



United Nations
Environment
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RESTRICTED

UNEP/WG.118/Inf.16
24 May 1985

Original: ENGLISH

Third Meeting of the Working Group for
Scientific and Technical Co-operation
for MED POL

Athens, 27-31 May 1985



Long-Term Programme for Pollution Monitoring and Research
in the Mediterranean Sea (MED POL - PHASE II)

REPORT ON THE IOC/UNEP/CSIC INTERCALIBRATION EXERCISE FOR OIL
AND PETROLEUM HYDROCARBONS

(Barcelona, 11-17 November 1984)

(document prepared by the International Oceanographic Commission)



INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS
UNITED NATIONS ENVIRONMENT PROGRAMME

Distribution restricted

IOC-CSIC-UNEP/MEDCAL-I/2
Paris, 20 May 1985
English only

IOC-CSIC-UNEP INTERCALIBRATION EXERCISE FOR OIL AND PETROLEUM HYDROCARBONS
Barcelona, 11-17 November 1984

DRAFT REPORT

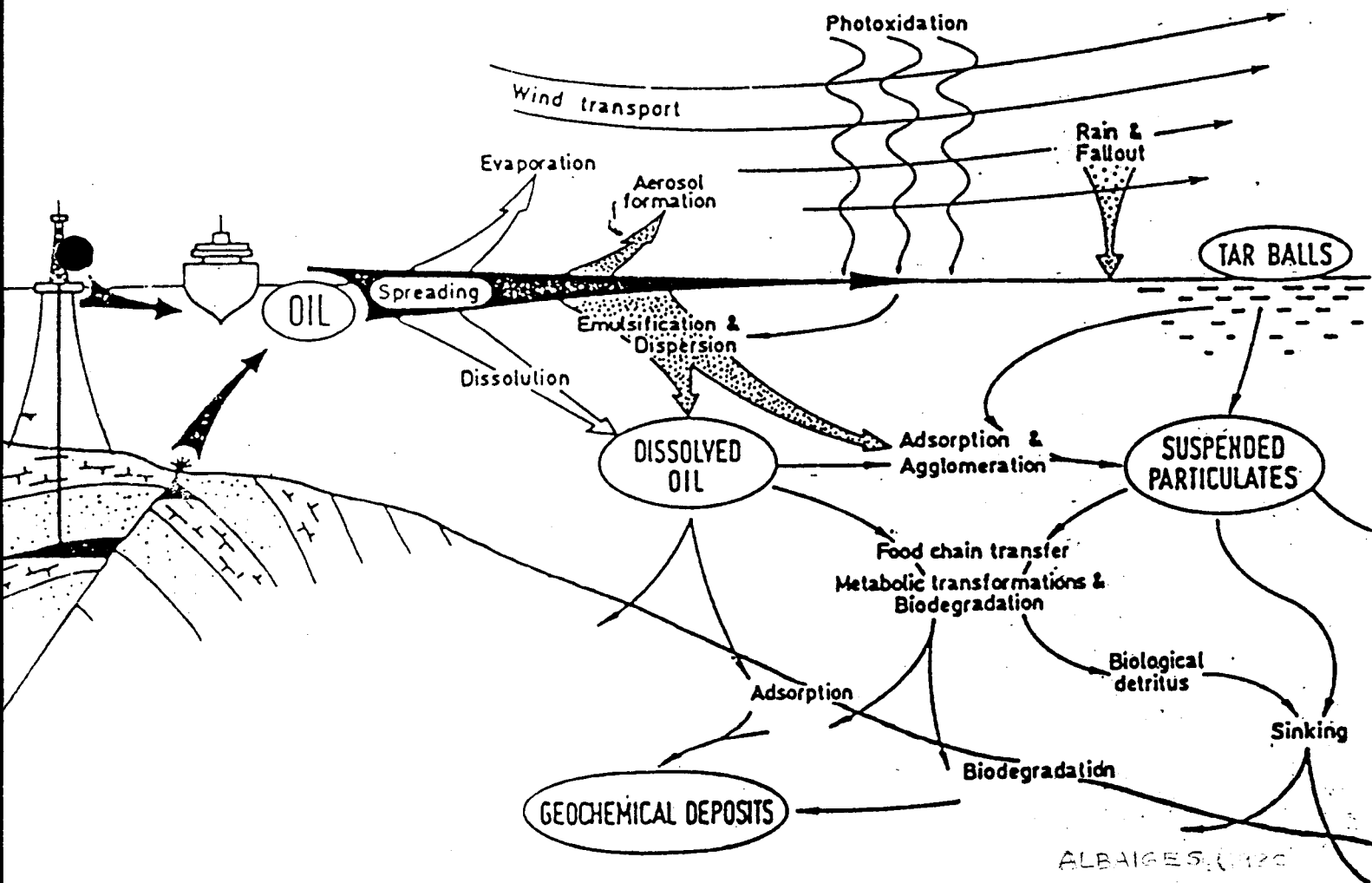


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1. INTRODUCTION

The IOC/CSIC/UNEP Intercalibration Exercise for Oil and Petroleum Hydrocarbons was held at the Instituto de Química Bio-Orgánica of the Consejo Superior de Investigaciones Científicas (C.S.I.C.), Barcelona, Spain, between 11 and 17 November 1984, following a recommendation by the Working Group for Scientific and Technical Co-operation for MEDPOL (Athens, 21-25 November 1983).

The Intergovernmental Oceanographic Commission (IOC) as an organization collaborating in MEDPOL-II, and as the co-ordinating Agency for MED-I, in line with its efforts to establish, in collaboration with the United Nations Environment Programme (UNEP), a global programme for oil pollution monitoring (MARPOLMON-P), undertook to organize this Intercalibration Exercise (MEDCAL). IOC gratefully accepted the offer of CSIC to host the exercise in connexion with the 3rd International Congress on Analytical Techniques in Environmental Chemistry, and the 2nd Workshop on the Chemistry and Analysis of Hydrocarbons in the Environment, organized jointly by the International Association of Environmental Analytical Chemistry (IAEAC) and the Catalan Society of Sciences (CSS) and EXPOQUIMIA, and sponsored by IOC and UNEP.

1.1 PARTICIPANTS

Participation was invited particularly from among participants in MEDPOL-II and participants in the ICES/IOC/MEDPOL Mussel Homogenate Intercalibration Exercise for Petroleum Hydrocarbons (Bermuda 1983). The MEDCAL was also announced by UNEP to the National Co-ordinators of MEDPOL-II, and by IOC at the Workshop on Marine Pollution of the Mediterranean, as well as at the Marine Chemistry Committee of the International Commission for the Scientific Exploration of the Mediterranean Sea (ICSEM) Congress, Lucerne, October 1984. It is therefore estimated that all, or most, of the scientists actively engaged in petroleum pollution monitoring in the Mediterranean region were contacted.

The participants in the experiments were from 9 countries. Two observers from the Kuwait Action Plan (KAP) region were accommodated as participants (see Annex III).

1.2 OBJECTIVES OF THE MEDCAL

The main objectives were to offer an opportunity to compare analysis by spectrofluorimetry and by GC for petroleum hydrocarbons in sediments during the exercise. In addition, demonstration of sampling and subsequent analysis for DDPH, as well as sampling of microlayer and beach tar sampling was to be organized. Subsequently, in each participant's home laboratory, analyses would be made by spectrofluorimetry and by GC whenever possible, using as references the samples of chrysene provided, topped crude oil and *n*-alkanes. If other methods (HPLC, or GC/MS) were operational, they were also to be employed as appropriate.

MEDCAL would also review the relevant reference methods, with a view to reporting any observations to the joint IOC/UNEP Group of Experts on Methods, Standards, Intercalibration (GEMSI) and, through the Inter-Agency Advisory Committee (IAAC), to the MEDPOL Working Group on Scientific and Technical Co-operation (WG/STC). Further, MEDCAL would make recommendations on any actions it considered necessary to promote the generating of more, and better, petroleum pollution monitoring data under MEDPOL. Whereas visual observations and collection of floating tar balls were not to be covered, demonstrations of gas chromatographic analysis of tar balls and of petroleum hydrocarbons in biological material would be used as a basis for discussion of those methods.

The timing of MEDCAL would allow an interface with the 2nd Workshop on the Chemistry and Analysis of Hydrocarbons in the Environment (19-20 November), expected to be of particular interest to participants through the opportunity if offered for exchange of information on the latest advances of analytical methodology and related research in this field.

1.3 ORGANIZATION

The Exercise was organized and co-ordinated by Dr. J. Albaigés, (Instituto de Química Bio-Orgánica, CSIC), and Dr. Leif Andren (IOC) acting as Technical Secretary.

To provide a theoretical framework for the Exercise, a series of lectures (see Annex VI) were given by some participants and by guest lecturers. In that context, ample time was set aside for related discussions. The laboratory work was organized, in principle, as one block of activities; participants were divided into eight groups with one laboratory assistant for every group, and with Dr. Grimalt as the overall co-ordinator.

2. LECTURES

A series of lectures were given by guest lecturers, and by some of the participants in the Group. These were intended to set a theoretical frame for the intercalibration exercise and the technical demonstrations, by describing the conceptual and strategic background for the monitoring of oil and petroleum hydrocarbons and by showing recent methodological developments. After each lecture, a brief discussion took place. Summaries of the lectures appear in Annex VI.

3. DEMONSTRATIONS OF SAMPLING TECHNIQUES

With a view to promoting uniform sampling techniques and demonstrating how sampling may introduce variance in results, approximately half a day was set aside for demonstration of sampling and related requirements and for related discussion of methods and equipment. These discussions led to a number of suggestions and recommendations, which are recorded in section 7 and Annex II of the present report.

3.1 MONITORING TAR ON BEACHES

A lecture on this subject was given by A. Golik (summary in Annex VI), who also demonstrated the technique for collection and measurement of beach tar and led a group discussion on the subject.

The demonstration was made on the beach in the vicinity of Barceloneta, on the basis of IOC Manuals and Guides No. 13 (M/G 13). Although very little material could be identified as tar, and much as debris, the demonstration clearly show the technique to be employed.

The related discussion gave rise to a number of observations and suggestions.

The group recognized the importance of determining residence time of tar balls on the beach as a clue to the assessment of tar pollution. It was suggested that research on the tar ball chemistry might be conducive to better evaluation of the residence time, although some of the participants expressed some scepticism in this regard.

Some participants felt that a clear definition of "beach width" is required. This definition is simple if the back of the beach is a cliff or a dune. However, where the beach is very wide, it was suggested that the landward border of the beach should be taken to be the line of the highest observed water level.

It was suggested that in any future tar monitoring activity a clear indication be given as to whether the monitoring is one of "tar standing stock" or of the rate of tar being washed up from the sea onto the beach. The group recommended the development of innovative methods for tar estimations, and especially the conducting of a feasibility study for estimating tar quantities, by means of low-altitude air photography or video recording, for example. One approach was described by the lecturer.

In this connexion it was also suggested that advantage be taken of the temperature difference between tar balls and sand, and that infra-red recording or photography be used as a means for determining tar quantity. Both the latter methods would require "ground truth" observations.

It was suggested that tar monitoring and studies on behaviour of tar should be co-ordinated with studies of drift card dispersal and research on current systems to determine the relationship between dispersion routes of oil from deballasting to its eventual deposition on beaches.

A suggestion was made to construct a tar trap to be deployed outside the surf zone in coastal waters. This trap would collect tar in the sea, thus providing an estimate for tar deposition rate. Field experiments must be conducted to construct and evaluate the functioning of such a trap.

It was also proposed to conduct a study on the degradation of tar balls in different regions. While V/Ni ratio and S content might provide an idea of the source of the tar, gas chromatography could give a clue to the age of the tar. If the ratio of "new" vs. "old" tar on a beach could be established, this could give some indication of the rate of tar deposition on the beach.

3.2 DEMONSTRATION OF WATER SAMPLING FOR SUBSEQUENT ANALYSIS FOR DDPH

Sampling of seawater for DDPH analysis was demonstrated in the Barcelona harbour using a weighted winchester bottle (Fig. 2) according to the design given in M/G-13. Samples were collected at 1 m depth and taken to the Institute for further analysis.

The procedure followed is described in M/G-13: n-hexane and CCl₄ were used for extraction of hydrocarbons. The utilisation of CCl₄ poses a health risk. But some participants felt that its greater density was a great advantage, especially during on-board sampling in rough sea. The addition of CCl₄ is relatively easy on a rolling ship, whereas adding n-hexane implies discarding approximately 50 cc of sea water and then adding the n-hexane. Sometimes this can be difficult without losses.

It was pointed out in this connexion that, during long passages from one station to another, DDPH sampling can be performed without costly extra stops if the research vessel is provided with a continuous water intake system arranged in such a way as to avoid contamination.

One participant suggested that if this cannot be realized, samples may be taken with a metal bucket sampler while the ship is cruising. Care should be taken not to throw the sampler too far away from the ship, because at a cruising speed of 10-15 knots this may result in the loss of the bucket. Shipboard contamination is a primary concern in this context and great care must be taken.

3.3 SAMPLING OF THE SEA SURFACE MICROLAYER

A demonstration of the technique for microlayer sampling took place in a water reservoir on the premises of CSIC. The sampler used had been manufactured on the basis of the description in IOC Manuals and Guides n° 15 (M/G-15). It had the corresponding size (80 x 60) and mesh size (15 wires/inch) Fig. 1. Its sampling efficiency was calculated as 0.4 mm.

It was noted that this sampler, by virtue of its simplicity, could be recommended for use in MEDPOL even though its sampling characteristics were not ideal. By comparison, the rotatory screen or a glass plate will sample 60 μ m, and the Bubble Interfacial Microlayer System (BIMS), approx. 5 μ m.

In this connexion, the value of collecting rainwater for analysis of atmospheric downfall, as ancillary data, was stressed, as such data could yield qualitative information on such input. At any rate, a sub-surface sample (1 m depth) should be taken whenever possible in conjunction with the microlayer sampling.

All participants who expressed a need for a microlayer sampler were provided with the recommended screen net to bring home after the Exercise.

4. ANALYTICAL WORK

The laboratory activities during the Exercise consisted of analytical work in connexion with the intercalibration of sediment analysis, analysis of dissolved/dispersed petroleum hydrocarbons in severely polluted sea water, a demonstration of analysis of petroleum hydrocarbons in weathered tar balls, and a demonstration of analysis of petroleum hydrocarbons in biological material (Figs. 3 and 4).

In connexion with the laboratory work and related discussions the question of need, choice and distribution of standards and reference materials was brought up several times. The Technical Secretary of IOC informed the participants about some on-going efforts in this regard and noted especially that GEMSI, at its forthcoming session, would seek solutions for provision of adequate standards, reference materials and uncompromised reference materials for international programmes dealing with, inter alia, petroleum hydrocarbon analysis.

It was agreed that efforts would have to be made to employ standard procedures in all MEDPOL laboratories. This implies not only using the same standard and reference materials but also giving great attention to details in the procedure for sampling and sample preparation.

The group was sub-divided into groups of two participants, with one laboratory assistant per group.

The great range of variability of the participants' experience necessitated considerable flexibility in planning.

4.1 ANALYSES OF SEDIMENT SAMPLES

Each laboratory group was provided with a freeze-dried sediment sample for analysis following the procedure given in Manuals and Guides No. 11. The saturated fraction was analyzed by gas chromatography and quantified using a reference mixture of C₁₄, C₂₂ and C₂₈ n-alkanes. The aromatic fractions were quantified only by UV-fluorescence owing to the lack of time, using standard solutions of a topped Arabian light crude oil.

The results are reported in Section 6.1 of the present report. The conclusions from related discussions are recorded in Sections 7 and 8.

4.2 ANALYSIS OF DISSOLVED/DISPERSED PETROLEUM HYDROCARBONS IN SEA WATER

Each laboratory group made an analysis for DDPH following the procedure given in Manuals and Guides No. 13.

The samples had been taken (see Section 3.2) from a polluted area, and it cannot be excluded that quenching occurred during the fluorometric measurement. Because of pressure of time, it was decided not to introduce an additional clean-up procedure but to evaluate the results in the light of this possibility.

The results of the exercise are reported in Section 6.2.

The related discussions are reflected in Sections 7 and 8 of the present report.

4.3 ANALYSIS OF BEACH TAR

An analysis of weathered tar lumps which had been collected on the beach was demonstrated.

The aim of this analysis was twofold: on the one hand, to evaluate the age or degree of weathering of tars and on the other to identify their possible origins. Based on the current experience at the Institute, a preliminary screening of the samples was carried out by gas chromatography, after deasphalting in n-pentane. The FID and FPD profiles were obtained simultaneously in a conveniently modified GC. A glass needle injector (Ros type) was used to reduce as much as possible the contamination of the glass liner.

Additional parameters for source identification are those corresponding to the elemental analysis (S, Ni, V, etc...). At this stage, the availability of the library with the characteristics of the crude oils or products carried in the area of study is very important.

Although the Group recognized the need to implement these methods according to the environmental policies of each country, it was considered premature to recommend such analysis on a more systematic scale within the framework of MEDPOL.

4.4 ANALYSIS OF PETROLEUM HYDROCARBONS IN BIOLOGICAL MATERIAL

The method description is given in Annex VIII. The Group expressed great interest in this method and in its wider use in the Mediterranean region and saw no objection to its inclusion in MEDPOL.

However, in view of the limited experience with this method among participants, it was felt necessary to arrange training in one form or another (group training or provision of individual fellowships).

The observers from the KAP region stated that it appeared to be of great interest to KAP to develop a Mussel Watch programme for that region, based on the same procedures as those considered for MEDPOL. This would require training but also a continued interchange of experience between the two regions.

5. INSTRUMENTAL ANALYSIS

The individual instrumental measurements were run on a UV spectrofluorometer (Perkin Elmer MPF3) and a high resolution gas chromatograph (Carlo Erba 4130). Quantitation and data analysis were carried out by micro computer (HP 86).

The participants' degree of experience with work on these instruments varied from good to none. The leader of the laboratory work therefore made provision for larger or smaller elements of training for this work, depending on individual needs.

The experience points to a great need for training in the MEDPOL region to allow for broad participation in any future intercalibration on petroleum hydrocarbon analysis. Thus, any intercalibration exercise should contain an essential training component.

Most participants were to a greater or lesser degree familiar with spectrofluorimetry. However, the great usefulness of GC for follow-up verification and for research on specific aspects was recognized. The more sophisticated and expensive GC-MS is out of reach for most participants.

Realizing its shortcomings, the participants nevertheless recommended the UV spectrofluorimetric method for use in any future MEDPOL programme for oil pollution monitoring. The possibility of using more performing instruments, thus permitting recording of synchronous excitation spectra, was emphasized.

With regard to selection of the most suitable instrumental method for analysis of petroleum hydrocarbons in water, one participant currently working with infra-red spectroscopy stressed this method's usefulness for quantification of high levels of oil pollution. However, it was recognized that comparison of such data with fluorescence data may pose a serious problem.

6. RESULTS OF THE INTERCALIBRATION EXERCISE

6.1 HYDROCARBONS IN SEDIMENTS

Aliquots of a freeze-dried sediment had been distributed among ten participants and analyzed accordingly (cf. 4.1). In order to improve the homogeneity of the sediment, it was first sieved through 250 μm .

The method was followed up with about 20 g of sediment, and 10 ml of distilled water were added before partitioning between methanol and hexane to facilitate phase separation. The results obtained in $\mu\text{g/g}$ dry sediment are summarized in tables 1 and 2.

6.2 DISSOLVED/DISPERSED HYDROCARBONS IN SEA WATER

Eight samples were collected using the sampling device described in M/G-13. As indicated in Section 3.2, the extraction was performed with *n*-hexane (four samples) and with CCl_4 (four samples), the latter added to bottle prior to sampling. The results obtained in $\mu\text{g/l}$ are indicated in Table 3.

TABLE 1 : FRACTION 1.- SATURATED HYDROCARBONS

Sample	g. sediment	Total n-alkanes	UCM ¹⁾	Pristane/Phytane
1	21.15	0.25	13	1.7
2	20.24	0.18	8.5	2.0
3	22.33	0.44	8.7	1.7
4	19.52	0.50	11	1.1
5	19.95	2.5	82	1.5
6	21.05	0.33	18	1.3
7	21.14	0.78	23	1.5
8	21.83	1.3	29.5	1.5
9	20.70	0.18	14	1.8
10	21.33	0.62	14	1.5
$\bar{X}(n=10)$	---	0.71	22.2	1.6
S(%)	---	100	99	16
$\bar{X}(n=9)$		0.51	15.5	
S(%)		70	45	

These values were calculated on the basis of a standard mixture containing C₁₄, C₂₂ and C₃₂ n-alkanes and with the help of a desk microcomputer. Representative chromatograms are shown in figures 5 (standard) and 6 (sample).

¹⁾UCM = UV-fluorescence screening method

TABLE 2 : FRACTIONS 3 AND 4.- AROMATIC HYDROCARBONS

Sample	Fraction 3 (in eq. Arabian light)	Fraction 4	Total A.HCs
1	14.6	14.9	29.5
2	10.7	11.1	21.8
3	18.4	10.4	28.8
4	16.1	9.9	26
5	44.1	6.1	50.2
6	--	6	--
7	--	5	--
8	13.25	5	18.2
9	6.1	7	13.1
10	12.3	9.4	21.7
$\bar{X}(n=8)$	17	8.5	26.16
S%	68	38	
$X(n=7)$	13		22.73
S%	31		

Owing to lack of time it was only possible to analyse these fractions by UV-fluorescence. Representative spectra are shown in figure 7. The results are expressed in μg eq. Arabian light crude oil./gr. of dry sediment.

The standard deviations were lower than for the saturated fraction, which is consistent with the easy manipulation of the samples for UV-fluorescence analysis. They can be considered as acceptable, bearing in mind the different degree of training of participants.

TABLE 3 : RESULTS OF SEA-WATER ANALYSES

Sample	eq. Arabian light	eq. chrysene
1	330	21
2	16	1.0
3	38	2.4
4	28	1.8
5	19	1.2
6	30	2.1
7	21	1.4
8	590	38
$\bar{X}(n=8)$	134	86
S(%)	160	160
$\bar{X}(n=6)$	25	1.65
S(%)	33	33

Samples 1-4 were extracted with CCl_4 and samples 5-8 with n-hexane. Apparently there is no major difference between the two methods. A standard deviation of 33% (excluding samples 1 and 8) can be considered as satisfactory, bearing in mind the site where the samples were collected.

It was commented among the participants that the ratio between crude oil-chrysene equivalents is usually 5-7, whereas in the present case it is higher than 10. This can be attributed to a lower degree of crude oil topping or to the nature of the oil itself, as the Arabian light is highly paraffinic.

7. AMENDMENTS OF IOC MANUALS AND GUIDES N° 11 AND 13

During the laboratory work and in connexion with lectures as well as during discussions of methods and results, a number of suggestions were made to improve or clarify the existing method descriptions. These suggestions are listed below. The related discussion benefited from the presence of two GEMSI members: Dr. K. Burns and Dr. J. Farrington.

7.1 DETERMINATION OF PETROLEUM HYDROCARBONS IN SEDIMENTS

The text of Manuals and Guides n° 11 should be amended as follows:

Page 5, Section 4 (Principle), line 1:

Should read: "After sampling of the sediment with a corer (to allow undisturbed sediments) or in coarse sediments, with a grab, or with the assistance of a diver....".

Pages 5-6, Section 5 (Reagents):

Generally the use of trade marks should be avoided. The solvents can be described as "fluorescence grade", "chromatography grade", etc... Trade marks to be used only in exceptional cases when it is considered absolutely essential, e.g. in the case of silica and alumina. Add also that "solid reagents must be washed before use".

Pages 7-8, Section 6 (Apparatus and equipment):

The above comments apply to this section as well. Trade marks should not be specified as advertisement should be avoided in a document of this nature.

Page 11, Section 7.3 (Sample collection and storage):

The use of grabs for sediment sampling should be avoided except when corers do not function well owing to the physical nature of the sediment.

Page 13 (Fig. 5):

The EPA-tag should be removed and replaced by another appropriate tag.

Page 13 (Section 8.1), line 3:

Replace "150 g" by "50 g" of wet sample.

Page 13 (Section 8.2), line 2:

Replace "100° C" by "105 C".

Page 14, para. 2, line 5:

Replace "5%" by "1%" (i.e., "dry until the difference between subsequent seighing is 1%").

Page 14 (Section 8.3), line 2:

Change weight of the sample to 50 g. The remaining part of this paragraph should be reconsidered by GEMSI especially with respect to the amount of internal standard needed.

Page 14 (Section 8.4), line 1:

If the methanol extract contains suspended material, centrifuging is recommended before transferring the sample to a separation funnel for extraction.

Note : Methanol and pentane are miscible unless some water is present. Please note also that any water used for addition has to be pre-extracted to avoid contamination.

7.2 DETERMINATION OF DISSOLVED/DISPERSED PETROLEUM HYDROCARBONS IN SEA-WATER

The following amendments are proposed for the IOC Manuals and Guides N° 13:

Page 1 (Section 1.1) (Sampling device and procedure)

After the second sentence, insert "it may be an advantage to use a sampler equipped with a device that allows the bottle to sink through the water surface closed, and to be opened at a desired depth, usually 1 m."

Page 2, first four lines: replace the text by the following:

- wash with detergent.
- subsequent wash with hydrochloric acid (three times).
- wash with distilled water (three times).
- wash with good quality acetone or methylene chloride (three times).
- wash with nanograde hexane (once).

Page 2, para. 4 (A second..... handling): GEMSI is invited to consider this working in the context of the proposed new text for page 1, section 1.1. Depending on the conclusion reached by GEMSI, it may amend the fourth line and the following text of the paragraph to read: "..... the ship. The bottle will sink closed; it should be lowered several metres below the sampling depth in order to eliminate possible contamination of the external wall of the bottle. Then, pull up the sampler to the desired depth, open it and let it fill. When back on deck, decant enough water to leave space for solvent addition."

Page 2, para. 5: Delete the two first sentences (upon retrieval... expansion volumes). In the following sentence, delete "if possible". What was stated with address to GEMSI in the paragraph above also applies here.

Page 9, (Section 2.8) Sample clean-up

Being aware of the risk of contamination of the sample during any clean-up procedure, the Group, mindful of the probability of interference from non-petroleum hydrocarbon substances in coastal waters and open ocean waters with high biological productivity, nevertheless recommends GEMSI to review the question of clean-up in the light of the latest experience in this field.

8. CONCLUSIONS

The Intercalibration Exercise gave rise to several important conclusions which should be borne in mind in connexion with the further efforts to develop a functioning regional programme for petroleum pollution monitoring as well as research efforts in this field.

Ideally, any intercalibration exercise consists of a gathering of experienced analysts who compare their individual methods and streamline the procedures to guarantee valid data on a regional basis.

The participants had a very varied background with regard to analytical experience. This made some detailed instruction or training in relation to the Exercise a necessary component of the activity, and such training was very well received because of the high motivation of the participants.

The results of the UVF analysis showed a reasonable range of variation, except for the two values that were clearly out of range. This was later established as being due to contamination during laboratory work. For the sediment analyses the picture was similar: two participants had used a non-prescribed solvent and obtained deviating results.

Generally, the more experienced participants obtained, not surprisingly, better (e.g. less contaminated) results.

The next intercalibration should be extended over a longer time (two weeks) to allow time for analyzing of a larger number of samples. This will enable participants to verify a larger number of aspects of petroleum analysis. Further, this will allow for a training element without loss of time for the intercalibration proper.

The procedure for quantification of GC-data with a microprocessor was outside the experience of all participants. It was therefore (with few exceptions) done by the laboratory work leader. Therefore, the intercalibration covered, strictly speaking, only the analytical work; the whole procedure from sampling to final data, would perhaps have yielded much greater variability if performed in the participants' home laboratories.

A major training effort will be required in the Mediterranean region to ensure that there is widespread participation in a petroleum monitoring programme.



Figure 1

Demonstration of microlayer sampler

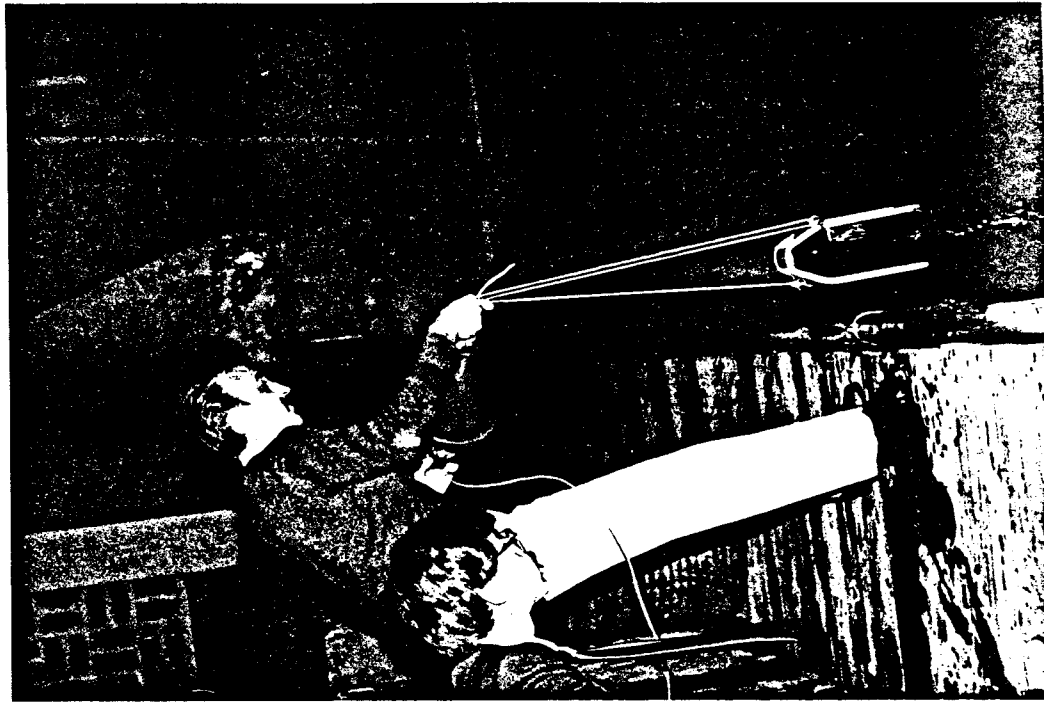


Figure 2

Demonstration of sampling of water for DDPH analysis



Figure 3

Director (right) of Exercise and laboratory assistants



Figure 4

Demonstration of computerized gaschromatography - mass spectrometry

Figure 5: Chromatogram of the n-alkane standard mixture

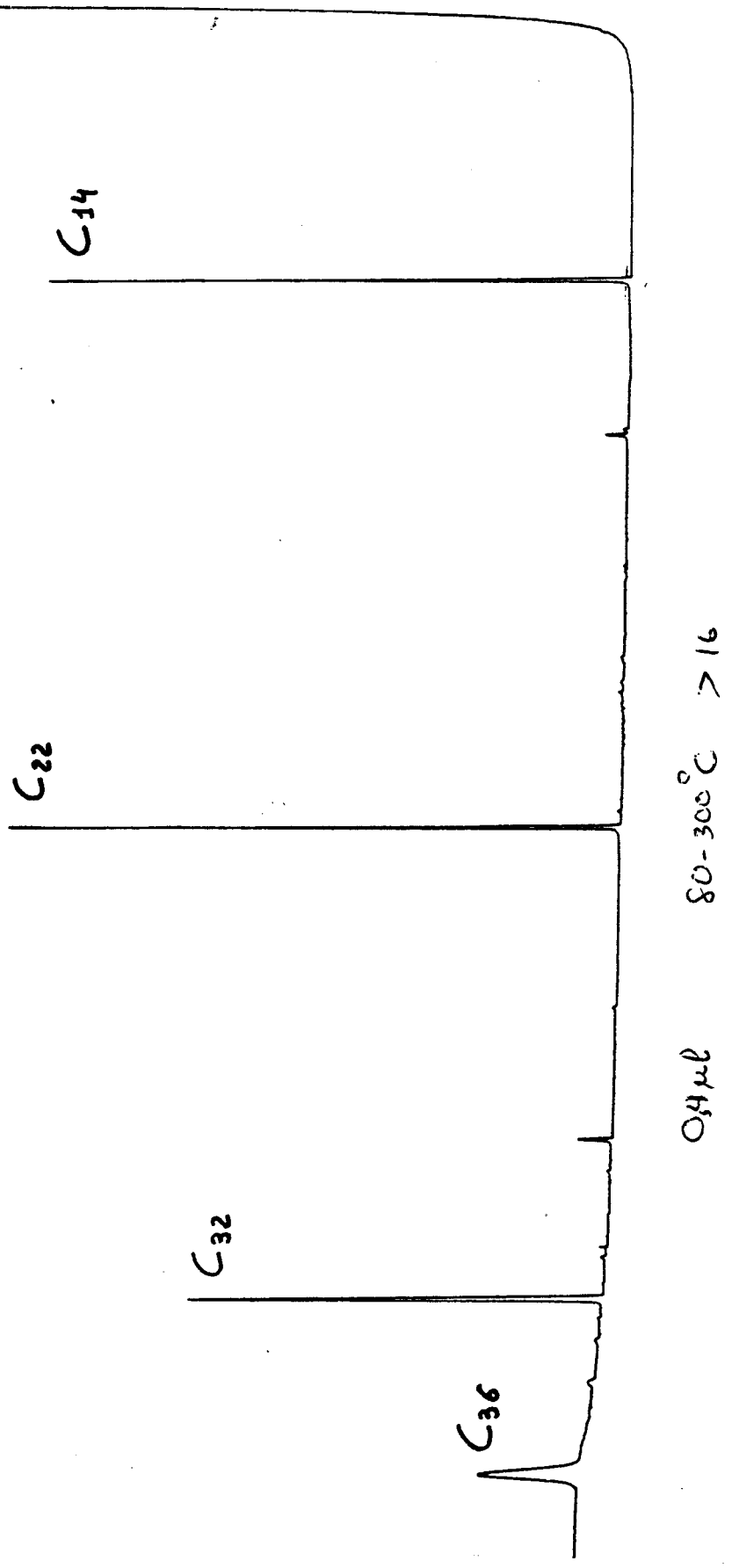
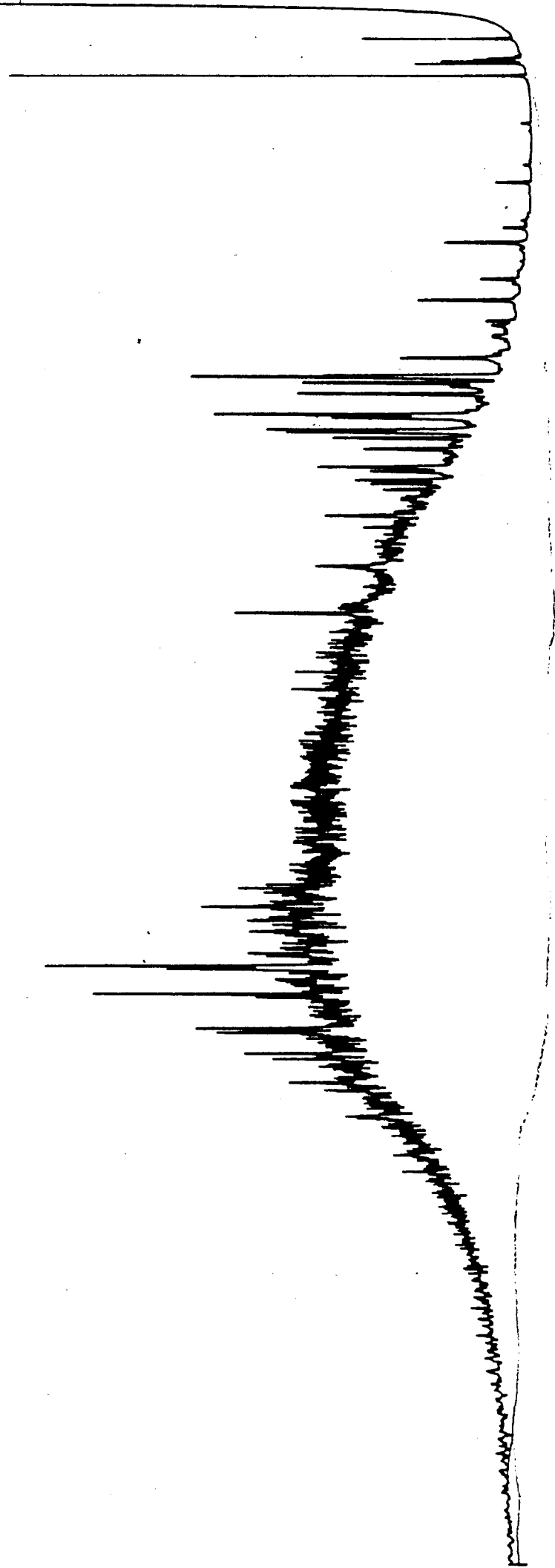


Figure 6: Chromatogram of a Sample



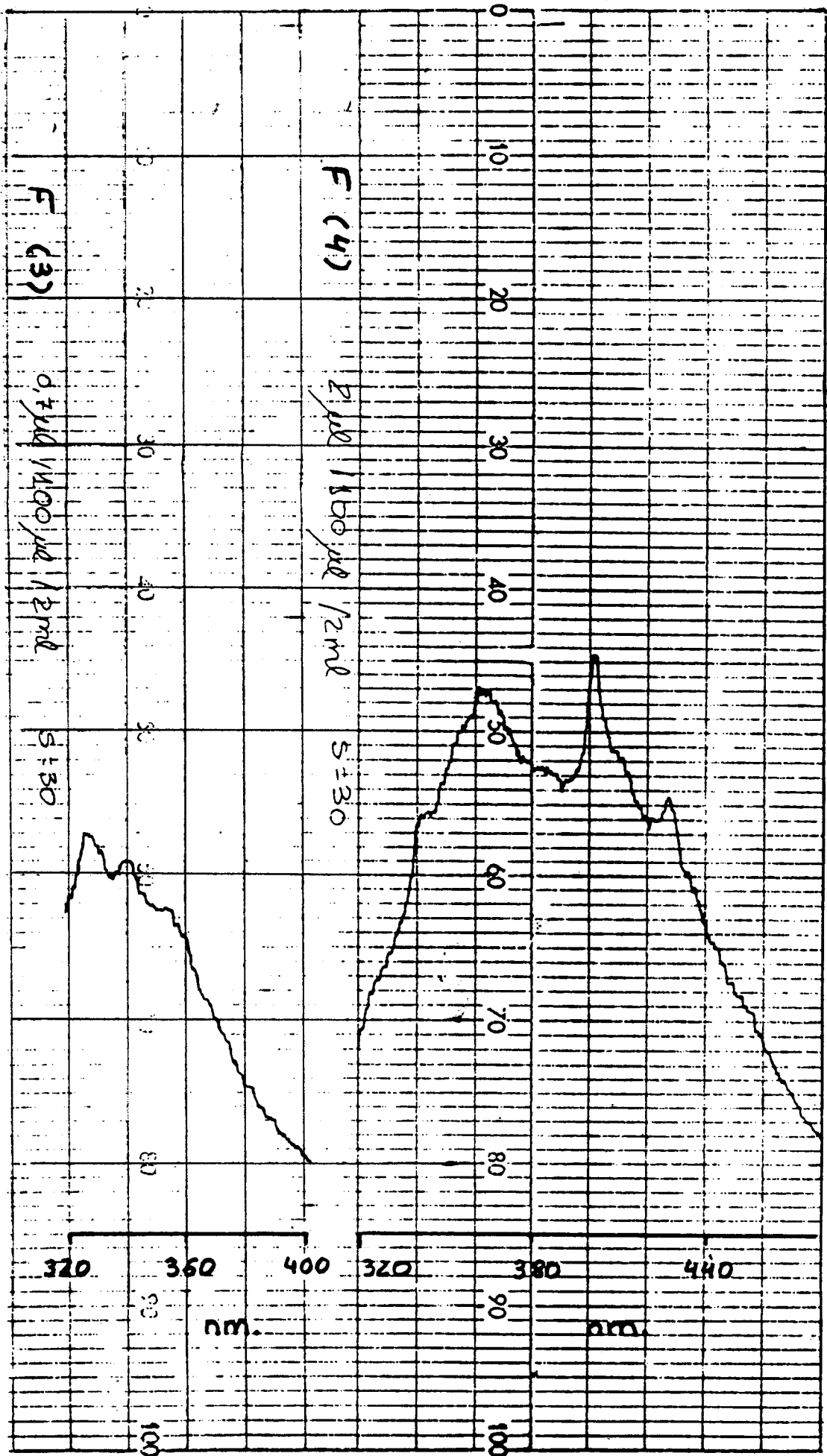


Figure 7: Uv-fluorescence spectra of Fractions 3 and 4

PROGRAMMESunday 11 November

Arrival: Gathering (at 20.30) at the reception of Hotel Residencia Monte Carlo, 124 Ramblas, Barcelona. Welcoming by organizers, general information.

Monday 12 November

Introduction: Demonstration of facilities at Instituto de Química Bio-Organica (of C.S.I.C.).

Lectures: International co-operation; objectives, strategy and approaches for petroleum pollution monitoring; equipment, sampling, storage and standard materials; recent developments in sample preparation and analysis, (see Annex VI).

Discussions of lectures.

Tuesday 13 November

Lectures: Monitoring of beach tar.

Field excursion: water sampling for subsequent DDPH-analysis; beach tar survey and sampling for analysis of weathered tar.

Visit at Instituto de Investigaciones Pesqueras with demonstration of facilities.

Discussion of sampling methods.

Wednesday 14 November

Analytical work: sample work-up; analysis of water and sediment samples measured with reference to chrysene and topped off crude oil, and to n-alkanes, respectively.

Discussion on interpretation of results and data reporting.

Thursday 15 November

Analytical work: continued: demonstration of, and individual analysis by UVF.

Discussion of result of analysis by UV-Spectrofluorimeter, and of report on beach tar sampling and an eventual revision of the prescribed method.

Friday 16 November

Lecture with associated discussion: Sampling in the dissolved and particulate phases of seawater.

Analytical work: Continuation of sediment analysis.

Demonstration of a) microlayer sampling, b) analysis of biological material and c) computerized gas chromatography-mass spectroscopy (GGC-MS)

Quantification of results from GC-analysis.

Discussion of results of analytical work. Drafting of report.

Saturday 17 November

Discussion of the results of the sediment analysis, drafting and approval of the recommendations of the Intercalibration Exercise.

Discussion of follow-up work distribution of samples for subsequent analysis in home laboratory.

ANNEX II

RECOMMENDATIONS

The participants in the IOC-CSIC-UNEP Intercalibration Exercise for Oil and Petroleum Hydrocarbons (Barcelona, 11- 17 November 1984) made the following recommendations :

1. Beach tar (3.1)*

Beach tar studies on a larger scale may yield valuable information on the fate and behaviour of tar and should be linked, wherever possible, with collection of floating tar balls and studies of current patterns. The IOC Manuals and Guides No. 13 provides useful guidance for the sampling of standing stock only; such data should if possible be complemented by input data obtained from qualitative studies of net input through tar-traps outside the surf-zone or large-scale beach cleaning prior to measurement. Chemical analysis of tar for age assessment is not considered an unambiguous and cost-effective approach at this stage.

2. Microlayer studies (3.3)

Recognizing the need to design a programme for microlayer studies in order to gain better understanding of its biogeochemical significance and to provide a basis for input estimates, it is recommended that MEDPOL provide support for and that IOC organize studies addressing, e.g. differences between day/night characteristics, geographically northerly/southerly positions, coastal vs. open ocean stations and seasons of high/low biological productivity. Attention should be paid to the length of the planned time series and need for ancillary environmental and biological productivity data.

3. Workshop on Mussel Watch Methods (4.4)

A Training Workshop on analysis of hydrocarbons in marine organisms should be arranged with a view to the establishment of a Mussel Watch programme for the Mediterranean. Participants should be senior active analysts and the host laboratory should have recognized experience in this field.

4. Reference materials (4.5)

IOC should give urgent attention to the need for supplying standards and reference materials to MEDPOL participants on a more regular or continuing basis.

It is recommended that at least 3 months before the next petroleum hydrocarbon intercalibration exercise, the following reference materials be sent out to participants in the present Exercise and to other Mediterranean scientists who declared an interest in participation: (1) chrysene, (2) set of n-alkanes, (3) topped off crude oil.

* this figure refers to the corresponding section of the Report.

It is further recommended that until such time as MEDPOL has decided on that matter and a continuing (regional or inter-regional) service for supply of standards for petroleum analysis has been established, the standards supplied should be as similar as possible to those provided under the IOC/UNEP/ICES Intercomparison Exercise (Bermuda 1983), and that recommendations for GEMSI should be followed in their preparation and handling.

5. Amendments to prescribed method descriptions (6)

It is recommended that the Secretary IOC bring the Amendments proposed in Section 6 of the report of the present meeting ("Amendments of IOC Manuals and Guides") to the attention of the IOC/UNEP Group of Experts on Methods, Standards and Intercalibration (GEMSI) at its next session (Woods Hole, 26-30 November 1984) for review and endorsement, and that the MEDPOL Working Group on Scientific and Technical Co-operation be informed of the proposed modifications.

With these modifications in mind, the MEDCAL group recommended the methods described in IOC Manuals and Guides No. 11 and No. 13 for use in MEDPOL. It also endorsed the use of the Draft IOC Manuals and Guides No. 15 in future programmes in the region.

6. Training and assistance

Aware of the great need for training in this field in most countries, it is recommended that an intensive training programme be established by IOC and UNEP with a view to training individuals or groups in all analytical methods employed during the Exercise. Provision of analytical instruments is essential to allow several countries to participate fully in any regional exercise.

7. Intercalibration

Further regional (or inter-regional) intercalibration exercises should be organized once per year. If possible, these should be hosted by CSIC in order to take advantage of the experience gained during the present exercise.

Initially these intercalibrations should allow for a degree of simultaneous training.

ANNEX III

IOC/UNEP/CSIC INTERCALIBRATION EXERCISE FOR OIL AND PETROLEUM HYDROCARBONS

Barcelona, 11-17 November 1984

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ANNEX IV

SUMMARY OF

Questionnaire on activities and interests related
to oil pollution monitoring and research

This questionnaire was designed to aid the organizers in the planning of the Exercise. The information obtained, although crude, gives an impression of the general needs and experience of the participants and their home laboratories.

1. My activity is mainly geared towards :

research monitoring administration other

2. My experience, concerns predominantly :

DDPH Oil in sediments Oil in biol. material Microlayer Beach tar

3. Analytical methods employed:

- (a) standards: chrysene (6), PAH (2), Not specified (1) { S. Louisiana (1)
n-alkanes (2), C₁₂-C₂₀ (1), crude oil { Egyptian (1)
Kuwait (2)
- (b) solvents: n-hexane (7), CCl₄ (7), methanol/benzene (1), n-pentane (1), methylene-chloride (1)
- (c) instrumental analysis: UV⁽³⁾ (10), GC (9), IR (2), GLC (1), HPLC (2), HLC (1), GC-MS (2)
- (d) equipment used: UVF (6), GC (3), HPLC (2), GC-MS (2), columns (1), Soxhlet (1)
Separation funnel (1)

4. Amount of work :

- (a) the work started in (year): 1970, 1974, 1977 (2), 1978, 1982, 1983 (2), 1984 (2)
- (b) number of samples of analysis per year: 700, >200, 150, 120, 10-100, 4,
not indicated (4)

- 2 -

6. I wish to participate in microlayer sampling
 I have access to have no access to a sampler
 I need a screen to manufacture a sampler
7. I need the following standards : Chrysene n-alkanes
 Topped-off crude
8. I do not wish } to participate in a follow-up intercomparison including
 I wish } analysis of standard samples in my own laboratory
9. I (my laboratory) have produced the following reports/scientific papers relevant to the subject matter :

(here, the information provided was very varying and often meager).

ANNEX V

LIST OF REFERENCE DOCUMENTS

- UNESCO (1984) Manual for monitoring oil and dissolved/dispersed petroleum hydrocarbons in marine waters and on beaches. IOC Manuals and Guides, No. 13.
- UNESCO (1982) The determination of petroleum hydrocarbons in sediments. IOC Manuals and Guides, No. 11.
- UNEP (1984) Report on the IOC/UNEP Mussel homogenate intercalibration exercise for petroleum hydrocarbons (Mediterranean Region). In collaboration with the International Council for the Exploration of the Sea (ICES) and the Bermuda Biological Station (In press).
- NAS (1980) The International Mussel Watch. Report of a Workshop sponsored by the Environmental Studies Board, the Commission on Natural Resources and National Research Council. Washington 1980.
- IOC (1984) Manual for microlayer sampling. IOC Manuals and Guides, No. 15 (in press).
- IOC (1984) Report of the IOC Symposium/Workshop on fate and fluxes of oil pollutants in the Kuwait Action Plan (KAP) Region, Basrah, Iraq, 8-12 Jan. 1984. IOC Workshop Reports Series (in press).

ANNEX VI

LECTURES

given at the Intercalibration Exercise, in order of presentation

- | | |
|---------------|---|
| J. Albaigés | The fate of hydrocarbons in the marine environment |
| R. Risebrough | Hydrocarbons in the water column: background and perspectives |
| J. Albaigés | Modern concepts in marine pollution monitoring with particular regard to petroleum pollution |
| J. Grimalt | Chromatographic methods for analysis of petroleum hydrocarbons in sediments and organisms |
| M. Picer | The use of spectroscopic techniques for determination of petroleum hydrocarbons in the marine environment |
| A. Golik | Tar pollution on beaches: processes, monitoring and new ideas |
| A. Saliot | Strategies for sampling and analysis of oil and petroleum hydrocarbons at the ocean surface interface |
| J. Albaigés | Initiation of a Mussel Watch activity in the Mediterranean region |

THE FATE OF PETROLEUM HYDROCARBONS IN THE MARINE ENVIRONMENT

(by J. Albaiges)

Fossil hydrocarbons released into the sea in bulk (oil spills) or within other effluents (urban and industrial wastes) are subjected to a series of diverse processes that cause distribution of the components into the environment and, at the same time, produce ageing (weathering), thus changing its physical and chemical characteristics. All these processes occur simultaneously and are interrelated. The changes are continuous and the reactions create a dynamic state with a great number of variables. Furthermore, the nature and extent of the changes that occur in hydrocarbons depend upon the particular set of physical, chemical and biological environmental conditions existing at the moment of the spill and the physical and chemical characteristics of the spill itself.

Despite the uniqueness of the fate of each spill, some general patterns can be drawn. Processes are of two types, dispersal and degradative. Dispersal systems do not remove the pollutants from the environment but only redistribute them into the various reservoirs, namely the atmosphere, sea surface, water column and sediments. However, during transport, hydrocarbons can be chemically fractionated according to their volatility, solubility and adsorptive properties.

Degradative processes are poorly understood, although they are mostly oxydative (chemical or biological) in nature. They also affect selectively the different chemical species.

A general presentation of these processes will be made with special attention to the ultimate fate of petroleum hydrocarbons in the marine environment as well as to the analytical criteria for the identification of their specific sources.

HYDROCARBONS IN THE WATER COLUMN: BACKGROUND AND PERSPECTIVES

(by R. Risebrough)

Except for a few areas where natural seeps introduce petroleum hydrocarbons into the marine environment, the presence of petroleum in seawater represents an alteration by man of the chemical composition of natural systems. Measurements of petroleum in seawater are therefore also a measure of man's impact upon the biogeochemical cycles of the oceans. Policy decisions that would reduce any impact are therefore dependent upon the accuracy of these measurements, including an ability to distinguish between petroleum hydrocarbons and the hydrocarbons and related compounds recently synthesized by organisms.

Reported concentrations of petroleum hydrocarbons in seawater may be :

- 1) too low because of low extraction efficiencies, or because of losses during sample workup;
- 2) too high because of : a) contamination, or b) contributions by other substances.

In selecting methodologies to be used within national and international communities for determining levels of petroleum compounds in seawater, a major consideration has been the availability of a common methodology in the different laboratories. Our immediate concern in this context is whether the UV fluorescence method is sufficiently accurate to justify its use.

The following assumptions yield an estimate in the order of 0.02 micrograms/liter (0.02 parts per billion) of total petroleum compounds to be expected in the top 100 meters of the open Mediterranean:

- 1) the yearly input from all sources is one million tons, one sixth of the estimated yearly input into all oceans;
- 2) the surface area of the Mediterranean is 2.5×10^6 square kilometers;
- 3) 90% of the input occurs in the nearshore areas;
- 4) the mean residence time in the top 100 meters, considering losses due to evaporation, degradation, deposition on shore, sinking to greater depths, etc. is two weeks.

Errors in these assumptions are highly unlikely to change this estimate by an order of magnitude. Values exceeding this level in offshore areas therefore most likely represent either contamination or a contribution by recently synthesized biological compounds. Almost all fluorescence measurements exceed this value.

To minimize the contribution by contaminants to the measured values, a number of laboratories are beginning to use solid adsorbants that permit the extraction of larger volumes of seawater. None of these techniques is as yet routine such that they can immediately be adopted by other laboratories without considerable experimentation.

Because of the difficulties in obtaining an accurate level of petroleum in seawater, many marine environmental chemists have adopted the concept of "indicator organism". Instead of seawater, an organism that accumulates petroleum compounds in its body lipids to levels many times higher than those in the ambient seawater is analysed. Because of their availability in many parts of the world, and because of their filter-feeding habits, bivalve molluscs, particularly mussels and oysters have been used to compare relative levels of petroleum contamination in coastal waters over both space and time. Many of the contamination problems encountered in the analysis of seawater are thereby avoided. Since the UV fluorescence measurements include contributions from aromatic compounds of pyrogenic origin in addition to those from petroleum, as well as an unknown contribution from natural compounds, a confirmatory method such as gas chromatography is also necessary.

It is evident that whatever method or methods are used should be thoroughly intercalibrated.

MODERN CONCEPTS IN MARINE POLLUTION MONITORING WITH PARTICULAR REGARD TO
PETROLEUM POLLUTION

(by J. Albaiges)

The ubiquitous occurrence of hydrocarbons in the marine environment is a problem we have been aware of for a long time. Therefore, much research has been undertaken during the last years for the development of analytical methods for the identification of the specific source of accidental or intentional oil spillages. From this standpoint two different situations may occur, macro (acute) and micropollution (chronic), which require different approaches and encompass different goals.

A general requirement to be met by analytical methods for petroleum pollution monitoring is to be able to deal with the whole spectrum of oil products as well as the naturally occurring hydrocarbons in the marine environment.

According to the previously discussed fate of hydrocarbons in the sea, the different marine compartments, namely water, sediments and organisms are of great significance for the assessment of the effects and sinks of these pollutants. The advantages and drawbacks of each one of these compartments will be exemplified.

Since it is impossible to select any particular technique as being suitable for the analysis of all compounds in all matrices, laboratories must continue to use the most appropriate techniques for their specific applications. However, steps should be taken to assure the quality of the data obtained. At this respect it is important to use standard reference materials and involve the laboratories in intercalibration exercises.

As the recognition of pollutant sources is concerned, recent advances of environmental analytical chemistry, particularly in the organic geochemistry of fossil fuels have led to the identification of series of hydrocarbons whose occurrence and distribution are related to the nature of the sources and the processes undergone throughout their biogeochemical cycles. These molecules, named "chemical markers", provide a good insight for marine pollution studies and illustrative examples have been shown.

Finally, it should be remembered that monitoring is not simply an exercise in data accumulation. Any monitoring programme needs to be designed to properly answer specific questions such as environmental effects, degradation processes, etc... Once the relevant questions are asked, decision on the sampling scales and analytical schemes to be used will become important. In addition, any monitoring programme should be coupled to concurrent research and should be flexible enough to be adjusted as new information becomes available.

CHROMATOGRAPHIC METHODS FOR ANALYSIS OF PETROLEUM HYDROCARBONS IN
SEDIMENTS AND ORGANISMS

(by J. Grimalt)

Petroleum hydrocarbons constitute very complex mixtures that require elaborated analytical protocols for their isolation from environmental matrices and high resolution techniques for their individual analysis.

The concurrence of hydrocarbons from biogenic sources in the marine environment stress the use of individual hydrocarbon analysis vs. total hydrocarbon measurements in marine pollution studies. In this respect, molecular criteria have been established for the differentiation between petrogenic and biogenic hydrocarbons in recent sediments and organisms. High resolution chromatography, both gas-liquid (GLC) and liquid-liquid (HPLC), provide multiparametric profiles, highly useful for hydrocarbon source identification. Pattern recognition techniques have been applied to improve the diagnostic performance of such profiles.

GLC using flame ionization detectors (FIDs) has long been one of the most widely utilized approaches to investigate a multitude of naturally occurring and petroleum hydrocarbons. Most early work depended primarily upon comparisons of n-alkane and isoprenoid distributions. The use of different types of detectors, particularly the flame photometric detector (FPD) that selectively detects sulfur-containing compounds, such as benzo and dibenzothiophenes affords complementary information. However, the most powerful tool for the exploitation of GLC profiles is the MS, applied in the selective ion monitoring mode, by using computerized GC-MS. In this way, COM-GC-MS allows multiple fingerprints from the same GC run, which is very convenient for a rapid recognition of any compound class. Of outstanding significance are the so called "geochemical markers" that reflect the geochemical history of petroleum hydrocarbons, thus enabling the univocal identification of such pollutants.

Recent analytical advances in HPLC have also enabled the use of this technique as a fingerprinting tool for petroleum hydrocarbons. HPLC offers the advantages of increased sensitivity and selectivity for aromatic hydrocarbons. The advantages are provided mainly by class-specific detectors as variable wavelength UV and fluorescence. The distributions of PAHs and their alkyl homologs are of diagnostic value for source identification.

Hydrocarbon distributions in sediments and organisms made evident with these chromatographic techniques reflect the different pathways (transport and degradation) of these compounds in the marine environment.

THE USE OF SPECTROSCOPIC TECHNIQUES FOR DETERMINATION OF PETROLEUM
HYDROCARBONS IN THE MARINE ENVIRONMENT

(by M. Picer)

Infrared spectroscopy, UV spectroscopy and UV spectro-fluorescence techniques for the determination of petroleum oils in the marine environment were described in many papers. The concentrations of petroleum hydrocarbons found in seawater by using the IR techniques were in the range from 1 ppb to more than 10 ppm. It has to be stressed that mere extraction and IR measuring of crude extracts give false concentrations of petroleum hydrocarbons in seawater samples because it is very probable that other extractable organic materials are also determined.

For the determination of petroleum hydrocarbons in seawater, the UV spectroscopic method is not as often described as the IR method. However, it seems that this method is also not sensitive and specific enough to be used for the estimation of petroleum hydrocarbons in seawater samples.

For the determination of petroleum hydrocarbons in the marine environment, the application of UV fluorescence techniques alone or in combination with TLC and/or HPLC is very popular. It has to be stressed, though, that by using the fluorescence techniques it is not possible to differentiate fluorescent hydrocarbons with respect to their sources (petroleum hydrocarbons, heating or energy production, coke production, etc.).

Using the fluorescence method it was observed that calibration curves obtained after the addition of the known amounts of crude oil into solvent extracts of the mussel and the sediment showed a significant decrease in the fluorescence of the oil added due to the quenching effect. It is possible to evaluate and accordingly correct the observed quenching by using the standard addition method.

The values of the quenching obtained are presented as the correction factor and should be used for correction of the measured fluorescence so that more real data of petroleum concentrations in marine samples are obtained.

The problem of the recovery of spiked wet or freeze-dried sediments and mussel samples with crude oil has also been described. Using identical extraction procedures it was found that the mode of spiking and the physical condition of sediments and biota samples have a great influence on the recovery of added crude oil fluorescence materials.

TAR POLLUTION ON THE BEACHES, PROCESSES, MONITORING AND NEW IDEAS

(by A. Golik)

The floating particulate petroleum residues that appear in different shapes commonly called "tar balls", "tar lumps" or "chocolate mousse" are transported by winds and currents and eventually reach a shore. Upon reaching a beach sand grains are attached to the balls which increases the specific gravity of the tar lumps as a whole. It therefore sinks to the seabed from where, owing to hydrodynamical conditions there is usually a net inflow of tar towards the beach.

The balls settle on the wash marks of the waves on the beach. With any advance of the waterline towards the back of the beach due to tide or storm, the waves will distribute the tar on the beach in lines oriented parallel to the shoreline. Each line is a remnant of a previous stand of water level.

Several processes are responsible for tar removal from the beach but not all of them are well studied. One of these processes is the wind-generated waves which cause a long-short transport of tar balls until they reach an area of wide beach, such as in an estuary. There, the higher waves are capable of transporting the tar quite far inland, but because the water percolates into the sand the tar does not return to the sea.

Over a period of months, the tar balls develop a hard skin which then gradually breaks into small (1-3mm) particles which can be blown away by the wind. This is a very slow process.

When monitoring tar on the beach, care should be taken not to confuse the standing stock of tar with the rate of net tar input to the beach. The standing stock of tar is the quantity of tar found at any point of time on the beach. Such data can be used for comparison of tar pollution on two comparable beaches, or on the same beach at different periods. It is also relevant for the planning of beach cleaning operations. Knowledge of the net rate of tar input from the sea to the beach is needed to calculate the tar balance. Measurement of the standing stock of tar should follow the procedure outlined in the IOC Manuals and Guides N° 13. The results should be given in grams per meter beach front and also in g/m divided by the length of transect (from the waterline towards the back of the beach) to yield a value of g/m². If measurement of the standing stock of tar is made during a long period of time at short time intervals, care should be taken to select a new strip each time to avoid underestimation of the amount of tar.

Monitoring of net tar input is rendered more uncertain because tar balls are moved along the beach and re-deposited by waves. Repeated sampling of a strip of beach will therefore yield tar deposited directly from the sea as well as tar coming from neighbouring beaches. Therefore, to obtain an expression for net input, a large (hundreds of meters) section of the beach must first be cleaned after which daily sampling of one meter beach face sections is made. In this case, the same section should be re-sampled every time and the results will be expressed in units of g/m/day.

Since measurements of tar is laborious and time consuming, ideas for new methods have been attempted. Under ideal conditions, photography of the beach from a plane at low altitude clearly shows the streaks of tar deposited on the beach. If photographed with TV camera and recorded on video cassette, the information of a picture can be put into digital form. The digitizing is done by computer where each dot on the TV screen is given a value proportional to the saturation of the black colour in that dot. With the additional use of ground truth data, the obtained values may be converted into crude estimates of the actual quantity of tar. Infr-red sensors may more easily distinguish tar from sand because of their different thermal properties.

STRATEGIES FOR SAMPLING AND ANALYSIS OF OIL AND PETROLEUM
HYDROCARBONS AT THE OCEAN SURFACE INTERFACE

(by A. Saliot)

Intense exchanges of organic pollutants occur at the ocean-atmosphere interface, leading to important transformations of various inputs of hydrocarbons introduced in the surficial ocean, such as biogenic production, wet and dry deposition from the atmosphere, river runoff, ship traffic and coastal industrial activities. Among complex physico-chemical processes, these exchanges are conditioned by the chemistry of the sea surface microlayer.

For evaluating the hydrocarbon pollution and the associated exchange processes at the ocean-atmosphere interface, it is recommended to sample, respecting ultra-clean conditions, simultaneously all reservoirs involved in exchange processes: atmosphere for gaseous and particulate phases and surficial waters with a special attention to the surface microlayer, and separating dissolved and particulate material. For surficial waters or rains, it will be useful to know general hydrological and meteorological conditions, and specific data on nutrients, primary productivity, bacterial populations (structure and metabolism), dissolved and particulate carbon and more specific organic species such as proteins, lipoproteins, surfactants, fatty acids, complex organic matter. A good utilization of data on atmosphere for both gases and aerosols necessitates the knowledge of air masses trajectories and analyses of sodium (as a marine reference term), aluminium (as a continental reference term) and the precedingly described organic matter parameters.

Most information on surface microlayer chemistry has been obtained from two types of sample collection: solid surfaces such as glass plates, germanium prisms, rotating drum and screens. Commonly, metallic screens are inserted vertically below the surface and then lifted horizontally through the interface, collecting a microlayer of 150-400 um thickness, according to the wire diameter.

Gaseous compounds in the atmosphere are commonly samples using adsorptive and cryogenic entrainment. Sampling tubes containing a porous material such as Tenax GC, XAD 2 resin, polyurethane foam are placed in-line behind an appropriate glass fibre filter series mounted in a cascade impactor for collection of the aerosols. Appropriate analysis of hydrocarbon using both global methods on a large scale and, for selected samples, fine methods belonging to the modern tools of environmental chemistry, will lead to an inventory of hydrocarbons, distinguishing between natural and anthropogenic compounds and finally to a budget of exchange processes using models of evaporation, formation of aerosols through bursting bubbles, dry and wet deposition from the atmosphere.

We propose the following recommendations:

- Define a good sampling strategy: choice of the area, location of stations, time and frequency of sampling. Collect historical data on meteorological and hydrological observations, hydrocarbons and other chemical pollutant analyses obtained during preceding cruises; organize the sampling in a multi-disciplinary context, it would be appreciated to have on board both physicists, chemists and microbiologists.

- The collection of microlayer, subsurface water and surficial water, and atmosphere should be realised simultaneously, taking all precautions against contamination (for example: collection of the microlayer from a small boat discarded upwind from the main ship, with a screen, which should be rinsed by pure organic solvent just before use, collection of the air from a platform unit located several metres forward of the ship-bow with an electric contact between the pumps and a wind direction and speed monitor.
- Realize a first screening for hydrocarbon pollution, using I.R. spectrophotometry, uv spectrofluorimetry on a large number of samples in order to evaluate the sites where more complete analysis should be made. On these samples, use the HPLC, GC, GC/MS, spectrofluorimetric techniques for applying the geochemical marker approach for distinguishing between various sources.
- Determine from the markers inventory specific compounds which indicate sources, i.e. marine (n-C15, n-C17, pristane), natural terrestrial as from the higher plant waxes (n-C27, n-C29, n-C31), petroleum compounds (unresolved branched and cyclic compounds, sulfur compounds, low molecular weight n-alkanes), pyrolytic-like products (alkylated homologues of parent polycyclic aromatic hydrocarbons).
- Filtration should be realized immediately on board for surficial waters to avoid the risks of adsorption of film material on the walls of the sampling bottle. Both dissolved (passing through a 0.7-1 um glass fibre filter) and particulate hydrocarbons should be analyzed as their nature and pathway differ.

INITIATION OF A MUSSEL WATCH ACTIVITY IN THE MEDITERRANEAN REGION

(by J. Albaigés)

The increasing pollution of coastal areas by anthropogenic substances has led to the search for an effective monitoring program that has the capability of identifying "hot spots", detecting spatial and temporal trends and assessing effects of pollutants on biological systems.

Random measurements of specific contaminants in arbitrarily selected field samples do not address issues such as those mentioned. Randomly accumulated data cannot often be applied to answer questions.

The analysis of sediments and water samples can be of great value in a monitoring programme for coastal areas but the experience has shown in the validity of the sentinel organisms concept and that valuable environmental data can be obtained from a monitoring programme that incorporates bivalves. Several workers have discussed the attributes of bivalves as sentinel organisms that can be summarized as follows:

1. They are cosmopolitan and sedentary, thus being representative of the study area.
2. They are abundant, easy to sample and give adequate tissue for analysis.
3. They tolerate a wide range of environmental conditions without being killed.
4. They are of commercial value so that work with them has immediate economic and sanitary value.
5. Background data on uptake and release kinetics, growth rates, etc., is available.
6. They have minimal metabolic activity so that many pollutants of concern are simply accumulated.

However, bivalves are not the only appropriate monitoring organisms. Other territorial species might be used to serve as monitors of regional areas or for specific pollutants. In some cases organisms with higher metabolic capacity can be useful for the monitoring of more recalcitrant contaminants.

Two main questions arise from the initiation of a Mussel Watch activity in the Mediterranean region. First, is the lack of bivalves in many coastal areas, particularly at the Southern coast. Therefore, basic information might necessarily be obtained for alternative sentinel organisms, although very recently we, among several authors, have suggested the possibility of using the "synthetic mussel" approach, consisting in pumping water through a polyurethane foam for the monitoring of organic pollutants.

Secondly, this activity requires trained personnel and sophisticated instrumentation that may not easily be available in many countries. Therefore, a realistic assessment of available resources should be obtained before the initiation of such a programme, that obviously should incorporate possibilities for training as well as inter-calibration exercises for data validation.

ANNEX VII

INSTRUCTION FOR INTERCALIBRATION IN HOME LABORATORY

As a continuation of the IOC/CSIC-UNEP Intercalibration Exercise held at the Instituto de Quimica Bio-Organica in Barcelona (11-17 November 1984), all participants received a second sample, consisting of freeze dried marine sediment for analysis in their own laboratories. Each participant was also provided with the following samples as reference materials: n-alkanes (C₁₄, C₂₂ and C₂₈), chrysene and topped Kuwait crude oil.

Methods

During the Barcelona Exercise, the IOC Method for Petroleum Hydrocarbons in Sediments (Manuals and Guides N° 11) was distributed among the participants as well as other background literature already indicated in Annex V. We realize, however, that not all laboratories have the same analytical capabilities. This makes the request for a specific procedure difficult to be followed, although Manuals and Guides N° 11 should be taken as the reference method. Thus, we suggest that at least the unresolved complex mixture of saturated and aromatic fractions (F1, F3 and F4) be analysed by gas chromatography, using the n-alkanes as reference material and/or the aromatic fractions (F3 and F4) be quantified with respect to chrysene and Kuwait crude oil by UV-fluorescence.

The participants are requested to make two separate determinations with the sample supplied, provided that half of it should be sufficient for analysis.

Reporting of the results

Participants are requested to report concentrations of as many of the following as possible:

F1.- Total resolved hydrocarbons
 n-alkanes (total and individual)
 pristane, phytane (ratio)
Total unresolved saturated hydrocarbons

F3, F4- Total resolved hydrocarbons
 individual components
Total unresolved hydrocarbons
Total aromatics (eq. chrysene and crude oil)

Please indicate also the weight of sample taken for analysis.

All results are to be reported on a dry-weight basis. Therefore, the water content of the sediment must be determined in a sub-sample (not that taken for analysis) by drying overnight at 105°C.

When reporting results we request that you provide a description of the methodology used for the analysis (extraction, isolation, analytical instruments and conditions, solvent dilutions, etc ...) and provide copies of the chromatograms and/or spectra.

Deadline

We expect to receive your results as soon as possible and not later than 20 January 1985.

ANNEX VIII

PROCEDURE FOR ANALYSIS OF PETROLEUM HYDROCARBONS
IN BIOLOGICAL MATERIAL

Solvents should be reagent grade and glass-distilled before use. Adsorbents (silica and alumina) should be extracted with methylene chloride-methanol (2:1) in a Soxhlet apparatus. Aqueous NaOH solution is pre-extracted with hexane. The glassware should be cleaned by sonication in a detergent solution (e.g. EXTRAN, Merck) and rinsed with distilled water and acetone before use.

Subsamples of the mussel homogenate (No. 96, 109, 214) (5-6 gr) are placed in centrifuge tubes together with 15 ml of 6N NaOH aq. solution and 200 μ l of a standard solution containing 111 μ gr/ml of d_{50} n-C₂₄ and 97.3 μ gr/ml of d_{66} n-C₃₂. The tubes are closed with teflon lined caps and shaken for several minutes, after which they are maintained at 30°C during 18 hours. The mixture is extracted five times with ethyl ether (15-10 ml each), the combined extracts are brought to dryness or near dryness and brought up in hexane (1 ml) and poured on top of a column (30 cm x 1 cm i.d.) filled with 8 grs of alumina (top) and 8 grs of silica (bottom), both deactivated with 5% water. Three portions are eluted: I) with 20 ml of hexane, II) with 20 ml of hexane-methylene chloride (9:1), III) with 40 ml of hexane-methylene chloride (8:2).

After concentration under nitrogen, avoiding complete dryness, the residues are diluted with iso-octane (750-200 μ l) and analyzed by UV-fluorescence and high resolution gas chromatography.

Aromatic hydrocarbon analysis is performed by means of a suitable UV-spectrofluorimeter. Aliquots of fractions II and III are placed in silica UV-F cells and irradiated with 310 nm (slit 20 nm). The fluorescence intensity is recorded at 360 nm (slit 20 nm). The instrument is calibrated using solutions of chrysene and Arabian crude oil provided for the exercise.

The gas chromatograph is equipped with FID and splitless injector and fitted with D8-5 fused silica column (30 m x 0.25 mm i.d.; 0.25 μ m film thickness). The operating conditions are : injector and detector temperatures, 300 and 340°C respectively; column temperature hold at 60°C for one minute and then programmed from 60°C to 310°C at 4°C/min, the carrier gas is hydrogen (50 cm/sec).

Recoveries are calculated comparing the peak areas of the internal standards with the reference solution. The values should be higher than 90%. Resolved and unresolved compounds are quantified by comparison with external standards (a solution of C₁₄, C₂₂, C₃₂ and C₃₆ n-alkanes). All these operations are carried out semi-automatically using a microprocessor equipped with a digital planimeter.