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A Quality Assurance Study for the Analysis of Hydrocarbons in Sediments

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Dedicated to Professor W. Haerdi on the occasion of his 60th birthday

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Two exercises (MEDCAL I and II) were conducted in our Department during November 1984 and October 1986, with participants from the Mediterranean region, for testing the IOC Manual for the determination of petroleum hydrocarbons in sediments (IOC, Manuals and Guides, No. 11).

The gas chromatographic analysis of the saturated hydrocarbon fraction provided, at the best, a precision of 60% (relative standard deviation RSD) for *n*-alkanes (mean conc. 0.89 µg/g) and 56% for the unresolved complex mixture (UCM) (mean conc. 16 µg/g). The CPI and the pristane/phytane ratio provided better results (13% RSD). The aromatic fractions, analysed by UV-fluorescence, yielded in total a mean concentration of 10 µg/g of chrysene equivalents with a 49% RSD.

The extraction-partition step was confirmed to be the main source of error in the analysis because when the results were corrected for recoveries, the RSD were reduced to 17, 30 and 6% for *n*-alkanes, UCM and total aromatics, respectively. Our reference intra-laboratory precision was, respectively, 18, 14 and 14%.

KEY WORDS: Reference methods for hydrocarbon analysis, quality assurance analysis, hydrocarbons in sediments, hydrocarbon analysis, oil pollution monitoring.

INTRODUCTION

The large number of analyses performed in marine monitoring studies necessitates the existence of a common basis for comparing data both temporally (in long-term studies) and geographically (from different laboratories). The field of trace organic analysis and particularly of hydrocarbons and organochlorinated compounds—the organic pollutants of major concern in the marine environment—is highly demanding in terms of quality assurance studies, because of the complexity of the samples, with their associated matrix effects, and the lack of unique methods and reference materials for this kind of determination.¹

Then, the “correctness” of the analytical values obtained can only be established on a comparative basis through intercalibration exercises performed on field sample replicates and trying to identify the sources of disagreement by further studies.

The International Oceanographic Commission (IOC) as an organization collaborating with the United Nations Environment Programme (UNEP) in establishing a global programme for oil pollution monitoring (MARPOLMON-P), developed in 1982 a Manual for the determination of hydrocarbons in sediment² and encouraged laboratories of the Mediterranean region engaged in petroleum pollution monitoring to join an intercalibration exercise to discuss the method, verify their capabilities and thereby improve the credibility of the data being generated in the region.

Two exercises were organized during November 1984 and October 1986 in our Department with the participation of 10 and 11 scientists, respectively, from 7 and 9 countries. The participants were provided with an aliquot of a freeze-dried, sieved ($<250\ \mu\text{m}$) and thoroughly mixed sediment sample collected off Barcelona and were asked to perform the analysis of hydrocarbons according to the IOC, Manuals and Guides, No. 11.² The exercise, considered here as an inter-laboratory comparison, was carried out in parallel with another where the same samples were analyzed repeatedly by a well trained analyst, this being considered as an intra-laboratory evaluation. The overall results are reported in this paper.

MATERIALS AND METHODS

The analytical method basically encompasses the extraction of the

sediment (10–20 g) with a solution of 3 g of KOH in 100 ml of redistilled methanol by refluxing the mixture during 1.5 h and back extraction or partitioning into pentane. This procedure was modified taking into account the addition of 10 ml of distilled water after saponification and the centrifugation of the mixture for facilitating the separation between the organic and the aqueous phases.

The pentane extract was vacuum evaporated almost to dryness and resolved into saturated and aromatic fractions on a dry packed fully activated alumina mini-column (1.15 g; 10 cm × 5 mm i.d.), using the following sequence of solvents (4 ml each): pentane (saturates, *F1*) pentane (blank *F2*), pentane-dichloromethane (7:3) (lower aromatics, *F3*) and pure dichloromethane (higher aromatics, *F4*). The saturated fraction, dissolved in *iso*-octane, was analyzed by high resolution gas-chromatography (Carlo Erba 4160), using fused-silica columns (30 m × 0.25 mm i.d.; DB-5, J & W Scientific), temperature programmed from 60 to 300 °C at 6 °C min⁻¹. Injector and detector temperatures: 280 and 300 °C, respectively. Carrier gas: hydrogen (1 ml/min). The aromatic fractions were analyzed only by UV-fluorescence (Perkin Elmer MPF3) measuring the emission at 360 nm (excitation at 310 nm).

Quantitations by GC and UV-fluorescence were carried out respectively with reference solutions of *n*-C₁₄, *n*-C₂₂, *n*-C₃₂ and *n*-C₃₆ and of chrysene or topped Arabian light crude oil. An internal standard solution (*iso*-octane) containing perdeuterated *n*-C₂₄ and *n*-C₃₂ was initially added to the methanolic solution and used for recovery calculations

RESULTS AND DISCUSSION

The sediment samples used for the exercises were collected at the coast, off Barcelona (50 m water depth). They were adequate for intercomparing hydrocarbon analysis considering those usually handled by the laboratories engaged in coastal monitoring studies. The gas chromatograms shown in Figure 1 indicate a moderate degree of petroleum contamination evidenced by the occurrence of an unresolved complex mixture eluting as a “hump” over the baseline, together with specific molecular markers, namely hopanes and steranes. The cluster of peaks eluting in the C₁₆–C₁₉ range (LAB) correspond to the series of linear alkylbenzenes, and are indicative of contamination by domestic effluents.³

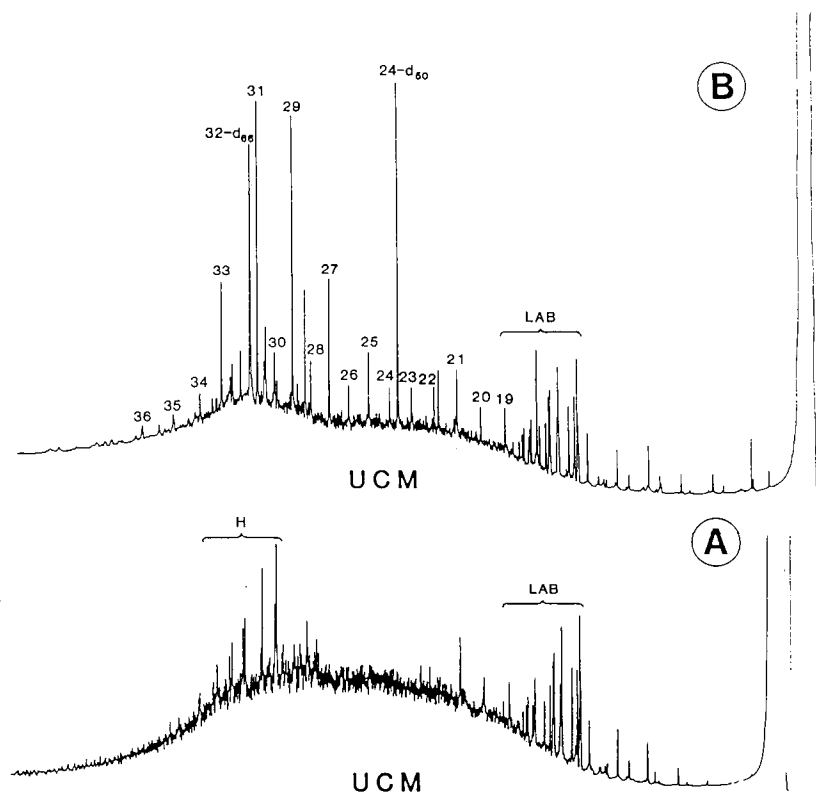


Figure 1 Gas chromatographic profiles corresponding to the aliphatic hydrocarbons analyzed in MEDCAL I (A) and II (B). UCM: unresolved complex mixture of aliphatic hydrocarbons; LAB: linear alkylbenzenes; H: hopanes.

As the sample used in MEDCAL I (Figure 1A) contained only minor quantities of *n*-alkanes we prepared another for MEDCAL II, in which these components should be easily measured. This was achieved by mixing the sediment used in MEDCAL I with 20% of another exhibiting the characteristic profile of terrestrial *n*-alkanes (higher plant waxes), that is, with an odd-to-even carbon number predominance in the C₂₅-C₃₃ range. The chromatogram of the resulting sample is shown in Figure 1B.

Although there is some controversy concerning the selection of the most suitable parameters for assessing petroleum contamination as

well as the methods for their determination, the unresolved complex mixture of alkanes (UCM) in the chromatogram of the saturated fraction and/or the UV-fluorescing aromatics are two main parameters regularly reported in petroleum pollution for monitoring studies.⁴ Individual components, like *n*-alkanes or isoprenoids (pristane and phytane) may also give an indication of petroleum contamination, particularly when it is fresh. However, the presence of coeluting or overlapping components in the chromatogram originated from other sources, namely biogenic, may induce to confusing conclusions, unless more sophisticated identification techniques, e.g. MS, are used. Bearing in mind that these techniques are not routinely applied in large survey studies, we entitled the participants to report, as a primary measurement of pollution, concentrations of unresolved hydrocarbons (UCM) and total aromatics in the corresponding fractions, respectively by GC and UV-fluorescence. Participants were also requested to determine in the chromatograms, *n*-alkane concentrations, *n*-alkane odd-even predominance (CPI) and pristane/phytane ratios whenever possible.

The results obtained are presented in Tables 1 and 2. As it can be observed, in both tables there are unreported values that correspond to situations where the analysts recognized significant losses during sample handling. There is also one case in MEDCAL I (E values in Table 1) where an external contamination of the extracts was realized. Out of these accidental cases two major trends are observed in the results of both exercises. First, the precision is generally better for the UV-fluorescence data (*F3* and *F4*) than for the gas chromatographic results. (*F1*). This may be explained by the major simplicity of the measurement together with the greater acquaintance of the analysts with the method. This UV-fluorescence analytical procedure was developed in 1978 for the IGOSS Pilot Project and since then has been routinely used for monitoring dissolved and dispersed hydrocarbons in the water column.⁵ Second, the precision improves slightly when the total aromatic hydrocarbons (*F3* + *F4*) are considered instead of the individual fractions (Tables 1 and 2), probably indicating that some dispersion is introduced in the chromatographic fractionation.

The results obtained during MEDCAL I provided for the first time a rough estimate of the precision that can be attained with the analytical method adopted by IOC for MARPOLMOL-P. However,

Table 1 Results of petroleum hydrocarbon analyses from MEDCAL I

	A	B	C	D	E	F	G	H	I	J	$\bar{X}(n=10)$	s°	$\bar{X}(n=9)^a$	s°
<i>F1</i> (aliphatic hydrocarbons)														
total <i>n</i> -alkanes ($\mu\text{g/g}$)	0.25	0.18	0.44	0.50	2.5	0.33	0.78	1.3	0.18	0.62	0.71	100	0.51	70
UCM ($\mu\text{g/g}$)	13	8.5	8.7	11	82	18	23	29	14	14	22	99	15.5	45
<i>F3</i> (eq. Arabian light; $\mu\text{g/g}$) monoaromatics	15	11	18	16	44	—	—	13	6.1	12	17 ^b	68	13 ^b	31
<i>F4</i> (eq. Arabian light; $\mu\text{g/g}$) polyaromatics	15	11	10	9.9	6.1	6	5	5	7	9.4	8.5	38	9.7	32
<i>F3 + F4</i>														
Total aromatics ($\mu\text{g/g}$)	29.5	22	29	26	50	—	—	18	13	22	26 ^b	42	23 ^b	26

*E not considered.

^bF and G are missing.

Table 2 Results of petroleum hydrocarbon analyses from MEDCAL II

MEDCAL II														CSIC lab.	
	A	B	C	D	E	F	G	H	I	J	K	$\bar{X}(n=11)$	s%	$\bar{X}(n=5)$	s%
<i>F1</i> (aliphatic hydrocarbons)	0.9	1.6	—	0.29	1.3	1.6	0.46	1.6	0.68	1.3	0.13	0.99 ^a	58	1.3	18
total <i>n</i> -alkanes ($\mu\text{g/g}$)	2.9	2.5	—	3.6	2.8	2.9	3.0	2.7	2.8	2.7	3.7	3.0 ^a	13	29	7
CPI	11.5	27	—	7.7	22	28.5	7.1	8.5	9.2	24	—	17 ^a	52	21	14
UCM ($\mu\text{g/g}$)	97	84	—	20	89	98	36	50	45	89	13	62 ^a	52	94	4
recovery % <i>n</i> -C ₂₄ (d)	91	92	—	23	93	100	40	38	47	94	12	63 ^a	54	96	3
recovery % <i>n</i> -C ₃₂ (d)	1.0	1.8	—	1.3	1.4	1.6	1.2	1.4	1.5	1.4	1.1	1.4 ^a	17	—	—
corrected <i>n</i> -alkanes	12	31	—	35	24	29	19	19	20	26.5	—	24 ^a	30	—	—
corrected UCM															
<i>F3</i> (chrysene units; $\mu\text{g/g}$)	9.9	11	3.3	3.7	8.9	8.4	3.3	4.2	8.1	9.3	0.7	6.4	53	9.9	16
monoaromatics	11	12.5	—	17	9.8	8.5	8.7	9.5	18	10	5.9	11 ^a	34	—	—
corrected monoaromatics															
<i>F4</i> (chrysene units; $\mu\text{g/g}$)	4.4	6.3	1.2	1.4	3.4	3.2	4.0	4.8	4.1	5.7	1.7	3.6	50	6.4	19
polyaromatics	4.7	7.2	—	6.5	3.7	3.2	11	11	9.0	6.2	7.8	7.0 ^a	39	—	—
corrected polyaromatics															
<i>F3 + F4</i> (chrysene units; $\mu\text{g/g}$)	14	17	4.4	5.1	12	12	7.3	9.0	12	15	1.7	10	49	16	14
Total aromatics	15	20	—	24	14	12	19	20	27	16	14	18 ^a	26	—	—
corrected total aromatics															

^aC results are missing.

a question may rise concerning the generalization of this estimate to other regions, where different analytical facilities and experience may exist. At this respect, other exercises have shown that this is not a relevant factor provided that the group of participants is large enough.⁶ Therefore, we may estimate that the results in this paper are of general application.

Taking into consideration the mean and standard deviation values after elimination of the outliers, according to the Anscombe's test,⁷ the level of precision was similar for both exercises, 45–52% RSD for the unresolved alkanes (UCM) and 26–34% for the total aromatics. The *n*-alkanes gave higher dispersion of values (70% RSD for MEDCAL I) which can be attributed to the low concentrations measured (0.5 $\mu\text{g/g}$), because when these were increased in MEDCAL II (1.2 $\mu\text{g/g}$) the RSD was reduced to 38%. However, surprisingly good precision was obtained for the CPI values, 5.6% RSD, although they were sometimes difficult to calculate due to the low concentrations of the components. On the other hand, both sets of data (MEDCAL I and II) show a fair agreement if we consider that the sediment added in a proportion of 20% to that used in MEDCAL I exhibited 4.1 $\mu\text{g/g}$ of *n*-alkanes and 26 $\mu\text{g/g}$ of UCM. Unfortunately, no comparison is possible for the aromatic fractions because of the different standards used (crude oil and chrysene eq.).

In order to investigate the sources of error in the determinations, we used in MEDCAL II internal standards for recovery calculations. As shown in Table 2 about 50% of the participants were able to obtain recoveries higher than 90%, two were in the 50% range and three obtained unacceptable recoveries. When the above reported results were corrected for such recovery estimations a significant improvement in precision was obtained, being now in the order of 20% of RSD in all cases (17% for *n*-alkanes and 28% for UCM). Assuming that the same recovery ratios correspond to the aromatic fractions, the corrected values for total aromatics also improve (from 34 to 26% RSD). However, the individual fractions show unreliable variations (decreasing for *F3* and increasing for *F4*), confirming the observations of MEDCAL I on the reproducibility of the column fractionation.

Apparently, the extraction-partition step is the main source of variability in the analyses. This is demonstrated by plotting the concentrations of UCM and total aromatics versus the recovery ratio (Figure 2). The points are distributed linearly (respective

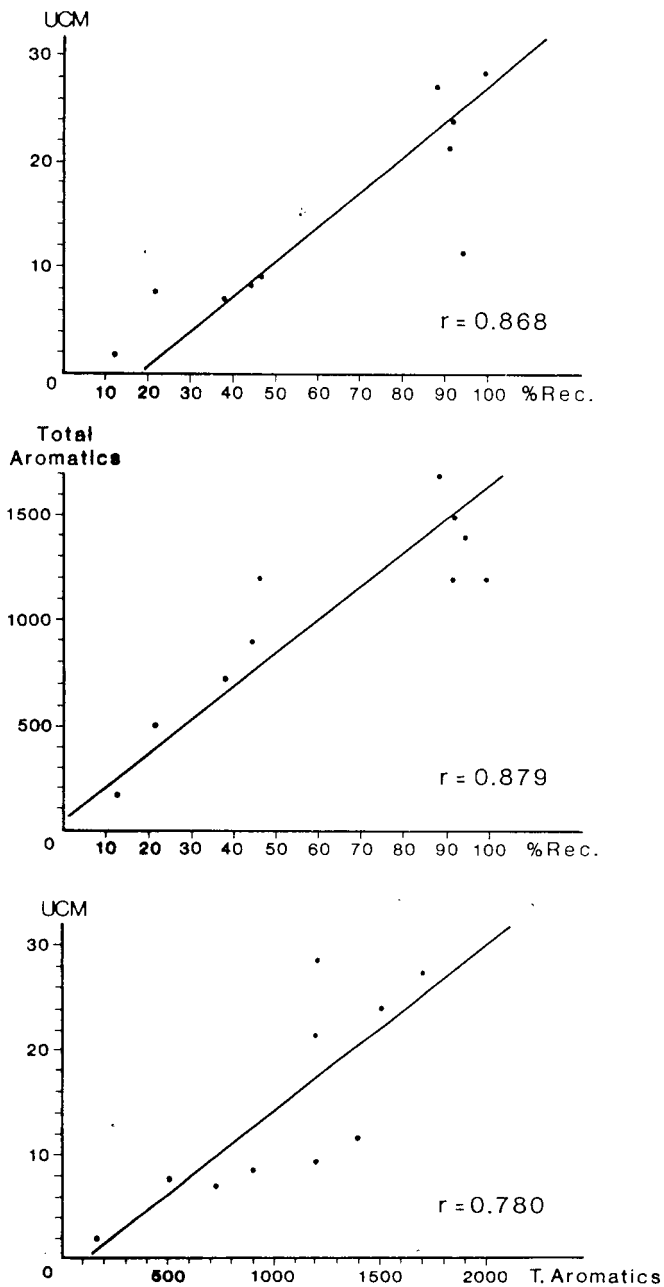


Figure 2 Linear regression between concentrations of UCM, total aromatics and recovery for the results of MEDCAL II (Table 2).

regression coefficients 0.87 and 0.88). This linear relationship is also maintained between the UCM and total aromatics (regression coefficient 0.78, Figure 2). Since no discrimination between losses of the original pollutants and the internal standards is expected during sample handling or instrumental analysis, these results indicate that the crucial step of the procedure is in fact the extraction.

The comparison of these results with other intercalibration tests described in the literature is difficult because most of them have been carried out without previous definition of the analytical methods, thus introducing greater variability. Comparison of analysis of alkanes in sediments among laboratories, each using its particular methodology, show a scattering of values between three orders of magnitude in the range of 1 $\mu\text{g/g}$.^{8,9}

However, differences are less when similar methods are used and concentrations are higher. Then, Ducreux and Bodennec,¹⁰ in an inter-laboratory comparison in which soxhlet extraction and IR or UV-fluorescence was respectively used for quantitation of hydrocarbons in the range of 300 $\mu\text{g/g}$, obtained 44 and 54% RSD, respectively.

Intra-laboratory precisions generally reached to 10–30% RSD for the different families of hydrocarbons using GC for quantitation.^{8,9} Gearing *et al.*,¹¹ reported relative standard errors of 16–24% for coastal sediments with hydrocarbons concentrations of 140 $\mu\text{g/g}$, also using GC. Scrupulous attention to sound analytical practices could enable inter-laboratory reproducibility to approach the intra-laboratory precision. In our case this has been situated between 14–18%, both for saturated and aromatic hydrocarbons.

An important consideration derived from these observations is the assessment of the real significance of the analytical results usually reported for sediments. In this sense, the *t* test for comparison of mean values of different populations allows an estimation of the level of differentiation between samples obtainable with the methodology intercalibrated here.

The test statistic has the form:¹²

$$t = \frac{\bar{X}_1 - \bar{X}_2}{s_p \cdot \sqrt{1/m_1 + 1/m_2}} \quad (1)$$

where X_i is the mean of population i
 m_i is the number of elements of population i
 and s_p is defined according to

$$s_p^2 = \frac{(m_1 - 1) \cdot s_1^2 + (m_2 - 1) \cdot s_2^2}{m_1 + m_2 - 2} \quad (2)$$

where s_i is the standard deviation of population i .

In our evaluation each population represents the replicated analyses performed on each sample. For simplicity it is assumed that they have been equally repeated in both samples ($m_1 = m_2 = m$). In addition, at this level of concentration, if the standard deviation is described as a function of the mean:

$$s_i = A \cdot X_i \quad (3)$$

where A is, respectively, 0.30 and 0.14, according to the inter- and intra-laboratory precisions reported above for the unresolved complex mixture of hydrocarbons (see Table 2).

Now, the test statistic (1) can be described as:

$$t = \frac{\sqrt{m} \cdot (1 - P)}{A \cdot \sqrt{1 + p^2}} \quad (4)$$

if $P = \bar{X}_2 / \bar{X}_1$, and this is compared with the Student's t distribution for testing the hypothesis of differentiation. Since the standard deviations are not estimated from the populations but calculated according to (3), the degrees of freedom are $2 \cdot m$. Ten percent has been selected as the level of significance ($\alpha = 5$).

The test can be used in order to calculate the minimal values of P necessary for observing a significant difference between the two means. In Table 3 several of these values are shown, they depend on the number of replicates per sample and the standard deviation of the analytical method. Thus, if four analyses are performed on each sample (a rather unrealistic situation) two samples will be differentiated for P values higher than 1.2 (intra-laboratory) and 1.5 (inter-laboratory). For duplicate analyses, the minimal ratios are respectively 1.35 and 2, that is more than 100% of difference

Table 3 Estimation of the minimal ratios between mean values of replicate analyses needed for the differentiation of sediments from their content in petroleum hydrocarbons (according to the Student's *t* test and the dispersions observed in MEDCAL exercises for the UCM)

	<i>Replicates per sample</i>			
	<i>1</i>	<i>2</i>	<i>4</i>	<i>6</i>
Precision:				
Intra-laboratory (14%)	1.87	1.36	1.21	1.16
Inter-laboratory (30%)	8.76	2.01	1.51	1.38

between means in the case of inter-laboratory comparison. When only one analysis is made on each sample (the most regular situation) the minimal values of *P* are 1.87 and 8.8 for, respectively, intra- and inter-laboratory comparisons (almost one order of magnitude in the latter case). The most important feature of this table is the strong difference in terms of statistical significance that is observed between single and duplicate analyses.

CONCLUSIONS

The results of the MEDCAL exercises indicate that the IOC method for determination of hydrocarbons in sediments² can be inter-calibrated, enabling large scale applications, e.g. in regional monitoring studies, provided that adequate sample collection and preparation as well as checking for recoveries throughout the analytical procedure are taken into account. Standard deviations in the range of 10–16% and 20–30% can probably be considered as the best that can be obtained, respectively, in intra and inter-laboratory comparisons. This is an important aspect to be examined for the assessment of spatial or temporal trends. As described in Table 3, the significance of the analytical differences depends on the number of replicates of each analysis, increasing importantly when passing from single to duplicate determinations. In any case, the implementation of an integrated data base for marine pollutants requires a continued effort for validation of data generated through monitoring programs.

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