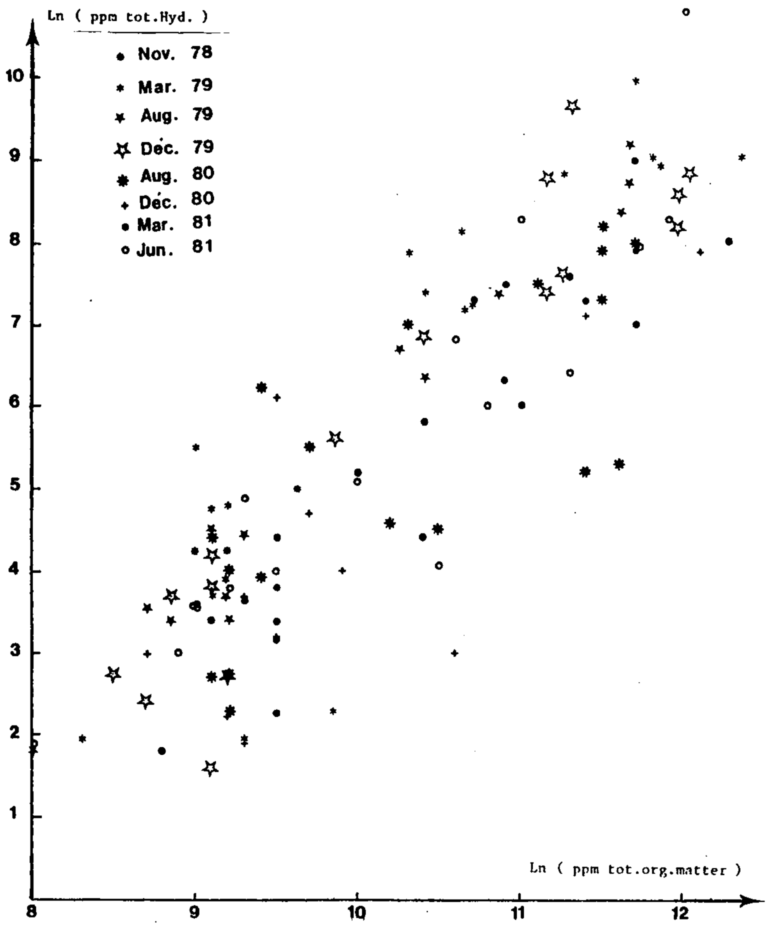

Figure 10 Correlation hydrocarbons—organic matter.

useful in trace analysis. Moreover, it makes it possible, as soon as samples have been taken, to treat any number of them simultaneously—thus precautions for conservation become unnecessary and work can be carried out *in situ* during oceanographic campaigns. Using this procedure, it is possible to bring the detectability threshold down to 1 ppm by IR, 10 ppb by HPLC, and 10 ppb by (GC).[2]

The working method we propose has the advantage of making it possible with one sample of reduced quantity (50 g), to determine the global hydrocarbon content using a non-destructive method of analysis such as infrared and HPLC, and to make a selective study of different hydrocarbons using a destructive method such as (GC).[2] This analytical procedure has made a study of hydrocarbon weathering in an estuarine zone possible on a large space-time scale.

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