

# **Intergovernmental Oceanographic Commission**

Workshop report No. 25

## **Workshop on the Intercalibration of Sampling Procedures of the IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-ocean Waters**

Bermuda, 11-26 January 1980



INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION

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PROCEDURES OF THE IOC/WMO/UNEP PILOT PROJECT  
ON MONITORING BACKGROUND LEVELS OF SELECTED  
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SUMMARY REPORT

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<u>No.</u>	<u>Title</u>	<u>Publishing Body</u>	<u>Languages</u>
1.	CCOP-IOC, 1974, Metallogenesis, Hydrocarbons and Tectonic Patterns in Eastern Asia [Report of the IDOE Workshop on]; Bangkok, Thailand, 24-29 September 1973. UNDP (CCOP), 138 p.	Office of the Project Manager UNDP/CCOP c/o ESCAP Sala Santitham Bangkok 2, Thailand	English
2.	CICAR Ichthyoplankton Workshop, Mexico City, 16-27 July 1974. (Unesco Technical Paper in Marine Science, No. 20)	Division of Marine Sciences, Unesco, Place de Fontenoy, 75700 Paris, France	English Spanish
3.	Report of the IOC/GFCM/ICSEM International Workshop on Marine Pollution in the Mediterranean, Monte Carlo, 9-14 September 1974.	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English French Spanish
4.	Report of the Workshop on the Phenomenon known as "El Niño", Guayaquil, Ecuador 4-12 December 1974.	FAO Via delle Terme di Caracalla, 00100 Rome, Italy	English Spanish
5.	IDOE International Workshop on Marine Geology and Geophysics of the Caribbean Region and its Resources, Kingston, Jamaica, 17-22 February 1975.	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English Spanish
6.	Report of the CCOP/SOPAC-IOC IDOE International Workshop on Geology, Mineral Resources and Geophysics of the South Pacific, Suva, Fiji, 1-6 September 1975.	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English
7.	Report of the Scientific Workshop to Initiate Planning for a Co-operative Investigation in the North and Central Western Indian Ocean, organized within the IDOE under the sponsorship of IOC/FAO (IOFC)/UNESCO/EAC, Nairobi, Kenya, 25 March - 2 April 1976.	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English (full text) Extract and Recommendations also in:  French Spanish Russian

<u>No.</u>	<u>Title</u>	<u>Publishing Body</u>	<u>Languages</u>
8.	Joint IOC/FAO (IPFC)/UNEP International Workshop on Marine Pollution in East Asian Waters, Penang, 7-13 April 1976	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English
9.	IOC/CMG/SCOR Second International Workshop on Marine Geoscience, Mauritius, 9-13 August 1976	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English French Spanish Russian
10.	IOC/WMO Second Workshop on Marine Pollution (Petroleum) Monitoring, Monaco, 14-18 June 1976	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English French Spanish Russian
11.	Report of the IOC/FAO/UNEP International Workshop on Marine Pollution in the Caribbean and Adjacent Regions, Port of Spain, Trinidad, 13-17 December 1976	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English Spanish
11. Suppl.	Collected contributions of invited lecturers and authors to the IOC/FAO/UNEP International Workshop on Marine Pollution in the Caribbean and Adjacent Regions, Port of Spain, Trinidad, 13-17 December 1976	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English Spanish
12.	Report of the IOCARIBE Interdisciplinary Workshop on Scientific Programmes in Support of Fisheries Projects, Fort-de-France, Martinique, 28 November - 2 December 1977	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English Spanish
13.	Report of the IOCARIBE Workshop on Environmental Geology of the Caribbean Coastal Area, 16-18 January 1978	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English Spanish
14.	IOC/FAO/WHO/UNEP International Workshop on Marine Pollution in the Gulf of Guinea and Adjacent Areas, Abidjan, Ivory Coast, 2-9 May 1978	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English French
15.	CPPS/FAO/IOC/UNEP International Workshop on Marine Pollution in the South-east Pacific, Santiago de Chile 6-10 November 1978	IOC, Unesco Place de Fontenoy, 75700 Paris, France  CPPS Señor Miguel BAKULA Secretario General de la Comisión Permanente del Pacífico Sur Vanderghem 590 Lima 27 Perú	English       Spanish

<u>No.</u>	<u>Title</u>	<u>Publishing Body</u>	<u>Languages</u>
16.	Workshop on the Western Pacific, Tokyo, 19-20 February 1979	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English French Russian
17.	Joint IOC/WMO Workshop on Oceanographic Products and the IGOSS Data Processing and Services System (IDPSS), Moscow, 9-11 April 1979	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English
17. Suppl.	Papers submitted to the Joint IOC/WMO Seminar on Oceanographic Products and the IGOSS Data Processing and Services System, Moscow, 2-6 April 1979	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English
18.	IOC/Unesco Workshop on Syllabus for Training Marine Technicians, Miami, 22-26 May 1978 (Unesco reports in marine science, No. 4)	Division of Marine Sciences, Unesco Place de Fontenoy, 75700 Paris, France	English French Spanish Russian
19.	IOC Workshop on Marine Science Syllabus for Secondary Schools Llantwit Major, Wales, UK, 5-9 June 1978 (Unesco reports in marine science, No. 5)	Division of Marine Sciences, Unesco Place de Fontenoy, 75700 Paris, France	English French Spanish Russian
20.	Second CCOP-IOC Workshop on IDOE Studies of East Asia Tectonics and Resources, Bandung, Indonesia, 17-21 October 1978	Office of the Project Manager UNDP/CCOP c/o ESCAP Sala Santitham Bangkok 2, Thailand	English
21.	Second IDOE Symposium on Turbulence in the Ocean, Liège, Belgium, 7-18 May 1979	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English French Spanish Russian
22.	Third IOC/WMO Workshop on Marine Pollution Monitoring, New Delhi, 11-15 February 1980	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English French Spanish Russian
23.	WESTPAC Workshop on the Marine Geology and Geophysics of the Northwest Pacific, Tokyo, 27-31 March 1980	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English Russian
24.	WESTPAC Workshop on Coastal Transport of Pollutants, Tokyo, 27-31 March 1980	IOC, Unesco Place de Fontenoy, 75700 Paris, France	English

<u>No.</u>	<u>Title</u>	<u>Publishing Body</u>	<u>Languages</u>
25.	Workshop on the Intercalibration of Sampling Procedures of the IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-Ocean Waters, Bermuda, 11-26 January 1980	IOC, Unesco Place de Fontenoy, 75700 Paris	English

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SUMMARY REPORT  
INTRODUCTION

- 1 The present report gives the background, a preliminary description and an assessment of a Workshop held at the Bermuda Biological Station for Research, Inc., St. George's West, Bermuda, at the kind invitation of the Government of Bermuda.
- 2 Upon the initiative of UNEP, a study of the feasibility of a programme for monitoring background levels of selected pollutants in open-ocean waters was undertaken by three consultants appointed by IOC, WMO and UNEP, using the recommendations of the GESAMP Working Group on the Scientific Bases for the Determination of Concentrations and Effects of Marine Pollution (GESAMP Reports and Studies No. 1) as a starting point. On the basis of their study, a proposed programme was developed by the IOC/WMO/UNEP preparatory meeting of experts (Geneva, 23-25 March 1976), and submitted to the IOC-WMO (IPLAN)/UNEP group of governmental experts (Geneva, 26 March 1976) for consideration and approval.
- 3 The Executive Committee of WMO approved the Programme in principle by its Resolution 16 (EC-XXVIII). The Executive Council of IOC, by the Resolution EC-VII.11, approved the general concept and intention of the proposed programme, and by Resolution EC-VIII.9 approved the joint IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-Ocean Waters.
- 4 Forty-two Member States have supported the Programme and expressed an interest in its implementation; of these, twenty-three Member States have nominated National Co-ordinators and forty-nine laboratories to participate in the intercalibration exercise. The International Council for the Exploration of the Sea (ICES) was invited to co-operate in this exercise, and nominated five laboratories to participate in the Pilot Project.
- 5 The guidelines for the intercalibration phase of the Pilot Project were formulated at the Second Session of the GIPME Group of Experts on Methods, Standards and Intercalibration (GEMSI) (Bergen, 1-4 May 1978), and further elaborated by a core group of GEMSI (Monaco, 12-14 March 1979). A detailed timetable of the intercalibration of the sampling procedures, which was to be followed in the Bermuda exercise, was formulated at a meeting of the Steering Committee in Bermuda, from 8 to 10 October 1979 (Annex I).
- 6 The action plan was frequently adjusted during the exercise to ensure the maximum possible scientific output. There were several reasons for such adjustments: the highly variable weather conditions which prevailed during the period of the experiment; the need to repair shipboard equipment; breakage of some samplers during transportation; malfunctioning of certain samplers; and the loss of a large-volume Bodman sampler. Such contingency plans allowed all the main objectives of the Workshop to be achieved.
- 7 It must be stressed, however, that the maximum benefit can only be gained from this exercise if the intercalibration of standard solutions for trace metals and chlorinated hydrocarbons is completed.

8 On 4 October 1979, high-level standard solutions were sent by the IAEA's International Laboratory of Marine Radioactivity (ILMR) in Monaco, to 41 laboratories participating in the intercalibration exercise of the Pilot Project. These solutions contained: Lindane, DDE, DDD, DDT, HCB and Aroclor 1254, but the internal standards recommended by the GIPME Group of Experts on Methods, Standards and Intercalibration were not included because they could not be obtained in good time.

9 To date, only five laboratories have sent their results and three laboratories have indicated that they could not do the analyses.

10 Low-level standard solutions were prepared and sets of vials labelled "spiked sea water" were sent by ILMR, but only to fourteen laboratories. These low-level standard solutions will be distributed to other laboratories only after they have submitted results of their analyses of the high-level standard solutions. To date, two laboratories have reported their results for the low-level standards.

11 Similar analyses of standard solutions of selected trace metals have yet to be initiated. This will be done as soon as appropriate funds are available. In this regard it is necessary to stress that, without the results of such analyses, not only will the value of this Workshop be significantly reduced, but a full report on the intercalibration exercise will not be possible.

12 The success of the Workshop in Bermuda was to a large degree due to the input of the Bermuda Biological Station for Research and its personnel, to the NOAA vessel R.V. GEORGE B. KELEZ and her captain and crew. This input is gratefully acknowledged.

#### 1. OPENING OF THE WORKSHOP

13 Thirty-five scientists from thirteen countries participated in the Workshop, and representatives of WMO and observers from UNEP were also present.

14 A list of Participants is given in Annex II. The Workshop was officially opened on 12 January 1980 by the Governor of Bermuda, Sir Peter Ramsbotham. Mr. Erling Naess, a Patron of the Bermuda Biological Station for Research, gave the keynote address. Dr. Slaczka, Assistant Secretary IOC, officially welcomed all participants on behalf of the sponsoring agencies (IOC, WMO and UNEP). He thanked the Government of Bermuda for hosting the Workshop, and the Bermuda Biological Station for Research, its Director and staff, for the use of its laboratories and other facilities. Dr. Slaczka especially thanked Dr. Tony Knap, Deputy Director of the Station, for the excellent preparation of the Station for the Workshop. He thanked the US National Oceanic and Atmospheric Administration for providing the Workshop with the R.V. GEORGE B. KELEZ and other equipment. He acknowledged with appreciation the high-quality analytical equipment provided by the Hewlett-Packard, Perkin-Elmer and Varian Companies, and thanked the UN Environment Programme for its valuable financial support for the Workshop.

15 Dr. Slaczka briefly described the origin, history and goals of the IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-Ocean Waters under which the Workshop had been organized.

16 On behalf of the IOC, as the leading sponsor of the Workshop, and of the WMO and UNEP as co-sponsors, he invited Dr. Neil Andersen to assume the scientific leadership of the Workshop, Dr. Mike Bowers, the responsibility for the conduct of the

trace-metal intercalibration, and Dr. Karsten Palmork, likewise, for the chlorinated-hydrocarbon intercalibration.

17 Dr. Andersen, who is Chairman of the IOC's GIPME Group of Experts on Methods, Standards and Intercalibration, briefly described the scientific basis of the experiment.

## 2. CONDUCT OF THE WORKSHOP

18 All the necessary facilities and chemicals were provided by the Bermuda Biological Station for Research, the Hewlett-Packard, Perkin-Elmer and Varian Companies, the US National Oceanic and Atmospheric Administration, the IAEA's International Laboratory of Marine Radioactivity, in Monaco, the Netherlands Institute of Sea Research, in Texel, the German Hydrographic Institute in Hamburg, the Skidaway Institute of Oceanography, Savannah, USA, and the Bedford Institute of Oceanography, Dartmouth, Canada (a list of the main facilities is given in Annex III).

19 The participants formed two action Teams:

- Chlorinated-hydrocarbon Team (leader Dr. K. Palmork)
- Trace-metal Team (leader Dr. M. Bowers).

Compositions of the Teams are given in Annex IV.

20 A Workshop Committee (Annex V) was also formed to take care of the proper execution of the exercise.

21 Ad hoc meetings of the Teams were organized to discuss the progress of the work, the incoming results, and any difficulties; and appropriate steps to solve them were taken.

22 The preparatory phase of the Workshop started on 13 January 1980. During this phase all chemicals, basic standard solutions and glassware were prepared, and the gas chromatographs and atomic absorption spectrophotometers were checked and calibrated. The seagoing phase of the experiment started on 15 January on the arrival of the R.V. GEORGE B. KELEZ, and continued until 21 January 1980, the appropriate onshore laboratory operations depending on what had been accomplished and on problems met during each cruise. The sea-water samples were collected at the Panulirus Station, 12 miles southeast of Bermuda (32° 10' N; 64° 31' W).

23 During the period 13-19 January 1980, two US satellites measured environmental conditions around Bermuda. TIROS-N measured water colour (i.e., chlorophyll-a) with the Coastal Zone Colour Scanner (CZCS). Results will provide insight into any unusual levels of productivity present during the sampling period. The Advanced Very High Resolution Radiometer (AVHRR) on NOAA-6 was used to record surface temperature. These results will provide information on any unusual circulation patterns (e.g., eddies) that occurred. Sea-truth measurements were made and are in hand. Tapes have been received and are presently being analyzed by Dr. Neil Andersen at the Remote Sensing Facility of the Scripps Institution of Oceanography.

### 3. INTERCALIBRATION OF CHLORINATED-HYDROCARBON SAMPLING PROCEDURE

- 24 Some participants who arrived at the Biological Station before the start of shipboard operations, undertook preparatory work such as checking the gas chromatographic procedures and instruments, checking and controlling blanks, and preparation of sampling equipment.
- 25 A first meeting of the participants in the chlorinated-hydrocarbon group was held on 11 January 1980. The scientists taking part in the exercise were identified (Annex IV), and an operational plan for the first sampling cruise was developed and is given in Annex VI.
- 26 The objective of the first cruise was to determine the concentration of chlorinated hydrocarbons at 1200- and 10-meter depths, in order to estimate the size of the sample required for the intercalibration experiment described in Annex I. Rough weather during the cruise resulted in the loss of one large-volume (90 l) Bodman sampling bottle, after obtaining only one sample at 10 m depth. Sampling with this device was thus abandoned because of the danger involved in its use. However, sub-surface water (10 m) was sampled, using the Tokar and Harvey gas-lift system, which resulted in the collection of 420 litres of seawater. The seawater was stored in two 210-litre stainless-steel drums which has been used previously only for the storage of sea water.
- 27 Sea water from the drums was immediately passed through glass columns containing XAD-2 resin (five bed volumes per minute:  $250 \text{ ml min}^{-1}$ ), resulting in two extracts of 50 litres each and one of 126 litres. These samples were transferred to the laboratory and analyzed according to the procedure given in Annex I. The resulting chromatograms appeared to be rather complicated, and their interpretation was hampered by the large number of peaks present. It was suspected that some of these peaks might not originate from the sample. Blanks were run through the entire procedure, using one XAD-2 column five times in succession. Resulting chromatograms showed relatively high blank values, especially before florisil treatment. It was decided, therefore, to improve the blanks by cleaning all XAD-2 resin to be used in the experiment, by acetonitrile Soxhlet extraction. The sodium sulphate and florisil were also cleaned in the same way.
- 28 The extract of each sample was analyzed by gas chromatograph equipped with electron capture detector (ECD); samples obtained in the Institute of Marine Research in Bergen and in the International Laboratory of Marine Radioactivity in Monaco (both from 10 m depth), obtained under similar chromatographic conditions, were available for comparison.
- 29 In the sea-water samples collected during the Workshop it was difficult to recognize the PCB patterns present in the Bergen and Monaco samples. This was due to the blanks and the relatively low contribution of highly chlorinated components in the samples collected during the Workshop. The concentration of PCB in sea water calculated on the basis of Aroclor 1254 and in terms of the standard formulation commonly used (the gas chromatograph with glass-packed column under isothermic conditions, and electron capture detector) resulted in a value of about  $0.05 \text{ ng l}^{-1}$ ; this is one order of magnitude lower than any value reported before. Unpublished results (Harvey, 1980 and Elder and Villeneuve, 1980), support these findings.

- 30 It was recognized that the retention times of the dominant peaks in the sample chromatogram are shorter than those of Aroclor 1254 peaks. Duinker and Hillebrand recently found that less highly chlorinated components represent the PCB composition in North Sea water better than the commonly accepted Aroclor 1254.
- 31 It appeared that several peaks in the sample chromatogram have retention times identical to peaks typical of Aroclor 1221 and 1242. Therefore, it was decided to compare the chromatograms of the samples with chromatograms of as many individual PCB components as were obtainable during the Workshop. For this purpose standard solutions of sixteen mono, di-, tri-, and tetra-chlorobiphenyls were prepared at various concentrations. These, and other standards still to be prepared, will be used in identifying the peaks present in the chromatograms obtained in the analyses of sea-water samples.
- 32 The preparations for the second cruise (Annex VI) were made according to the requirements set forth in the operational plan for sea-water sampling for chlorinated-hydrocarbon analysis, and further developed as a result of knowledge gained from the analyses of samples collected on the first cruise. For storage of the sea-water samples, eight 50-litre glass carboys were cleaned with chromic acid, concentrated hydrochloric acid, water, acetone and hexane. The last hexane washing was evaporated down to appropriate volume and analyzed by gas chromatograph to check the quality of the carboys.
- 33 A 1000-litre steel tank, supplied by the Bermuda Biological Station for Research, steam-cleaned and washed with sea-water, was used to store sea-water obtained through the gas-lift system, so as to minimize any inhomogeneity that might arise when using individual glass carboys as originally proposed in the operational plan.
- 34 All samples foreseen in the operational plan were obtained, except for samples for a time-variation experiment.
- 35 The samples for intercalibration between the participants were prepared on board the R.V. GEORGE B. KELEZ from sea water collected in the large tank, from the stainless-steel drum containing water from the Bodman sampler, and from the stainless-steel drum containing sea water from the gas-lift system. The effects of storage of sea water in various containers were minimized by immediate extraction through XAD-2 column on board the ship.
- 36 For comparison, hexane extracts of sea water were obtained directly from glass samplers (Gaul-type) provided by the German Hydrographic Institute in Hamburg.

#### 4. INTERCALIBRATION OF TRACE-METAL SAMPLING PROCEDURES

##### Objectives

- 37 The objectives of the experiment were the intercomparison of different types of sampling bottles (modified GO-FLO, HYDRO-BIOS and NISKIN) and three different types of hydrowire (Kevlar; plastic-coated, galvanized steel; and unlubricated 302 stainless steel). Each of these types of sampling bottles and

hydrowires is widely used in various combinations for the collection of sea-water samples for trace-metal analysis. An ancillary objective was to determine the intercomparability of laboratory analyses, particularly in those cases where multiple determinations on single samples can be carried out. However, the major aspects of analytical performance remain to be assessed through the proposed IOC Standards and Sea Water 'Round-robin' Intercalibration.

#### Experimental design

- 38 In the chosen experimental design each type of sampling bottle was deployed on each type of hydrowire in a water mass or layer which may be assumed to have a homogeneous trace-metal distribution over spatial and temporal dimensions larger than those bounding the sampling experiment. There was sufficient replication in the design to enable an analysis of variance to be made to determine any differences between types of sampling bottles and hydrowires. Furthermore, the design contained considerable redundancy, so that, even if sample losses or adverse weather conditions forced a reduction in the degree of replication, the integrity of the comparison would nevertheless be maintained.
- 39 One or more of each type of sampling device was to be first deployed on a single hydrowire cast at depths below 1500 metres at the Panulirus Station ("S"). Previous assessments of the hydrography at this station (Pocklington, 1972), have shown that gradients in temperature and salinity in time and space at such depths are small (Annex I). Previous measurements of the vertical distribution of trace metals indicate that their concentrations are invariant at intermediate depths. The bottle spacings were such that the depth range covered by the sample set was as small as feasible. The cast was to be repeated a sufficient number of times to enable each participant to draw four water samples from each type of sampler on an individual cast. The participants were asked to analyze each of these water samples at their home laboratories for the following trace-metals:
- Priority 1: mercury, cadmium, lead, copper, zinc, nickel, selenium, and cobalt
  - Priority 2: chromium, arsenic, manganese, iron, tin, molybdenum, and vanadium.
- 40 Each participant's data could then be used to assess the intercomparability of sampling bottles. The comparison of hydrowires could be made by using a single sampler type but, because individual wires may mask some of the differences between bottles and vice versa, it was decided to deploy the three types of bottle on each of the three types of hydrowire. Thus the sampling sequence had to be repeated for the other two hydrowires. This in turn yields additional bottle-to-bottle comparisons as well as an assessment of differences between hydrowires.
- 41 The design included a test of the vertical and temporal homogeneity of the trace-metal distributions in the region of the water column used for the inter-comparison. The design allowed for the collection of additional replicate samples at the spatial and temporal extremities of a sampling sequence for later analysis by participant laboratories with known analytical precisions. The resulting data should enable the homogeneity assumption, implicit in the intercomparison experiment, to be tested.

Execution of the experiment

- 42 The first day's ship operations (Annex VII) were intended to allow the deployment of enough mixed casts of modified GO-FLO, NISKIN and HYDRO-BIOS bottles on Kevlar hydrowire to provide each participant with four replicate samples from each bottle type. The original intention to deploy the sampling bottles at depths exceeding 1500 metres had to be abandoned because the greatest length of Kevlar hydrowire which could be handled by the ship was 1400 metres. A decision was therefore made to deploy the bottles in the 1200- to 1300-m depth range despite the closeness of the oxygen minimum to this depth. This is therefore a technical restriction which makes the testing of the homogeneity of the trace-metal distribution with depth even more crucial.
- 43 Owing to adverse weather conditions and malfunctioning of the HYDRO-BIOS bottles, the operations were altered to cover the deployment of modified GO-FLO and NISKIN bottles on the Kevlar hydrowire followed by the deployment of unmodified and modified GO-FLO samplers on stainless-steel hydrowire. These latter operations were completed successfully during a cruise of 48 hours' duration.
- 44 Since the experimental design needed revision following the experience gained and operations during the first period at sea, the design was altered to take advantage of the redundancy in the original design, to carry out comparisons of pairs of bottle types only on single hydrowires and to use a single sampling bottle (modified GO-FLO) for the comparison of hydrowires.
- 45 Therefore, on the second day of shipboard sampling for the trace-metal programme (Annex VII) modified GO-FLO and HYDRO-BIOS bottle were deployed on plastic-coated galvanized wire. Samples from the GO-FLO samplers will be used for the wire-to-wire comparison; the results from this sequence of casts will suffice for the comparison of HYDRO-BIOS and GO-FLO samplers. Additional replicate samples drawn from modified GO-FLO bottles on the first and last casts of the second day's operations were also collected for testing the vertical and temporal homogeneity assumption. The second day's ship operations were completed in 24 hours.
- 46 The action plan of the Workshop required the participants to analyze their samples in their respective home laboratories, but, because of the very good facilities in the laboratories of the Bermuda Biological Station for Research (clean laboratory with positive pressure inside, high quality flameless atomic-absorption spectrophotometers), some samples were analyzed by participants immediately (Drs. Church and Lee). These results will be included in the Final Report of the Intercalibration Exercise.
- 47 During the Workshop it was decided to conduct an evaluation of sample changes during storage in each of the three types of sampling bottle (Annex VIII). For this purpose a 200-litre sample of sub-surface sea water was collected just outside St. George's Harbour (Contingency Surface Sample - CSS) and placed in a large-volume polyethylene tank. Each type of sampling bottle was filled with water from this tank and samples were withdrawn at intervals thereafter for analysis by participants at their home laboratories. Typically, samples were drawn from the sampling bottles within 5 or 10 minutes of filling, 2 hours later and 10 hours later (see Annex VIII). These samples should enable changes in sample composition resulting from effects during sample collection to be assessed.

- 48 At the end of the Workshop a questionnaire was prepared and distributed among the members of the Trace-metal Team (Annex IX). Each participant was asked to complete his questionnaire and return it with his analytical results.

5. SHIPBOARD OPERATIONS ON THE R.V. GEORGE B. KELEZ

15 January 1980: First day of sea-water sampling for chlorinated-hydrocarbon analysis

- 49 The purpose of the first day's operation was twofold:
- (i) to collect sufficient surface water to allow for enough analyses to determine the concentrations of the compounds to be analyzed, thus providing a basis for designing a final sampling strategy (Annex VI);
  - (ii) to give all interested participants and observers an opportunity to take part in the shipboard operations.

- 50 The R.V. GEORGE B. KELEZ left St. George's at approximately 0800 hours and arrived on the Panulirus Station at 1030 hours. Winds were 20 to 30 knots and seas ran between 2 and 3 m. throughout the day. One successful surface BODMAN-bottle cast was conducted. However, during the second cast (1230 hours), the vessel took a heavy roll, catching the BODMAN bottle under the starboard bilge keel. The Kevlar cable parted, resulting in the loss of the bottle. At this time, BODMAN casts were suspended and a contingency sampling plan, using a gas-lift pump designed by George Harvey and John Tokar of the NOAA Atlantic Oceanographic and Meteorological Laboratory in Miami was implemented. This system worked and allowed pumping of sufficient water to permit the day's sampling goals to be met. Operations were stopped at 1430 hours to return to port to change personnel for trace-metal sampling that night. At 1600 hours, weather forecasts resulted in the Commanding Officer of the GEORGE B. KELEZ cancelling the night operations and delaying trace-metal sampling until 0700 on 16 January 1980.

16 January 1980 First day of sea-water sampling for trace-metal analysis

- 51 The purpose of this operation was:
- (i) to compare HYDRO-BIOS, NISKIN and modified GO-FLO sampling bottles on Kevlar cable;
  - (ii) to compare stainless steel (SS) wire and the Kevlar cable, using modified GO-FLO and NISKIN bottles.
- 52 R.V. GEORGE B. KELEZ left St. George's at approximately 0830 hours and arrived on the Panulirus Station at 1100 hours. Winds were sustained at 30 to 35 knots and gusted to 45 knots. Seas ran at 2 to 3 m throughout the day.
- 53 Initial casts on Kevlar cable failed owing to premature tripping of the HYDRO-BIOS bottles. After two failures and one success, a decision was made to try one more cast with HYDRO-BIOS bottles and, if it failed, to drop the HYDRO-BIOS bottles and work only with the modified GO-FLO and NISKIN bottles.

This cast was probably successful; however, the protected thermometer in the NANSEN bottle at the bottom of the cast flooded, prohibiting a calculation of the sample depth. The unprotected thermometer in the same bottle read 14.2<sup>0</sup> C indicating that the cast was probably successful. However, given the time constraints and the problem with the HYDRO-BIOS bottle, use of these bottles was discontinued. Subsequent operations using Kevlar cable with modified GO-FLO and NISKIN bottles went smoothly as did scheduled work using the stainless-steel hydro-wire.

54 At 1630 hours on 17 January 1980, the R.V. GEORGE B. KELEZ steamed to the Spit Buoy off St. George's to transfer two sick scientists to the M.V. FOX and returned to the Panulirus Station at approximately 2000 hours to complete work with the stainless-steel hydro-wire. The R.V. GEORGE B. KELEZ returned to St. George's at 0730 on 18 January 1980, and laid alongside until approximately 0700 on 19 January 1980.

19 January 1980: Second day of sea-water sampling for chlorinated-hydrocarbon analysis

55 The cruise had the following objectives:

- (i) To compare three different methods of sample collection and storage
  - (a) an all-glass sampler (German Hydrographic Institute) with in situ extraction with solvent;
  - (b) collection of water in steel drums filled with water taken with a 90-litre BODMAN sampler followed by XAD-2 resin column extraction;
  - (c) collection of water in steel drums through the gas-lift pumping system followed by the XAD-2 resin column extraction.
- (ii) To fill a 1000-litre steel container and simultaneously pass water from it through 14 XAD-2 resin columns, to allow each participant to analyze one sample at the Bermuda Biological Station for Research, and one simultaneous sample later in his home laboratory.
- (iii) To fill glass and steel containers with 700 litres of water for multiple analyses by all participants in the Bermuda Biological Station for Research.
- (iv) To compare an in situ XAD-2 pumping system with the other methods of collection and extraction.
- (v) To perform the standard Panulirus Station hydrographic cast.
- (vi) To make a NISKIN bottle cast to 900 m for nutrient, dissolved oxygen, and chlorophyll samples.

56 All of the above objectives were achieved except that the NANSEN hydrographic cast had to be cut short owing to deteriorating weather conditions. To achieve the above objectives, 48 discreet samples were taken which amounted to approximately 4000 litres of water. Of the 20 hours spent on station, 17 hours were used for sampling.

57 Considering the multiple objectives and the poor weather, the trip was considered successful.

20-21 January 1980: Second day of sea-water sampling for trace-metal analysis

- 58 The purpose of this cruise was to obtain samples from modified GO-FLO and HYDRO-BIOS samplers using the plastic-coated steel wire. Initially, two GO-FLO and eight HYDRO-BIOS bottles, and one NANSSEN sampler with reversing thermometers for depth determination, were used. The NANSSEN sampler was positioned 50 metres from the weight and all other samplers were separated by eight metres. Each cast was lowered 1300 metres. The wire angle was kept as nearly vertical as possible as the messenger was dropped.
- 59 The first cast was unsuccessful owing to the failure of the NANSSEN bottle to reverse. After a minor modification on the NANSSEN bottle, the next two casts were successful. On the fourth cast, one HYDRO-BIOS sampler came apart and could not be repaired. However, the sampling was completed with only three more casts using seven instead of eight HYDRO-BIOS samplers.
- 60 Samples from the GO-FLO and HYDRO-BIOS samplers were collected for each participant. Samples for salinity determination were collected from the NANSSEN bottle. Additional samples were collected from the GO-FLO bottles on the second and last casts to check temporal and spatial homogeneity.

6. DEMONSTRATION OF SURFACE MICRO-LAYER SAMPLING

- 61 Knowledge of the physico-chemical properties of the sea surface is fundamental to an understanding of processes by which chemicals move between air and sea and vice versa. The surface micro-layer is a unique element of the marine environment. Many kinds of marine organisms inhabit this upper layer of the sea. At the same time the surface micro-layer (typically organic films produced by lipid secretions of marine organisms and by oil spills) can accumulate various pollutants such as chlorinated hydrocarbons, heavy metals, etc. Such films can alter a surface micro-layer community and can modify mass and energy transfer between the atmosphere and the ocean.
- 62 For these reasons, at the Steering Committee Meeting in Bermuda from 8 to 10 October 1979, the Representative of WMO proposed that an intercalibration for sampling the surface micro-layer be incorporated into the exercise. The Committee agreed to this. To save time and money that could be spent in future for developing the surface-sampling technique independently in the countries involved in this Pilot Project, the screen method of surface micro-layer sampling was demonstrated during the Workshop (Annex XI) to the participants of the intercalibration exercise; their reaction to the demonstration was positive. The scientists involved could easily serve as a core of researchers who would be interested in developing a co-ordinated international effort for monitoring the surface micro-layer.

7. SEMINAR AND CLOSURE OF THE WORKSHOP

- 63 On 22 January 1980, a seminar was held during which the participants discussed available results and problems met during the exercise, and began to develop preliminary conclusions and recommendations which will be refined for inclusion in the Final Report. The Report of this Seminar is given in Annex XI.

64 The exercise was officially closed on 26 January 1980. However, several participants from the Chlorinated-hydrocarbon Team remained at the Station to complete laboratory experiments that were underway, and the results of these experiments will be included in a report to be published in September 1980 on the results of the intercalibration exercise.

## 8. CONCLUSIONS AND RECOMMENDATIONS

65 The following conclusions and recommendations were drawn up during the Workshop by the Chlorinated-hydrocarbon and Trace-metal Teams, as well as during the seminar at the end of the Workshop, on 22 January 1980.

- (i) All the objectives of the Workshop were achieved with only minor modifications due to the difficult weather conditions during vessel operations.
- (ii) All participants received a set of sea-water samples for analysis in their home laboratories, for chlorinated hydrocarbons or trace metals.
- (iii) The following chlorinated hydrocarbons should be estimated in the samples: PCBs, DDT, DDE, DDD, DDMU, HCB and Lindane.
- (iv) The following trace metals should be estimated in the samples:  
Priority 1: mercury, cadmium, lead, copper, zinc, nickel, selenium, and cobalt.  
Priority 2: chromium, arsenic, manganese, iron, tin, molybdenum and vanadium.
- (v) Analytical results should be sent not later than May 1980 to Dr. Palmork (chlorinated hydrocarbons) and Dr. Bowers (trace metals).
- (vi) For analysis of PCBs, the standard solutions of less chlorinated components should be used, preferably those corresponding to the composition of Aroclor 1221 and 1242 rather than Aroclor 1254 which is commonly used as the standard.
- (vii) Bearing in mind the very low level of PCBs in open-ocean waters (about  $0.05 \text{ ng l}^{-1}$ ), all glassware, solvents, resins and other chemicals should be of a very high grade of purity and cleaned-up carefully before using.
- (viii) For analysis of chlorinated hydrocarbons, temperature-programmed gas chromatography with capillary columns (glass or fused silica) and electron capture detector is recommended.
- (ix) During collection of sea-water samples for chlorinated hydrocarbon analysis, a closed sampling system should be used to avoid contamination of samples on board the ship (by paints, fuels, etc.)
- (x) Preparation of individual sea-water samples for trace-metal analysis should be done on board ship in a "clean" laboratory.

- (xi) It is strongly recommended that the intercalibration of trace-metal standard solutions be initiated as soon as possible. Without these data the value of the Workshop on Intercalibration of Sampling Procedures will be severely limited.
- It is necessary to stress that one of the purposes of the intercalibration of standard solutions is also to facilitate an evaluation of other laboratories of the IOC Member States that could eventually participate in the Pilot Project.
- (xii) Bearing in mind the difficulty in the interpretation and calculation of the chlorinated-hydrocarbon chromatograms derived from the analysis of the sea-water samples, additional studies should be undertaken in home laboratories.
- (xiii) It is recommended that a small chlorinated-hydrocarbon action group meet in April or May 1980 to discuss the results obtained and decide the form of the part of the Final Report dealing with chlorinated hydrocarbons.
- (xiv) For the preparation of the Final Report of the intercalibration exercise, three consultants should be engaged not later than May 1980: one for the chlorinated-hydrocarbon section; one for the trace-metal section; and one for compilation and technical editing of the whole document.
- (xv) The Final Report of the intercalibration exercise should be ready in August 1980 for consideration at the Third Session of the GIPME Group of Experts on Methods, Standards and Intercalibration (September 1980).
- If results of the intercalibration of the trace-metal standard solutions (high and low level) are not available in good time, the trace-metal section of the Final Report will only contain the results of the intercalibration of sampling procedures.
- (xvi) It is recommended that a method of sampling the sea-surface micro-layer be further developed for use in the Pilot Project.

INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION

MEETING OF THE STEERING COMMITTEE FOR THE WORKSHOP ON THE  
INTERCALIBRATION OF SAMPLING PROCEDURES OF THE IOC/WMO/UNEP  
PILOT PROJECT ON MONITORING BACKGROUND LEVELS OF  
SELECTED POLLUTANTS IN OPEN-OCEAN WATERS +)

Bermuda, 8-10 October 1979

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+ ) The Annexes referred to in this Report of the Steering Committee are retitled Appendixes in the Report of the Intercalibration Exercise of which this Steering Committee Report is itself Annex I.

The meeting was opened at the Bermuda Biological Station for Research at 10.00, 8 October 1979 by Dr. Neil R. Andersen, Chairman of the GIPME Group of Experts on Methods, Standards and Intercalibration. The list of participants is attached as Annex I. Dr. Anthony Knap, Acting Director of the Bermuda Biological Station, welcomed the participants. Dr. Wojciech Slaczka, Assistant Secretary IOC, reported on the recent developments concerning the intercalibration exercise developed at GEMSI-II (Bergen, 1-4 May, 1978) and at the IOC/WMO/UNEP Joint Secretariat Meeting (Paris, 25 September 1978), and later refined by a GEMSI Core Group (Monaco 12-14 March, 1979); The details concerning the experiment are contained in the reports of these meetings and are not reiterated here, except that the following trace-metals: mercury, cadmium, lead, copper, zinc, nickel, selenium and tin, and the following chlorinated hydrocarbons: PCB's, DDT, DDE, DDD, DDMU, lindane, hexachlorobenzene will be included in the intercalibration exercise.

To date, 13 Member States have responded positively regarding their participation in the Workshop on Intercalibration of Sampling Procedures (Bermuda, 11-26 January 1980) with fourteen participants in the chlorinated-hydrocarbon analyses, and 15 in the trace-metal analyses; Colombia requested on-the-job training for two individuals. The Congo indicated its wish to participate but did not specify the nature of its participation. Dr. Slaczka also provided the latest information on available resources for the Workshop.

Mr. Desmond Scott, IOC Secretary, and Dr. Stjepan Keckes, Director of the UNEP Regional Seas Programme Activity Centre, provided additional background information on this matter.

The schedules, dates, experimental designs, equipment and expendable supplies described in Annexes II-V are based on the obtained information and findings of previous meetings on this matter. The following assumptions have been made regarding organization of the Workshop.

Drs. Palmork and Villeneuve reported on Dr. Palmork's recent visit to the IAEA International Laboratory of Marine Radioactivity in Monaco where they discussed the instruments to be used in this exercise and went through the methods of chlorinated-hydrocarbon analysis. Information from their report, supplemented by the discussion that followed, constituted the basis for Annex II. This Annex describes in detail the part of the exercise dealing with chlorinated hydrocarbons.

Dr. Villeneuve reported on the distribution of chlorinated-hydrocarbon standards; high-level standards have been sent to all laboratories participating in the Pilot Project. However, no internal standard (as recommended by the GEMSI Core Group) was available. Therefore, an attempt will be made to acquire appropriate compounds (e.g., from Dr. Duinker, Netherlands) to include in a second distribution of standard solutions. The second set of chlorinated-hydrocarbon standards to be added to seawater samples and analyzed as recommended by the GEMSI will be distributed before January.

Dr. Bowers presented the experimental design for the trace-metal sampling. Dr. Bower's exposition has been combined with information provided by Dr. Atwood and the Steering Committee in Annex III.

On the topic of availability of trace-metal standard solutions, the Steering Committee considered that under no circumstances can the analyses of standard trace-metal solutions, discussed in the Report of GEMSI-II, and later by Dr. Andersen on his visit to the Sagami Chemical Research Center, be omitted. To do so would seriously undermine the proper interpretation of results of the trace-metal analysis of samples collected during the Workshop.

The standard solutions, which will be employed as standards for analyses conducted at the Bermuda Biological Station, will be provided by:

Dr. M. Bowers: Trace Metals

Dr. J.P. Villeneuve: Chlorinated Hydrocarbons and XAD resin.

Facilities at the Bermuda Biological Station will be available for the period 1-26 January 1980, and Dr. Knap will be responsible for this aspect of the Workshop. Details are given in Annex II.

The timetable requires participants to be at the Bermuda Biological Station no later than 11 January 1980 (the ship is scheduled to arrive at 0900, 13 January 1980, and may commence operations immediately; participants are expected to depart no later than 26 January 1980. Dr. Knap indicated that the Station could accommodate 40 people. The Grotto Bay Hotel will be used to accommodate any participants in excess of this number. There is also available at the Station a seminar room having a capacity for 80 people. This will be used for discussions following sample collection, and analysis from 21 to 25 January 1980, but will be also available for other purposes throughout the total period of the experiment. The sea-water samples will be taken at the Panulirus Station (32°10'N; 64°31'W).

The hydrography of the Station has been studied continuously since 1954. Several analyses of the physical oceanographic conditions at this station have been conducted (Schroeder & Stommel, 1969; Pocklington, 1972; Worthington, 1976). Since the experiments require the repeated sampling of as near a homogeneous water mass as possible, the majority of the sampling work will be conducted in depths exceeding 1000m, where gradients in the hydrographic properties with depth are minimal and temporal changes in physical conditions are small and documented (Annex IV).

Lt. Pawlowski reported to the Committee on various matters relative to the R/V KELEZ. This information, and data provided by Dr. Atwood, are incorporated in Annex V on shipboard operations, plans and schedules.

As with all oceanographic field operations, a schedule of ship operations was developed assuming reasonable weather conditions and having a small (i.e., one day) time contingency built in. However, there is always the possibility that unforeseen circumstances (e.g., unsafe weather conditions, engine breakdown, etc.) would require major decisions and schedule adjustments. Therefore, the responsibility for making such decisions must reside with the Scientific Committee to enable on-site alterations in the operation to be made (see below). Any modifications made to the plans and schedules contained in the attached Annexes must follow the basic tenet that the scientific viability of the experiment, insofar as is possible, not be compromised. All scientific operations aboard the R/V KELEZ will be under the supervision of Dr. Atwood, the Chief Scientist. Decisions regarding ship operations, especially the safe operation of the vessel, will be the responsibility of the Commanding Officer of the R/V KELEZ.

Discussing the responsibility of preparation and execution of the Workshop, the Steering Committee agreed that two committees should be formed:

1. The Scientific Committee - scientific aspects of the Workshop and preparation of the final report on the whole intercalibration exercise (intercalibration of standard solutions, sea-water samples and sampling procedure). This committee would be composed of Dr. N. Andersen, Dr. K. Palmork, Dr. M. Bewers, Dr. D. Atwood, Dr. G. Harvey, and Dr. H. Windom.

The Steering Committee noted that in order to ensure that all common sampling equipment was made available for the experiment, additional scientists would be invited to participate in the Workshop. These are, in order of priority:

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3. Dr. J. Duinker,  
Netherlands Institute for Scientific Research,  
Den Burg,  
Texel  
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4. Dr. Manfred Ehrhardt,  
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  5. Mr. A. Holden,  
Freshwater Institute  
Department of Agriculture and Fisheries for Scotland  
Pitlochry,  
Scotland, U.K.
  6. Dr. G. Topping,  
Department of Agriculture and Fisheries for Scotland  
Torry  
Aberdeen  
Scotland, U.K.
2. The Administrative Committee - administrative aspects of the Workshop. This Committee would be composed of Dr. W. Slaczka (IOC), Dr. T. Knap (Bermuda Biological Station), and Lt. R. Pawlowski (R/V KELEZ).

At the same time IOC will take overall responsibility for the Workshop and be also responsible of all administrative arrangements preceding the Workshop.

Regarding funds needed and available at present, the Steering Committee was informed that:

1. The estimated contribution of IOC will be \$32,000; and UNEP has been asked to provide an additional US\$ 60,000. These resources are required immediately.
2. There will be a minimum of \$165,000 provided by the National Oceanic and Atmospheric Administration of the United States (\$130,000 for the operations of the R/V KELEZ, shipboard services and associated costs, e.g., docking fees, pilot, etc.) and, by the Bermuda Biological Station for Research, \$ 35,000 for use of facilities. Additional undetermined resources will also be contributed by Canada, Norway and the U.S.A., as well as by the IAEA's International Laboratory of Marine Radioactivity. The Steering Committee stressed that without these resources, the Workshop on Inter-calibration of the Sampling Procedures would not be scientifically successful.

Dr. Smagin (WMO) briefly discussed WMO interests in marine pollution monitoring, and the role that the air/sea interface plays in affecting mass and energy transfer. It is with this regard that WMO is interested in marine environmental monitoring. He pointed out that the surface microlayer (typically an organic film arising from natural processes) can act as an important

reservoir for various substances, including halogenated hydrocarbons and trace metals. He suggested that the Steering Committee consider incorporating an intercalibration of sampling methods of the surface microlayer into the exercise. The Committee concurred with Dr. Smagin's assessment of the importance of the air/sea interface and the need for conducting an intercalibration of surface microlayer sampling methods. However, the Committee pointed out that such a sampling intercalibration had not been considered during previous GEMSI meetings which have led to the presently planned and scheduled intercalibration of water samples for chlorinated hydrocarbons and selected trace metals. The Committee took the view that because the surface microlayer had not previously been considered in the development of intercalibration plans, the necessary expertise for designing an appropriate experiment is lacking. Nevertheless, in response to Dr. Smagin's request, the Committee agreed that time would be made available and shipboard capabilities provided to undertake surface microlayer sampling, provided that circumstances do not arise that would jeopardize the major objective of the water-sampling intercalibration. The development of an experimental design, the invitation of three or four participants, the costs required for transporting people and equipment to Bermuda, and their subsistence at the Bermuda Biological Station must be the responsibility of WMO. Also, the timely reporting to IOC and the Bermuda Biological Station of developments and plans is absolutely necessary, because of the limited time available before the Workshop starts.

The meeting was closed by Dr. Andersen at 1500 hrs on 10th October, 1979.

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OUTLINE OF THE METHOD TO BE USED FOR THE DETERMINATION OF  
CHLORINATED HYDROCARBONS IN SEA WATER

by

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and

J.P. Villeneuve

IAEA

International Laboratory of Marine Radioactivity, Monaco

A draft prepared on the basis of IOC/GGE(MSI)-II/3, Annex IV (Appendix 4), and the methods used at the International Laboratory of Marine Radioactivity, Monaco and the Institute of Marine Research, Bergen, Norway.

The draft will be discussed by the Steering group of the IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-Ocean Waters, at the meeting 8-10 October 1979 at the Bermuda Biological Station for Research.

OUTLINE OF THE METHOD TO BE USED FOR THE DETERMINATION OF  
CHLORINATED HYDROCARBONS IN SEA WATER

Introduction

At the second session of the GEMSI, in Bergen, Norway, May 1978, IOC/GGE(MSI)-II/3, Annex IV, a paper (appendix 4) was produced on "ANALYSIS OF CHLORINATED HYDROCARBONS IN SEAWATER BY ABSORPTION ON AMBERLITE XAD-2 RESIN". This paper is used as the basis for the "outline of the method" described here, with a few modifications made by The International Laboratory of Marine Radioactivity, Monaco and The Institute of Marine Research, Bergen, Norway.

In the method described here, seawater is passed through glass cartridges containing Amberlite XAD-2 resin which adsorbs the desired chlorinated hydrocarbons. The resin is then eluted with water miscible organic solvent to remove the adsorbed compounds. The eluate is diluted with water and extracted with hexane. The hexane extract, containing chlorinated hydrocarbons is then subjected to solid-liquid column chromatography to remove unwanted substances, reduced in volume to give a convenient concentration, and finally analysed by gas chromatography. The overall efficiency of the method is about 90% ( $\pm 10\%$ ), for a number of chlorinated compounds including polychlorinated biphenyls and the DDT series.

The main advantage of the method is that after the adsorption step, the resin can be stored for many weeks without adversely affecting the results. So, the adsorption step can be effected with relative ease aboard ship, after which the cartridges are sealed and shipped to a land based laboratory for further analysis. Thus, need for sophisticated laboratory facilities at sea are reduced.

In addition, since the adsorptive capacity of the resin is quite high, the upper limit on sample size is imposed only by the ability to collect large volumes of seawater. In sampling surface waters, this difficulty can be overcome by drawing water directly from the ocean through a cartridge or resin.

#### Sampling from ships.

Most oceanographic vessels are floating contamination problems. Contaminating substances, especially PCBs, are potentially present in the ships paint, hydraulic fluids, lubricating oils, anti-corrosives, hoses, bilge water, seawater plumbing systems, etc., etc. Every effort must be made to prevent seawater samples from coming in contact with these and other sources of contamination. It is essential to gain the co-operation of the officers and crew of the ship during a sampling programme in order to avoid such operations as bilge pumping or paint chipping when sampling gear is being used over the side.

Obviously, as with most analytical methods, certain steps require a log of familiarity before they become routine, and probable sources of contamination must be minimized. Various aspects of the technique are presented in more detail below.

#### Sampling

The analyses of seawater for chlorinated hydrocarbons require collection of volumes in the order of 50-100 liters. The sampling can then either be done by collecting sea water by suction directly from the surface and upper layers of an appropriate

volume through tygon or teflon tubing connected to a column with amberlite XAD-2 resin using a pump (Fig. 1). The speed of the pump should be adjusted to deliver 250 ml/min. When samples below the surface are desired, the use of a Bodega-Bodman Sampler should be preferred (Fig. 12).

Adsorption of chlorinated hydrocarbons from seawater

Pack a 2 cm (I.D.) glass column with 50 ml of precleaned XAD-2 resin in pesticide-free water. Make sure that all air bubbles are removed. Pass the desired (measured) amount of seawater through the column at a rate of 200-250 ml/min. (The adsorption efficiency of the resin is a function of the flow rate; the rate given here is 4-5 bed volumes/min which has been experimentally determined to be the optimum and gives about 95% adsorption efficiency for PCBs and DDTs) (Harvey, Steinhauer and Teal, 1973). This can of course be accomplished by gravity flow or with a pump (Fig. 1. 11.).

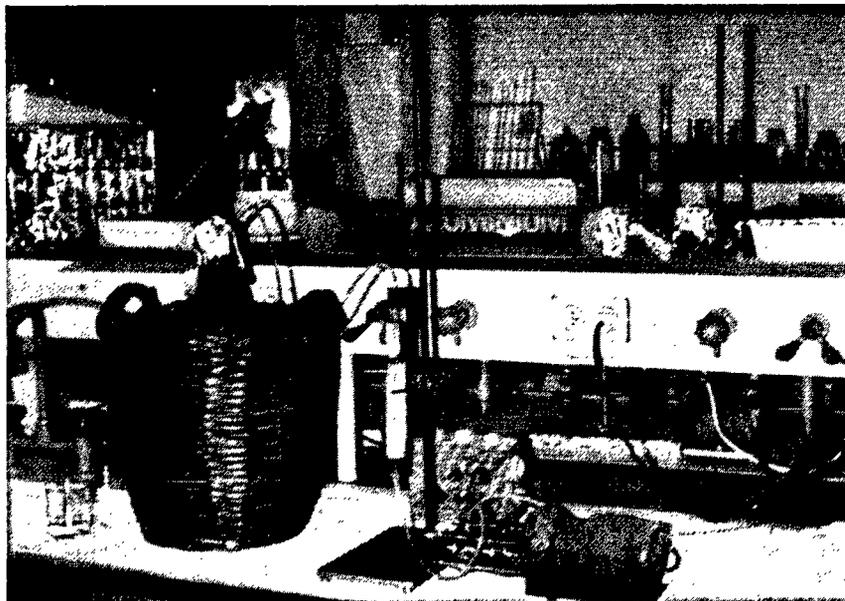


Fig. 1. Set up for the adsorption of chlorinated hydrocarbons on XAD-2 resin in the Monaco laboratory.

When using a pump it should be placed down stream of the column to avoid contamination.

It may be of interest to determine the relative amounts of chlorinated hydrocarbons in the dissolved and particulate states. However, filtering seawater before subjecting it to XAD-2 adsorption presents a problem because membrane, paper and glass fibre filter materials adsorb organic matter.

Furthermore, membrane and paper filters usually contain substances which interfere with the analysis so that only pre-cleaned glass fibre filters are suitable. So, if one filters the sample of water and then analyzes the filter for particulate chlorinated hydrocarbons, the results tend to be high because the total amount of chlorinated hydrocarbon present is due to particulate content plus that adsorbed on the filter. By extension, if the filtrate is subjected to the resin adsorption technique, the "dissolved" concentrations will tend to be low because some of the chlorinated hydrocarbons will have been lost on the filter. This problem can be overcome somewhat by first subjecting the sample to XAD-2 adsorption followed by filtration.

The reasons the latter is more accurate are two-fold. First of all, since the resin beads are large compared to most seawater particulates, the particulates tend to pass through the resin bed and out of the column. Secondly, XAD-2 tends to pick up only those chlorinated hydrocarbons in the dissolved state rather than those adsorbed to particles. Only rarely does a sample of open ocean seawater contain particles large enough to be held up by the column. These are readily visible at the top of the column and can be carefully removed before the column is eluted.

In the open ocean, the amount of chlorinated hydrocarbons associated with particulates is usually less than 10% of the total, whereas in coastal zones, it may account for 90% or more. Therefore, the necessity for filtering seawater depends on the overall aims of the monitoring programme and the prevailing conditions at the sampling locations.

#### Internal standard

Before the elution of the XAD-2 column, an internal standard

should be added to the top of the column if the behaviour is the same as that of the compounds investigated. The internal standard will then go through the entire work-up procedure and simplifies the quantitation because there is no longer any need for exactly measured volumes and injections. The internal standard used is a PCB with four chlorine atoms, which is not found in measureable amounts in the Chlophene A50, used as standard in our laboratory (Institute of Marine Research, Bergen).

#### Extraction of resin and work-up of extract

The work-up of the resin can vary a little depending on the concentration of the chlorinated hydrocarbons in the area to be monitored, the presence of interfering substances and the amount of water sampled. The following is suggested:

Elute the resin column with 200 ml of boiling acetonitrile under gravity flow.

The eluate is transferred to a separating funnel (specially made for bromine analysis) containing 600 ml pesticide-free water.

The acetonitrile/pesticide-free water mixture is extracted twice with 80 ml portions of hexane (redistilled).

Dry the extracts with a minimal amount of  $\text{Na}_2\text{SO}_4$ . After decanting the combined hexane fractions, wash the  $\text{Na}_2\text{SO}_4$  with a few ml's of fresh hexane and decant this into the combined hexane fraction. Carefully reduce the volume of the hexane solution to approx. 10 ml on a rotary evaporator (do not exceed this limit or chlorinated hydrocarbons can be lost!), a Kuderna-Danish evaporator might also be used.

The next step in the procedure is to remove interfering substances from the extracts - that is compounds which have GC retention-times that are the same or close to retention times of the target chlorinated hydrocarbons. Quite often at this stage in the procedure the presence of interfering substances is

exhibited by a yellow to brown tint in the extract. If not then a preliminary check by electron capture gas chromatography should be carried out.

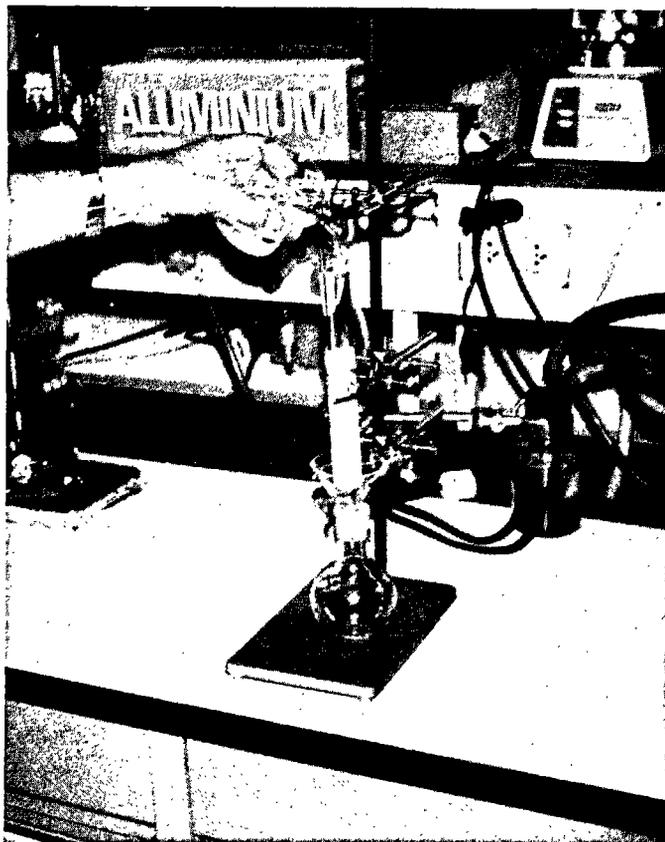


Fig. 2. Separating funnel for the hexane (C) extraction of the acetonitrile eluate (A), mixed with water (B).

If interfering substances are present they can usually be removed as follows:

Pass the concentrated extract through a micro-chromatography column (a Pasteur pipette will suffice) containing 2-4 cm. of Florisil<sup>(R)</sup>. Wash the column with one bed volume of 5% ether in hexane. The extract and ether-hexane washings are then combined and evaporated in a Kuderna-Danish concentrator to 0.5-1.0 ml or in a stream of pure nitrogen.

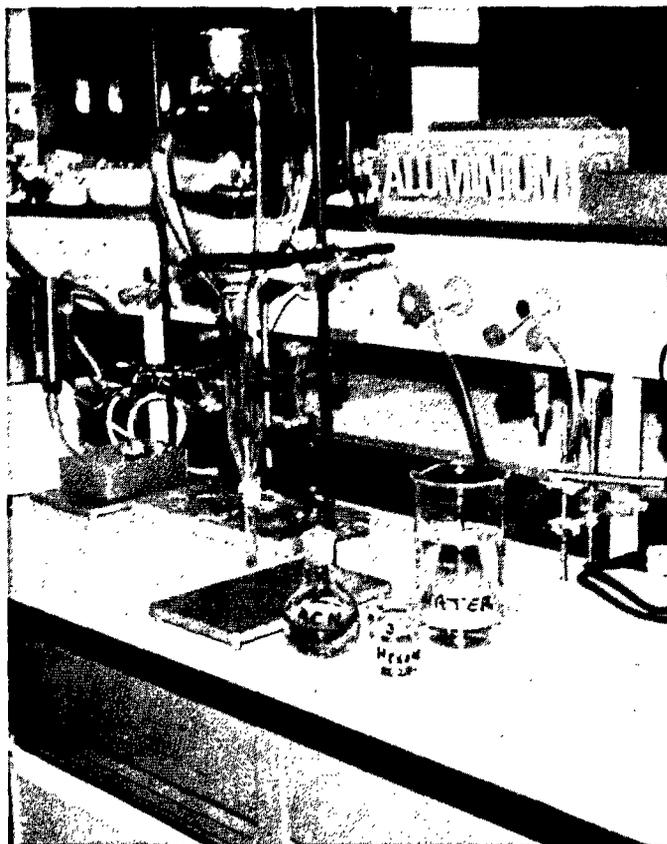


Fig. 3. Elution of the adsorbed chlorinated hydrocarbons from the XAD-2 resin with boiling acetonitrile.

It is important to quantify this volume for the final gaschromatographic analyses if an internal standard is not used.

After removing interfering substances, PCBs and *p,p'*-DDE can be separated from *p,p'*-DDT and *p,p'*-DDD before electron capture gas chromatographic analysis on packed columns as follows:

First, prepare deactivated silica by baking 100-200 mesh silica for 8 hrs at 140°C, then add to it 3% (W/W) water. (Some experimentation with conditions using standard chlorinated hydrocarbon solutions as yield determinants is necessary). Pass the extracts (0.5-1.0 ml) through a micro-chromatography column packed with 2 grams of the deactivated silica. It is recommended that the microcolumns are treated with dichloromethane and subsequently with *n*-hexane in order to remove interfering substances (Duinker and Hillebrand, 1978). Elute the column with hexane (10-15 ml) which removes PCBs and *p,p'*-DDE, then elute with a 10% ether-

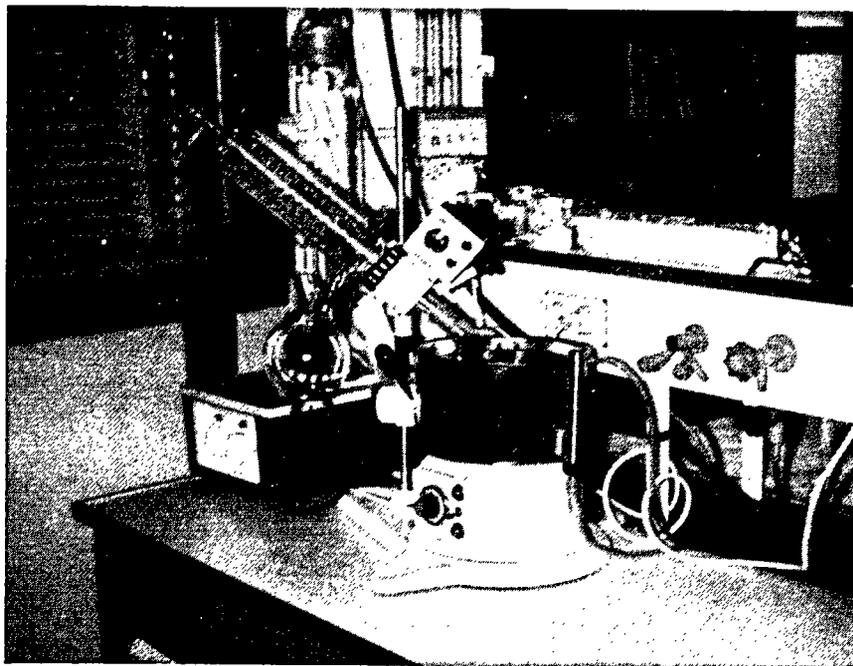


Fig. 4. Rotavapor for the reduction of the extraction volume.

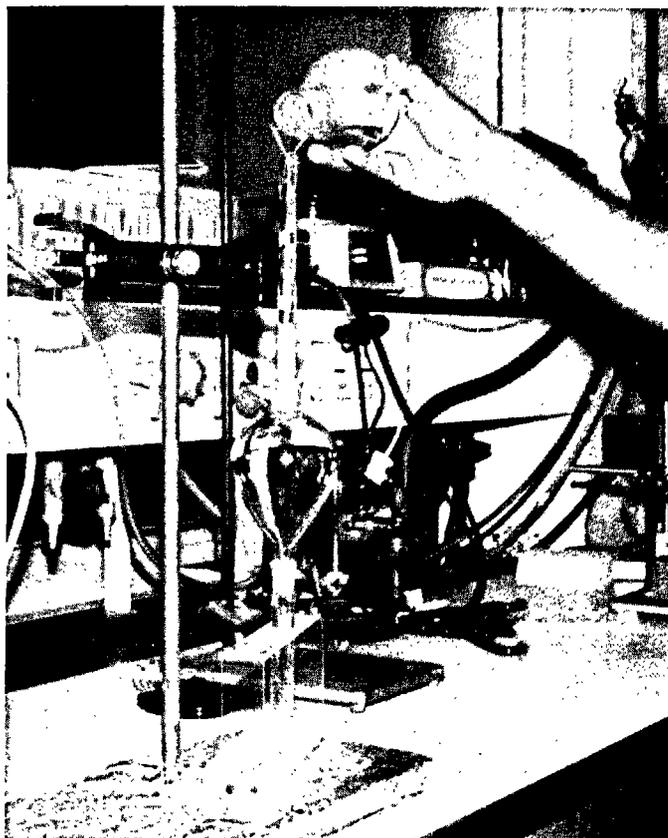


Fig. 5. Short column with Florisil for the clean up of the extract (to remove for example phthalates and other organic compounds).

hexane solution (10-15 ml) or toluene which removes p,p'-DDT and p,p'-DDD. The eluates are then concentrated to a convenient volume for gas chromatographic analysis. Appropriate blanks should be run, repeating the analytical procedure using water that was extracted already. This gives an estimate of the presence of any contamination source, with the exception of the sampling procedure.

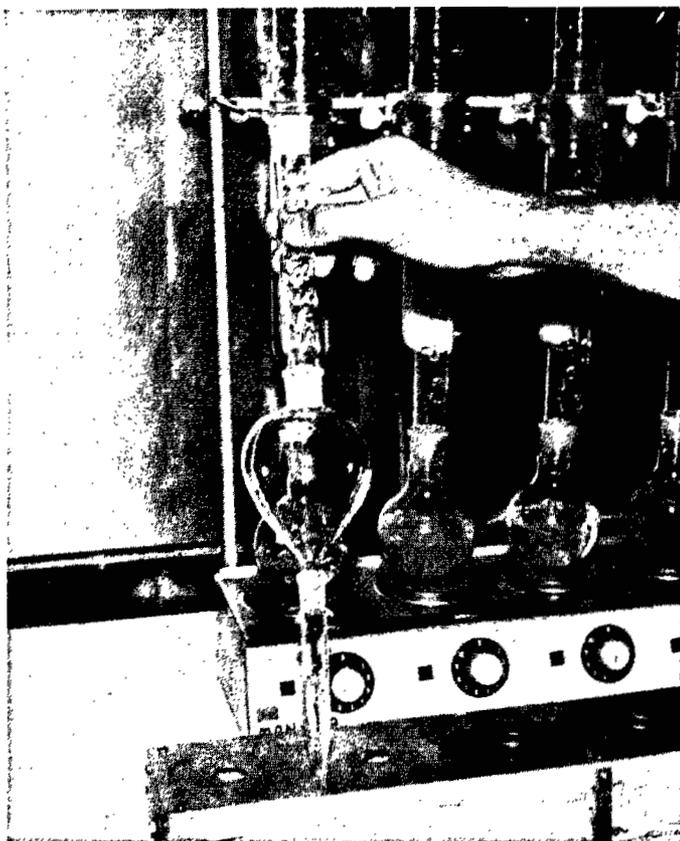


Fig. 6. Kuderna-Danish concentrator for final volume reduction.

### Gaschromatographic analysis

There are a number of suitable gas chromatographic stationary phases for chlorinated hydrocarbon analysis. Information contained in the references at the end of this paper may serve as a starting point for familiarization with materials commonly used.

Glass capillary columns are also in use for these analyses and in that case the separation of PCBs and p,p'-DDE from the p,p'-DDT and p,p'-DDD is not necessary.

The gas chromatograph should be equipped with electron capture detector. It should also have glass column(s) and all-glass injector and detector systems in order to avoid losses of samples by thermal "cracking".

Sample extracts are injected into the GC using standard techniques. However, due to the small quantities of chlorinated hydrocarbons normally dealt with, special care should be taken (see Appendix).

#### Gas chromatographic analyses using packed columns.

The analysis is performed on a Varian 3700. The chromatographic column used is a glass column filled with gas chrom Q coated with 10% OV 101 or with 10% DC 200.

For PCBs analysis, different types of packing are used by laboratories which make routine analysis:

- 5% DCFS 1265 + 4% DC 200 on chromosorb W 80/100
- 3% OV 210 + 3% OV 17 on gas chrom Q 100/120
- 6% QF1 on chromosorb W 80/100
- 10% OV 17, 10% OV 210 (1:4) on chromosorb W 80/100
- 1.5% SP 2250 + 1.95% SP 2401 on Supelcon aw
- 4% SE 30 + 6% OV 210 on gas chrom Q
- 5% SE 30 on Varaport 30

The main problem is the homogeneity of the phase. Normally with 10% (or more) of coating material there is no difficulty in obtaining an efficient column.

#### Experimental conditions:

- t<sup>o</sup> column: 200<sup>o</sup>C
- t<sup>o</sup> injector: 210<sup>o</sup>C
- t<sup>o</sup> detector: 260<sup>o</sup>C
- N<sub>2</sub> flow rate: 50-70 ml/min
- Volume injected: 1-10 µl

Gas chromatographic analyses using capillary columns.

The analyses of the PCB and pesticides were performed on a Hewlett Packard 5710 A gaschromatograph equipped with a HP 1874 A Capillary column control and a 45 m long glass capillary column coated with SE-54. The construction of the electron capture detector (ECD) permits the make up gas to flow directly into the detector housing via a built in metal coil which is heated by the detector and maintained at a constant temperature. Since the volume of the carrier gas entering the detector is very small compared to the make up gas (~ d 1:50). The temperature variation in the oven has little or no influence on the detector temperature and the capillary column can therefore be temperature programmed.

The conditions for the analyses were as follows:

Sample injection splitless,  
Oven programmed from 100-230°C at 8°C/min,  
Injector temp.: 250°C  
Detector temp.: 250°C  
Paper speed: 20 mm/min.

GC/MS analyses of a PCB- and pesticide-mixture

A mixture of PCB (Chlophene-A50) was analysed on a computerized gas chromatograph mass spectrometer (Finnigan GC/MS/DS Model 9000/3200F/6100) under the same chromatographic conditions and the same chromatographic columns as for the analyses performed using ECD-detector with temperature-programming (Fig. 7). The degree of chlorination (Chlorine number) of the different PCB components was determined and this chromatogram was compared with the chromatogram obtained using the same column type, electron capture detector and temperature programming. No attempt was made to determine the structure of the different isomeres.

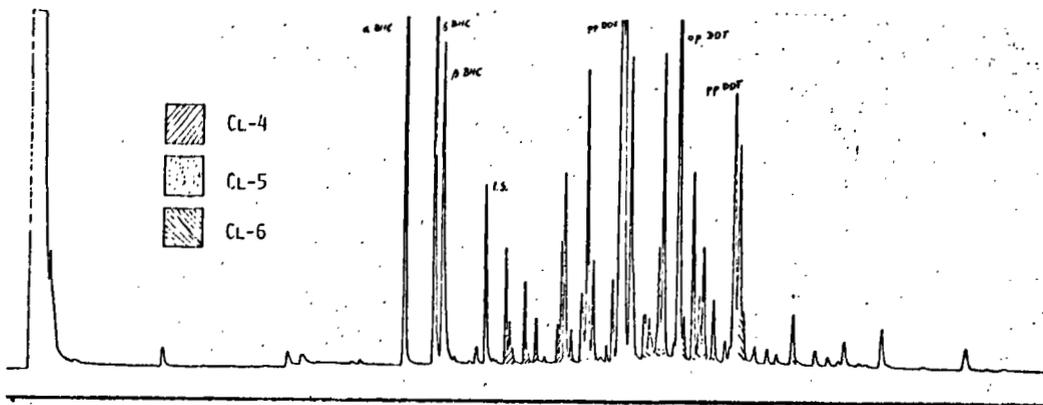


Fig. 7. Gas chromatogram of Chlophene-A50 and pesticidemixture using EC-detector and temperature programming.

For the quantitation of the pesticides the following standard solution was used:

0.260 ng	α BHC	
0.529 ng	β BHC	
0.268 ng	γ BHC	
0.510 ng	pp DDE	pr. μl
1.077 ng	op DDT	hexane
1.009 ng	pp DDT	
0.600 ng	internal standard (a PCB-Cl <sub>4</sub> isomere).	

Water sample from Monaco July 1979

The sample was subjected to the procedure described above and the Na<sub>2</sub>SO<sub>4</sub> dried sample was reduced to 10 ml.

The 10 ml sample was divided into two parts A and B.

- A. The 5 ml sample was mixed vigorously with conc. H<sub>2</sub>SO<sub>4</sub> and centrifuged. The hexane-phase was evaporated by a stream of dry nitrogen and then redissolved in 70 μl of hexan. 0.5 μl of this solution was injected on the gas chromatograph (Fig. 8).

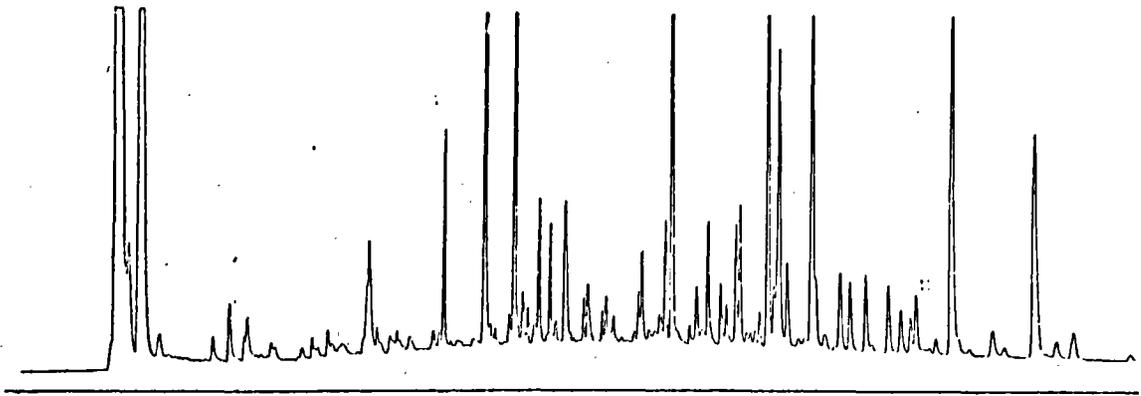


Fig. 8. Gas chromatogram of sample after conc.  $H_2SO_4$  clean-up.

One half of the sulphuric acid washed sample (A) was taken to dryness and redissolved in 2 ml of 4N KOH in Methanol in a 10 ml Sovirel tube with teflonlined screw cap. The tube was left at  $80^{\circ}C$  for one hour. The sample was diluted with approx. 0.5 ml distilled water and extracted with 2 x 3 ml of hexane. The hexane-phase was evaporated to dryness and redissolved in 50  $\mu$ l of hexane and 0.7  $\mu$ l was injected in the gaschromatograph (Fig. 9).

- B. The volume was adjusted to 10 ml and subjected to clean up on a Florisil column ( $\sim 0.5 \times 4$  cm). The eluate was evaporated to dryness, redissolved in 100  $\mu$ l of hexane and 0.5  $\mu$ l was injected on the gaschromatograph (Fig. 10).

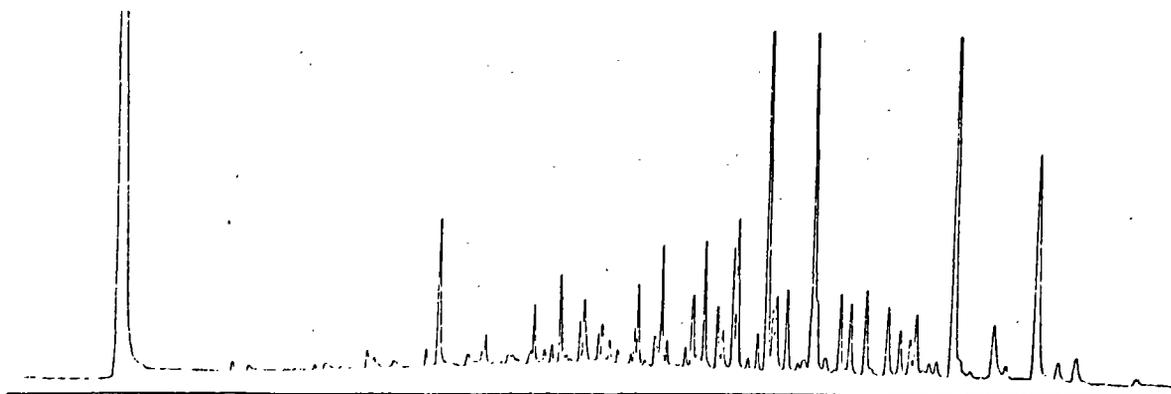


Fig. 9 . Gas chromatogram of sample after conc.  $H_2SO_4$  and KOH/methanol clean up.

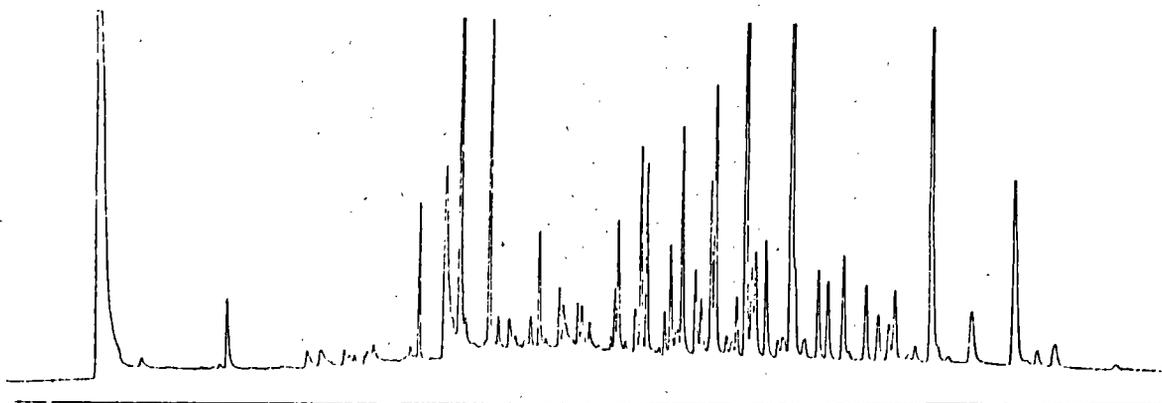


Fig. 10. Gas chromatogram of sample after Florisil clean-up.

Table 1. Content of PCB and pesticides in nanogram per liter sea water, H<sub>2</sub>SO<sub>4</sub> clean-up. (Perkin Elmer PEP-1 data system.)

THRESHOLDS 256 16

ST 1 MONACO HOLONNE 2 H2504 1A-9-79

ST 4 METHOD 4 FILE 10 31

TIME	AREA	RRT	RF	C	NAME
14.59	.0683	.810	.0000	.0000	1
14.75	.0446	.818	.0000	.0000	1
14.80	.0448	.821	.0000	.0000	1
14.98	.3721	.831	.0000	.0000	1
15.11	.3069	.838	.0000	.0000	1
15.32	26.6889	.850	.3162	1.5096	ALFA-BHC1 HEXAKLOROBENZEN1
15.55	1.1011	.863	.0000	.0000	1
15.71	.7341	.872	.0000	.0000	1
16.00	.1058	.888	.0000	.0000	1
16.07	.0715	.892	.0000	.0000	1
16.16	1.1744	.897	.0000	.0000	1
16.30	24.4416	.905	.3152	1.3672	GA44A-BHC1
16.61	2.1062	.922	.3995	.1494	BETA-BHC1
16.80	.9382	.932	.0000	.0000	1
17.04	1.1864	.946	.0000	.0000	1
17.16	4.4830	.952	.0000	.0000	1
17.41	.2967	.966	.0000	.0000	1
17.51	3.5308	.972	.0000	.0000	1
17.72	1.0532	.983	.0000	.0000	1
17.84	.0689	.990	.0000	.0000	1
18.01	4.5049	1.000	1.0000	.8000	INTERNAL STANDARD1
18.07	2.5641	1.003	1.0000	.4553	1
18.21	.3009	1.011	.0000	.0000	1
18.33	.1569	1.017	.0000	.0000	1
18.49	.1010	1.026	.0000	.0000	1
18.65	1.2641	1.035	1.8491	.4150	7 PCB-CL41
18.79	2.6540	1.043	.9413	.4436	8 PCB-CL41
19.09	.0837	1.059	.0000	.0000	1
19.27	.9950	1.069	.9900	.1749	11 PCB-CL41
19.40	1.5246	1.077	.0000	.0000	1
19.52	.2719	1.083	.0000	.0000	1
19.64	1.2592	1.090	.4347	.0972	13 PCB-CL41
19.91	.3143	1.105	.0000	.0000	1
20.09	.1520	1.115	.0000	.0000	1
20.34	.5323	1.129	.4754	.0449	15 PCB-CL41
20.48	1.7369	1.137	.5679	.1753	16 PCB-CL41
20.59	3.0278	1.143	.6325	.3400	17 PCB-CL51
20.82	.6977	1.156	.4629	.0573	18 PCB-CL51
20.99	.6874	1.165	.0000	.0000	1
21.14	1.9122	1.173	.2595	.0881	19 PCB-CL51
21.34	4.1318	1.184	.3316	.2432	21 PCB-CL51
21.55	19.5603	1.196	.3731	1.2956	22 PCB-CL51
21.96	.1686	1.219	.3426	.0102	23 PCB-CL51
22.16	.6867	1.230	.3623	.0441	24 PCB-CL51
22.37	2.5510	1.242	.0969	.0438	PP-DD1
22.54	.5349	1.251	.1245	.0118	DIELDRIN1
22.62	.7224	1.255	.1245	.0159	DIELDRIN1
22.76	4.7523	1.263	.2318	.1956	29 PCB-CL51
23.00	2.3484	1.288	.1864	.0777	30 PCB-CL61
23.39	1.8882	1.298	.1063	.0356	31 PCB-CL61
23.73	4.2638	1.317	.2238	.1694	33 PCB-CL61
23.87	5.0445	1.325	.1210	.1084	34 PCB-CL51
24.09	.6238	1.337	.0000	.0000	1
24.23	.5931	1.345	.0000	.0000	1
24.40	.6863	1.354	.3710	.0452	PP-DDD-OP-DDT1
24.56	15.2054	1.363	.2305	.0493	36 PCB-CL61
24.86	16.3014	1.380	.0989	.2860	37 PCB-CL61
25.06	2.3341	1.391	.1976	.0819	38 PCB-CL61
25.24	15.0214	1.401	.1022	.2720	39 PCB-CL51
25.53	3.9404	1.417	.0710	.0496	40 PCB-CL61
25.78	.0866	1.431	.0000	.0000	1
25.91	.5202	1.438	.0000	.0000	1
26.07	.4403	1.447	.0000	.0000	1
26.18	.4781	1.453	.3493	.0466	PP-DDT1
26.38	17.2108	1.464	.0691	.2108	42 PCB-CL61
26.51	2.6006	1.471	.0691	.0318	42 PCB-CL61
26.80	1.0094	1.488	.0000	.0000	1
27.13	.2284	1.506	.0000	.0000	1
27.31	3.3273	1.516	.0000	.0000	1
27.62	3.0499	1.533	.0000	.0000	1
28.15	3.4651	1.563	.0529	.0324	43 PCB-CL61
28.34	.4352	1.573	.0000	.0000	1
28.90	3.1355	1.604	.0000	.0000	1
29.31	2.1676	1.627	.0000	.0000	1
29.44	1.5803	1.645	.0000	.0000	1
29.84	2.6908	1.656	.0000	.0000	1

Table 2. Content of PCB and pesticides in nanogram per liter sea water, H<sub>2</sub>SO<sub>4</sub> and KOH/meth clean-up.

TIME	AREA	RET	RF	C	NAME
14.75	.0548	.819	.0000	.0000	I
14.96	.8621	.831	.0000	.0000	I
15.15	.1983	.841	.0000	.0000	I
15.26	.1485	.847	.3162	.0125	ALFA-BHC:
15.33	.0684	.851	.3162	.0057	ALFA-BHC:
15.43	.4554	.857	.0955	.0116	HEXAKLOROBENZEN:
15.56	1.1134	.864	.0000	.0000	I
15.81	.1747	.878	.0000	.0000	I
16.08	.1541	.893	.0000	.0000	I
16.35	.6093	.908	.3152	.0512	GAMMA-BHC:
16.45	.4569	.913	.0000	.0000	I
16.61	.2130	.922	.3995	.0227	BETA-BHC:
16.70	.1226	.927	.0000	.0000	I
16.79	.1141	.932	.0000	.0000	I
17.05	.7395	.947	.0000	.0000	I
17.17	1.7264	.953	.0000	.0000	I
17.38	.1486	.965	.0000	.0000	I
17.51	.5409	.972	.0000	.0000	I
17.74	.7255	.985	.0000	.0000	I
18.00	2.9976	1.000	1.0000	.8000	INTERNAL STANDARD:
18.13	.2099	1.007	.0000	.0000	I
18.23	.2823	1.012	.0000	.0000	I
18.33	.1650	1.018	.0000	.0000	I
18.50	.1842	1.027	.0000	.0000	I
18.66	1.1192	1.036	1.8491	.5521	7 PCB-CL4:
18.80	2.7265	1.044	.9413	.6848	8 PCB-CL4:
19.03	.1143	1.057	.0000	.0000	I
19.13	.1259	1.062	.0000	.0000	I
19.28	.9675	1.071	.9930	.2556	11 PCB-CL4:
19.41	1.3973	1.078	.0000	.0000	I
19.65	1.0380	1.091	.4347	.1204	13 PCB-CL4:
19.93	.5236	1.107	.0000	.0000	I
20.10	.2198	1.116	.0000	.0000	I
20.24	.3428	1.124	.0000	.0000	I
20.36	.3422	1.131	.4754	.0434	15 PCB-CL4:
20.48	1.0559	1.137	.5679	.1600	16 PCB-CL4:
20.60	2.4882	1.144	.6325	.4200	17 PCB-CL5:
20.81	.3714	1.156	.4629	.0459	18 PCB-CL5:
21.16	1.6808	1.175	.2595	.1164	19 PCB-CL5:
21.35	4.3332	1.186	.3316	.3834	21 PCB-CL5:
21.54	.9524	1.196	.3731	.0948	22 PCB-CL5:
21.77	.3254	1.209	.0000	.0000	I
21.97	.1376	1.220	.3426	.0125	23 PCB-CL5:
22.17	.7241	1.231	.3623	.0703	24 PCB-CL5:
22.41	3.3579	1.245	.0969	.0868	PP-DDE:
22.55	.4544	1.252	.1245	.0150	DIELDRIN:
22.63	.6233	1.257	.1245	.0207	DIELDRIN:
22.77	4.3872	1.265	.2318	.2713	29 PCB-CL5:
23.20	2.3783	1.288	.1864	.1182	30 PCB-CL6:
23.40	1.6402	1.300	.1053	.0465	31 PCB-CL6:
23.74	4.2664	1.318	.2238	.2548	33 PCB-CL6:
23.87	5.5743	1.326	.1210	.1800	34 PCB-CL5:
24.24	.5384	1.346	.0000	.0000	I
24.42	.1186	1.356	.3710	.0117	PP-DDD-OP-DDT:
24.57	1.3135	1.365	.2305	.0809	36 PCB-CL6:
24.87	16.2931	1.381	.0989	.4296	37 PCB-CL6:
25.07	2.3645	1.392	.1976	.1248	38 PCB-CL6:
25.19	3.4953	1.399	.1022	.0952	39 PCB-CL5:
25.54	3.6960	1.418	.0710	.0700	40 PCB-CL6:
25.78	.0623	1.432	.0000	.0000	I
25.92	.4670	1.440	.0000	.0000	I
26.15	.9818	1.452	.5493	.1439	PP-DDT:
26.39	18.1254	1.466	.0691	.3340	42 PCB-CL6:
26.52	2.5748	1.473	.0691	.0474	42 PCB-CL6:
26.81	1.0300	1.489	.0000	.0000	I
27.13	.1765	1.507	.0000	.0000	I
27.31	3.5110	1.517	.0000	.0000	I
27.47	3.0632	1.535	.0000	.0000	I
27.94	.0458	1.552	.0000	.0000	I
28.15	3.8857	1.563	.0529	.0548	43 PCB-CL6:
28.34	.4374	1.574	.0000	.0000	I
28.90	3.2577	1.605	.0000	.0000	I
29.15	.0635	1.619	.0000	.0000	I
29.31	2.1982	1.628	.0000	.0000	I
29.65	1.6590	1.647	.0000	.0000	I
29.85	2.4483	1.658	.0000	.0000	I

Table 3. Content of PCB and pesticides in nanogram per liter sea water, Florisil clean-up.

THRESHOLDS	256	16			
EST	4	METHOD	1	FILE	10 31
TIME	AREA	R:1	RF	C	NAME
14.61	.0684	.811,	.0000,	.0000,	!
14.84	15.6908	.824,	.0000,	.0000,	!
15.32	23.4137	.851,	.3162,	1.5104,	ALFA-BHC:
		.857,	.0955,		HPAAALDORP.CFNI
15.55	2.4216	.863,	.0000,	.0000,	!
15.80	.8506	.877,	.0000,	.0000,	!
16.07	.4448	.892,	.0000,	.0000,	!
16.31	11.3100	.906,	.3152,	.7276,	GAMMA-BHC:
16.44	.9587	.913,	.0000,	.0000,	!
16.64	1.1873	.924,	.3995,	.0968,	BETA-BHC:
17.00	1.4422	.944,	.0000,	.0000,	!
17.20	.5449	.955,	.0000,	.0000,	!
17.37	.1045	.965,	.0000,	.0000,	!
17.51	.4627	.972,	.0000,	.0000,	!
17.73	1.3096	.985,	.0000,	.0000,	!
18.00	3.9190	1.000,	1.0000,	.8000,	INTERVAL STANDARD:
18.22	.3342	1.012,	.0000,	.0000,	!
18.33	.1041	1.018,	.0000,	.0000,	!
18.51	.1337	1.028,	.0000,	.0000,	!
18.66	1.7055	1.036,	1.8491,	.6437,	7 PCB-CL4:
18.80	3.1187	1.044,	.9413,	.5992,	8 PCB-CL4:
19.27	1.6357	1.070,	.9900,	.3305,	11 PCB-CL4:
19.40	1.5786	1.077,	.0000,	.0000,	!
19.64	1.3436	1.091,	.4347,	.1192,	13 PCB-CL4:
19.92	.2213	1.106,	.0000,	.0000,	!
20.14	.0223	1.118,	.0000,	.0000,	!
20.23	.0632	1.123,	.0000,	.0000,	!
20.35	.4706	1.130,	.4754,	.0456,	15 PCB-CL4:
20.48	1.8369	1.137,	.5679,	.2129,	16 PCB-CL4:
20.59	4.1118	1.143,	.6325,	.5308,	17 PCB-CL5:
20.81	.5360	1.156,	.4629,	.0506,	18 PCB-CL5:
21.15	2.0829	1.175,	.2595,	.1103,	19 PCB-CL5:
21.34	6.5504	1.185,	.3316,	.4432,	21 PCB-CL5:
21.55	6.4227	1.197,	.3731,	.4890,	22 PCB-CL5:
21.76	.3553	1.208,	.0000,	.0000,	!
21.97	.3443	1.220,	.3426,	.0240,	23 PCB-CL5:
22.17	1.5580	1.231,	.3623,	.1152,	24 PCB-CL5:
22.37	4.1049	1.242,	.0969,	.0811,	PP-DDT:
22.55	.7885	1.252,	.1245,	.0200,	DIELDRIN:
22.63	.9328	1.257,	.1245,	.0237,	DIELDRIN:
22.76	8.0873	1.264,	.2318,	.3324,	29 PCB-CL5:
23.20	3.3360	1.288,	.1864,	.1268,	30 PCB-CL6:
23.40	2.4016	1.300,	.1063,	.0520,	31 PCB-CL6:
23.73	6.1632	1.318,	.2238,	.2814,	33 PCB-CL6:
23.87	9.6313	1.326,	.1210,	.2376,	34 PCB-CL5:
24.24	.6689	1.346,	.0000,	.0000,	!
24.40	.5670	1.355,	.3710,	.0429,	PP-DDD-OP-DET:
24.57	2.0590	1.365,	.2305,	.0968,	36 PCB-CL6:
24.86	20.6572	1.381,	.0989,	.4168,	37 PCB-CL6:
25.07	3.4169	1.392,	.1976,	.1377,	38 PCB-CL6:
25.20	4.5241	1.400,	.1022,	.0943,	39 PCB-CL5:
25.54	5.0256	1.418,	.0710,	.0728,	40 PCB-CL6:
25.92	.8550	1.440,	.0000,	.0000,	!
26.09	1.5120	1.449,	.0000,	.0000,	!
		1.457,	.5493,		PP-DLT:
26.39	23.2243	1.466,	.0691,	.3264,	42 PCB-CL6:
26.51	3.3347	1.472,	.0691,	.0469,	42 PCB-CL6:
26.85	1.4712	1.491,	.0000,	.0000,	!
27.12	.1536	1.506,	.0000,	.0000,	!
27.31	3.8182	1.517,	.0000,	.0000,	!
27.43	3.4809	1.535,	.0000,	.0000,	!
28.16	4.7886	1.564,	.0529,	.0516,	43 PCB-CL6:
28.34	.4504	1.574,	.0000,	.0000,	!
28.63	.1949	1.590,	.0000,	.0000,	!
28.91	3.6080	1.606,	.0000,	.0000,	!
29.32	2.2690	1.628,	.0000,	.0000,	!
29.66	1.6956	1.647,	.0000,	.0000,	!
29.85	3.7435	1.658,	.0000,	.0000,	!

ADDENDUM

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PREPARATION OF XAD-2 RESIN	p	23
GAS CHROMATOGRAPHIC ANALYSIS AND CONFIRMATORY TESTS	p	24

ADDENDUM

Apparatus.

The apparatus described here will mainly be those used at the International Laboratory of Marine Radioactivity, Monaco and the Institute of Marine Research, Bergen, Norway.

1. The pump used is a Cole-Parmer pump ser. 6LS 93581 WZIR051.

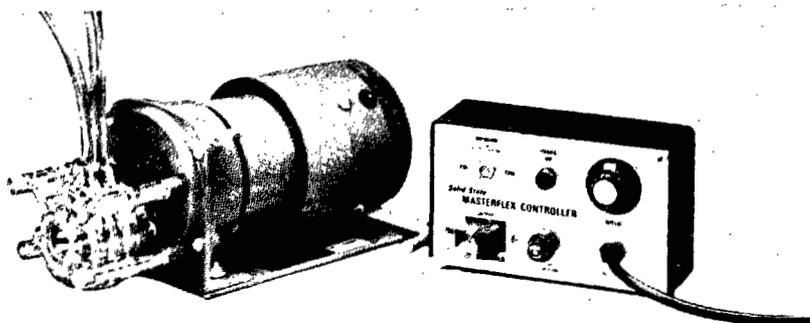


Fig. 11. Cole-Parmer pump for the suction of seawater through the XAD-2 resin.

2. The Seawater sampler suggested to be used for collection of water volumes up to 90 liters, is the Bodega-Bodman sampler. This is a modification of the Bodman Sampler (Bodman et al., 1961) made by Bodega Marine Laboratory in collaboration with R. Hamblin, Oceanic Industries, Osterville, Mass. USA (Fig. 12).

1) construction with non-contaminating materials, - anodized aluminum, stainless steel, teflon and viton; 2) 100 lb disk lead weights bolted directly to the bottom of the sampler and a one-way relief valve in the lid to permit subsurface cocking, such that the sampler could pass closed through the surface film, thereby minimizing a potential source of contamination; 3) the cylinder, constructed of aluminum, was maintained at its full diameter at both ends, facilitating cleaning and enhancing flushing as it descends through the water column; 4) the use of a Kullenberg piston core release mechanism allows sampling at pre-

cise distances from the bottom; 5) a magnetic switch on the upper plate of the sampler switches an integrally mounted 12 KHZ pinger to double pulse rate at the time of the trip, thus permitting continuous shipboard monitoring of the position and condition of the sampler; 6) a Swagelok Quick-connect purge valve in the lid for the attachment of a nitrogen gas line and a stainless steel ball valve with standard Swagelok connections at the bottom of the sampler allows the contents of the Bodega-Bodman to be transferred directly to a cleanroom for processing with limited exposure to the shipboard atmosphere; 7) positioning of the outlet valve in the center of the flat bottom plate reduces the potential for loss of larger settling particulates between sample collection and processing, which has been reported as a deficiency in similar samplers (Gardner, 1977).

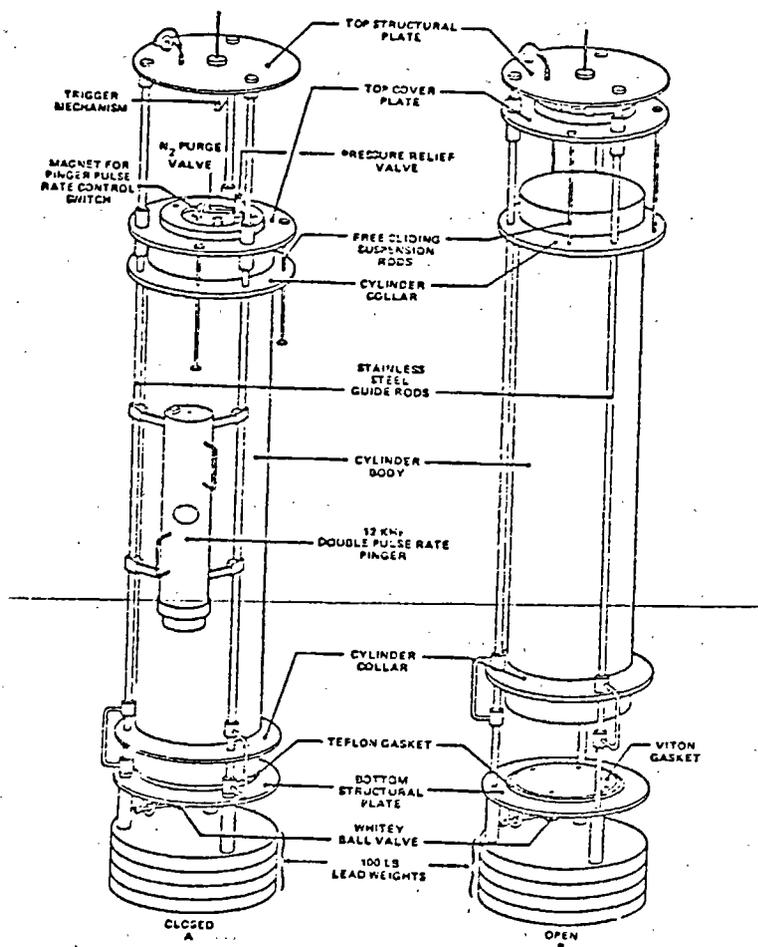


Fig. 12. The Bodega-Bodman sampler.

The figur nr.12 and the description of the sampler is copied from:

THE SAMPLING AND MEASUREMENT OF HYDROCARBONS IN NATURAL WATERS, by B.W. de Lappe, R.W. Risebrough, A.M. Springer, T.T. Schmidt, J.C. Shropshire, E.F. Letterman and J.R. Payne University of California, Bodega Marine Laboratory Bodega Bay, California 94923 (unpublished paper).

Chemicals and glassware.

Common sources of interference in the laboratory originate from glassware, chemicals and other materials used in the extraction and workup procedure, which have not been properly treated. Therefore, it is necessary to do routine and periodic checking of glassware and chemicals in order to ensure low blank values. For cleaning glassware the following procedure is recommended:

Wash all items in hot, soapy water and rinse thoroughly. Rinse each piece of glassware with pesticide-free acetone. Without drying the glassware, rinse each piece with pesticide-free hexane. Transfer the glassware to a drying oven and bake at 300°C for at least four hours, or at 250°C overnight.

A convenient procedure is to wash glassware by the described method each afternoon, place it in an oven equipped with an automatic timer set to shut off in the morning, so that it has time to cool by the time work commences each day. In this way, it can be used immediately and not exposed unnecessarily to the possibility of contamination.

The oven used in baking glassware and heating chemicals should be dedicated to chlorinated hydrocarbon analysis. Contamination, especially of chemicals such as  $\text{Na}_2\text{SO}_4$ , can take place if they are heated in an oven that has been used for other work.

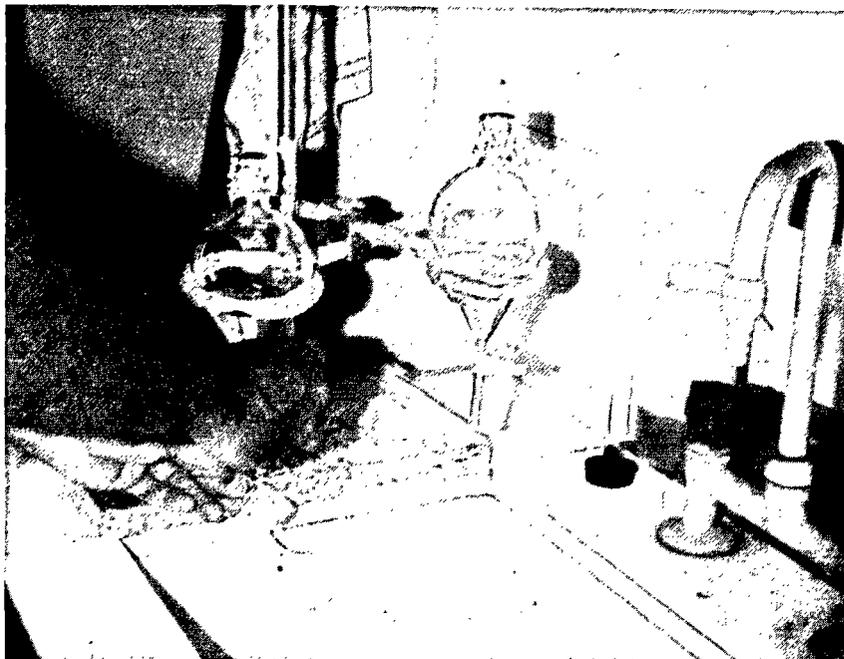


Fig. 13. Final rinse of glassware with acetone and hexane before baking at 250°C overnight.

The analyst should become familiar with other sources of contamination such as plastic wash bottles, plastic screw caps on glass or metal containers, PCB treated fibre glass used in air conditioning systems and as insulation, lubricating fluids, hydraulic fluids, paint chips, etc.

It should not be assumed that pesticide grade solvents are suitable for immediated use. Each new batch when received should be checked for background contamination by running blanks.

Chemicals such as  $\text{Na}_2\text{SO}_4$  and especially Florisil<sup>(R)</sup> have a tendency to adsorb contaminants from the atmosphere and should be periodically checked.  $\text{Na}_2\text{SO}_4$  can be cleaned by thoroughly washing with benzene and methylene chloride, followed by heating to 300°C in a clean oven. For details about handling Florisil<sup>(R)</sup>, the analyst should request the free bibliographies supplied by the manufacturer. (Floridin, 3 Penn Center, Pittsburgh, Pa. 15235).

Injection syringes must be kept clean. It is not unusual for a highly contaminated needle to need intensive cleaning before residual chlorinated hydrocarbons are removed. This could require 30-50 washings. Periodically, the syringe should be dismantled and soaked overnight in a suitable organic solvent such as acetone or ethylacetate. Since most new syringes are contaminated during manufacture, they should be thoroughly cleaned before use.

#### Preparation of XAD-2 resin

The commercially supplied XAD-2 resin beads are usually contaminated with a variety of organic compounds and fine particles formed by mechanical agitation during processing. Since batches vary, trial and error during the cleaning procedure is to be expected. The following has been fairly successful.

Shake the beads in a 50-60 mesh sieve to remove fine material and then wash those retained by the sieve with 30-50 volumes of tap water. Extract the beads in a Soxhlet for at least 24 hours using acetonitrile as a solvent. Change the solvent and repeat the extraction for an additional 24 hours.

Sometimes at this stage the resin is sufficiently clean to use; if not, additional extraction with different solvents such as benzene or acetone is necessary.

To check the progress of the clean-up procedure, a background blank determination is carried out.

To do this, pack a clean glass column (2 cm I.D.) with 50 cm<sup>3</sup> of extracted resin. Elute the column by gravity flow with 200 ml of boiling acetonitrile. Dilute the eluate with 600 ml of pesticide-free water. Extract this aqueous acetonitrile solution with two 80 ml portions of hexane. Extract the combined hexane fractions with 10 ml of pesticide-free water. Dry the hexane extract over a minimum amount of anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrate it to 0.5 ml in a Kuderna Danish concentrator or in a stream of dry

nitrogen. Analyze the extract for interfering compounds on a gas chromatograph using the same procedure that will be employed for seawater extracts. Calculate the interference on the basis of units of weight (usually ng) per litre. To do this, you must, of course know at this point the amount of seawater to be sampled.

If the blank is not acceptable, continue the cleaning process. When a satisfactory blank is obtained, the resin may be air dried and stored under pesticide-free water until needed.

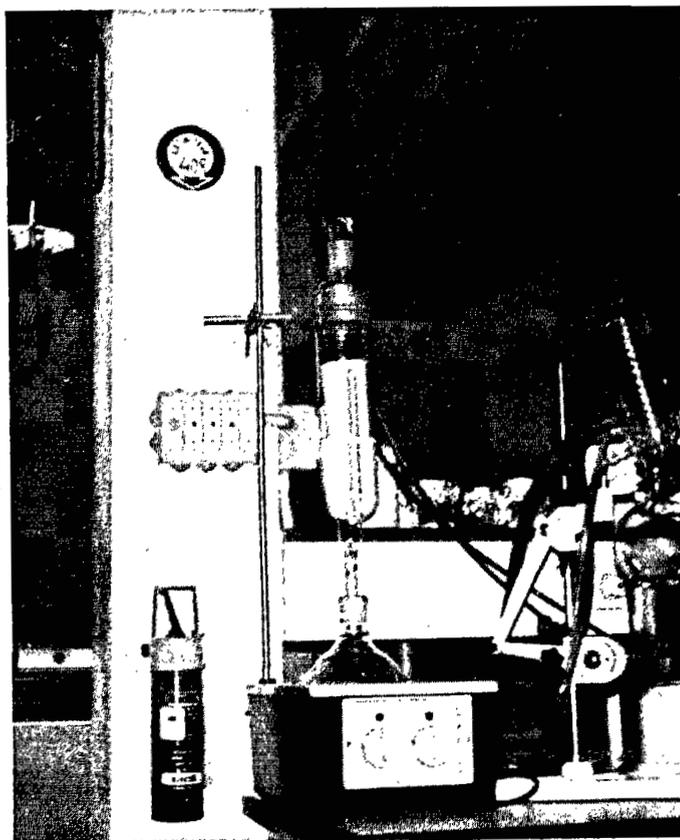


Fig.14. Reflux of XAD-2 resin with acetonitrile in a Soxhlet apparatus.

#### Gas chromatographic analysis and confirmatory tests.

Before injecting the sample, each syringe should be checked for the amount of residual solvent contained in the needle portion. Generally, liquid contained in the needle at the completion of an injection is also evaporated onto the column due to the high

temperature of the injector. In some cases, the amount of residual solvent can be in the range of 0.05-0.5  $\mu$ l. This can change the calculated results considerably if not accounted for when injections in the  $\mu$ l range are being used.

Qualitative analysis of the chlorinated hydrocarbons in question is done by comparison of retention times for samples with standard solutions, preferably on at least two columns which differ considerably in the polarity of their stationary phases. Additional identification of the compounds of interest can be done by chemical alteration followed by qualitative analysis (as well as quantitative analysis in some cases). Such confirmation procedures are exemplified by the following procedure for the dehydrochlorination of p,p'-DDD and p,p'-DDT to form p,p'-DDMU (2-chloro-1,1-bis (p-chlorophenyl) - ethylene and p,p'-DDE respectively:

To each of two 0.1-0.5 ml aliquots of concentrated extract, contained in graduated centrifuge tubes, add 1 ml of 0.1 N NaOCH<sub>3</sub>/methanol solution. Heat the two mixtures to 50°C in a water bath. For DDT confirmation heating should be for 30 mins; for DDD heat for 1 hr. Allow the two reaction mixtures to cool and then add 5 ml of pesticide-free water and 1 ml of pesticide-free hexane. Extract the newly formed derivatives by shaking the reaction mixtures vigorously; then let stand until the hexane and aqueous phases separate. Remove the hexane phases. Re-extract the aqueous phases with an additional 1 ml portion of hexane. Combine the two extracts for each of the two experiments and reduce each in volume to a suitable concentration for gas chromatographic analysis. DDE oxidized by chromic acid.

Whenever possible confirmation should be carried out using GC-MS techniques (mass-fragmentography).

For chemical derivation procedures to confirm the presence of other chlorinated hydrocarbon compounds the reader is referred to standard references such as "The Pesticide

Analytical Manual" (Vol. I. U.S. Department of Health, Education and Welfare, Food and Drug Administration, Rockville, Md.)

Quantification of PCBs and DDT residues is accomplished by comparing peak heights in sample chromatograms with those produced by reference standards. The peaks in the chromatograms of sample extracts should be bracketed by those of standards because of the limited range of linear response by the ECD. In the case of PCBs the sum of the 5 major peaks in the standard solution should be used (if a peak is missing in the sample chromatogram the quantity zero is used in the summation).

The following formula will give the concentration of a chlorinated hydrocarbon in a water sample:

$$[\text{CH}]_{\text{ng/l}} = \frac{\text{Ht}_{\text{sam}}}{\text{Ht}_{\text{std}}} \times \frac{\text{Wt}}{\text{V}_{\text{samp}}} \times \frac{\text{V}_{\text{ext}}}{\text{V}_{\text{inj}}} \times 10^3$$

Where:

$[\text{CH}]_{\text{ng/l}}$  = concentration of chlorinated hydrocarbon in nanograms/liter.

$\text{Ht}_{\text{sam}}$  = peak height of chlorinated hydrocarbon on sample chromatogram.

$\text{Ht}_{\text{std}}$  = peak height of chlorinated hydrocarbon on standard solution chromatogram.

$\text{Wt}$  = weight in nanograms of chlorinated hydrocarbon giving  $\text{Ht}_{\text{std}}$ .

$\text{V}_{\text{samp}}$  = volume in liters of water extracted.

$\text{V}_{\text{ext}}$  = final volume of extract in ml.

$\text{V}_{\text{inj}}$  = volume of extract in microliters giving  $\text{Ht}_{\text{sam}}$ .

It should not be implied that the method outlined is the only method or necessarily the best method. It can, however, be

considered as "state-of-the-art" along with other methods presented in recent literature references.

The following list of references include those which describe techniques for isolating chlorinated hydrocarbons from seawater. In addition, there are some references which discuss problems with contamination; a few references reporting results on samples using the techniques referenced and some containing descriptions of the advantages and disadvantages of the various techniques.

This list is by no means exhaustive, but contains the most important references describing the three main techniques commonly used for chlorinated hydrocarbon analysis.

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## SAMPLING INTERCALIBRATION OF TRACE-METALS

### Introduction

The recently completed ICES Fourth Round Intercalibration for Trace Metals in Seawater has enabled the analytical procedures for the determination of trace metals to be evaluated. The results from higher precision laboratories show that, whilst different sample treatments can have systematic influences upon analytical data, differences in instrumental techniques (e.g., atomic absorption versus anodic stripping voltammetry) have small effects. The purpose of the IOC Sampling Intercalibration Workshop is to examine biases, or differences between alternative sampling techniques that can influence the results of seawater analyses.

### Experimental Design

The most commonly used sampling techniques for trace-metal determinations in seawater are the use of General Oceanics<sup>R</sup> GO-FLO or NISKIN samplers or HYDRO-BIOS bottles deployed on various types of hydrographic wire. Although in most cases the samplers are modified to some degree to minimize contamination problems, the basic devices differ little throughout the developed countries. The preferred types of hydrowire are plastic-coated stainless steel, Kevlar, and nylon. Nevertheless, until recently, much use was made of stainless steel, and many surveys have been carried out using this type of hydrographic wire.

The chosen design seeks to ensure the influences of these different sampling bottles and hydrowires upon the resultant analytical data. The design involves two experiments to examine differences between a) sampling bottles and b) hydrowire.

#### a) Sampling bottle intercomparison

The three most common sampling bottles used in trace metal work -GO-FLO, NISKIN, and HYDRO-BIOS - will be deployed in series on a single wire (Kevlar) in a deep water mass which, from hydrographic considerations, can be assumed to be homogeneous over depth scales greater than the sampling depth sequence. Sets of 4 to 6 samples will then be drawn directly from each sampling bottle and frozen or acidified (according to the participant's needs) and shipped to his laboratory for analysis. One such cast will be carried out for each participant. Thus each participant will receive up to 18 samples for analysis in triplicate at his home laboratory. If sufficient participants have adequate precision and detection limits, this should enable a detailed assessment of the relative sampling bottle influences to be made.

#### b) Hydrowire intercomparison

Sets of single GO-FLO bottles will be deployed sequentially on different hydrowires to examine hydrowire influences. Each participants will receive six samples from a single GO-FLO sampler

deployed in a common water mass on each of three hydrowires (Kevlar, stainless steel, and plastic-coated stainless steel). Thus a total of 18 samples will need to be analyzed in triplicate by each participant so as to determine the relative differences between hydrowires as exhibited by the analytical data.

#### On-Site Intercalibration

In addition to the core experiments proposed above it is also intended to enable participants to undertake, at their discretion, an examination of sample-handling techniques at the BBS. A large volume sample 4500 litres will be collected and placed in a large polyethylene container with teflon enclosure manifolds. Participants will be able to draw water from this container to test the effects of various treatments especially the effect of different filters and filter holders. Analytical facilities including clean bottles, laminar-flow hoods and atomic absorption spectrophotometers will be available at the BBS for the analysis of samples from this container.

#### Operations

As described in the R/V KELEZ schedule of operations.

#### Participants' Requirements

Each participant will be required to bring a minimum of 36 precleaned sample storage bottles to BBS. If he wishes to join in the optional third stage of the trace-metal intercalibration, he should also bring additional pre-cleaned sample bottles and any filtration equipment they wish to test to Bermuda. He should also ensure that an adequate supply of high purity acid is brought if he intends to acidify his samples prior to shipment from Bermuda to his home laboratory. Facilities for freezing samples will be provided by BBS. Participants must undertake to arrange the shipment of sample sets from Bermuda to home laboratory, to conduct the analyses of the samples before 1 May 1980, and return the analytical data to the Scientific Committee by 15 June 1980.\*

In the event that a participant is unable to pre-clean his sample storage bottles prior to his arrival in Bermuda, some facilities for bottle washing are available at BBS but are likely to be severely limited. High purity water will be available on site.

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\* assistance with transportation arrangements will be provided by BBS staff and the Administrative Committee.

FACILITIES AND SERVICES OF THE BERMUDA BIOLOGICAL STATION

The Bermuda Biological Station for Research, Inc. (BBS), has offered its facilities for the Workshop of the IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-Ocean Waters. The BBS will make available facilities (room/board/laboratories) for 40 participants from January 1st to January 26th, 1980. BBS will provide transport from the research ship "KELEZ" to the BBS laboratory by one of its research boats at no additional charge to IOC. If ferrying of participants to Station 'S' ("Panulirus" Station) is required, BBS will provide ship time at no extra cost.

BBS will provide: a room for seawater sample storage; 1 room for pre-treatment of seawater samples for chlorinated-hydrocarbon analyses; and one room for trace-metals; a room for gas chromatographs (GC); an additional room for gas chromatograph and mass spectrometer (GC/MS); and a room for atomic absorption spectrophotometers (AAS). Varian Associates and Perkin-Elmer will each provide two (2) Gas Chromatographs with electron capture detectors (1 capillary, 1 packed column), and one (1) flameless AAS each. The factories will provide also appropriate technical service. It is expected that BBS will provide laminar flow hoods. Drs A. Knap and K. Palmork will contact Hewlett-Packard for a temperature-programmed glass capillary ECD/GC, and the Finnegan Corporation for the loan of a (OWA) GC/MS.

Full room and board will amount to \$320 per week per participant.

BBS will also be responsible for necessary glassware and chemicals.

The IOC will provide BBS with \$10,000 to cover partially the BBS costs (see BBS expenditure). UNEP was asked for an additional \$5,000 for expendable equipment.

FACILITY UTILIZATION COSTS

Ship time	\$	5,000
Expendable equipment:		
Glassware, gases, solvents, acids	\$	15,000
Salaries (50% overhead)	\$	15,000
Secretarial (photocopying)	\$	2,000
Preparation of laboratories	\$	13,000
		<hr/>
Total costs	\$	50,000
IOC contribution	-	\$ 10,000
Expected UNEP contribution	-	\$ 5,000
		<hr/>
BBS contribution	\$	35,000
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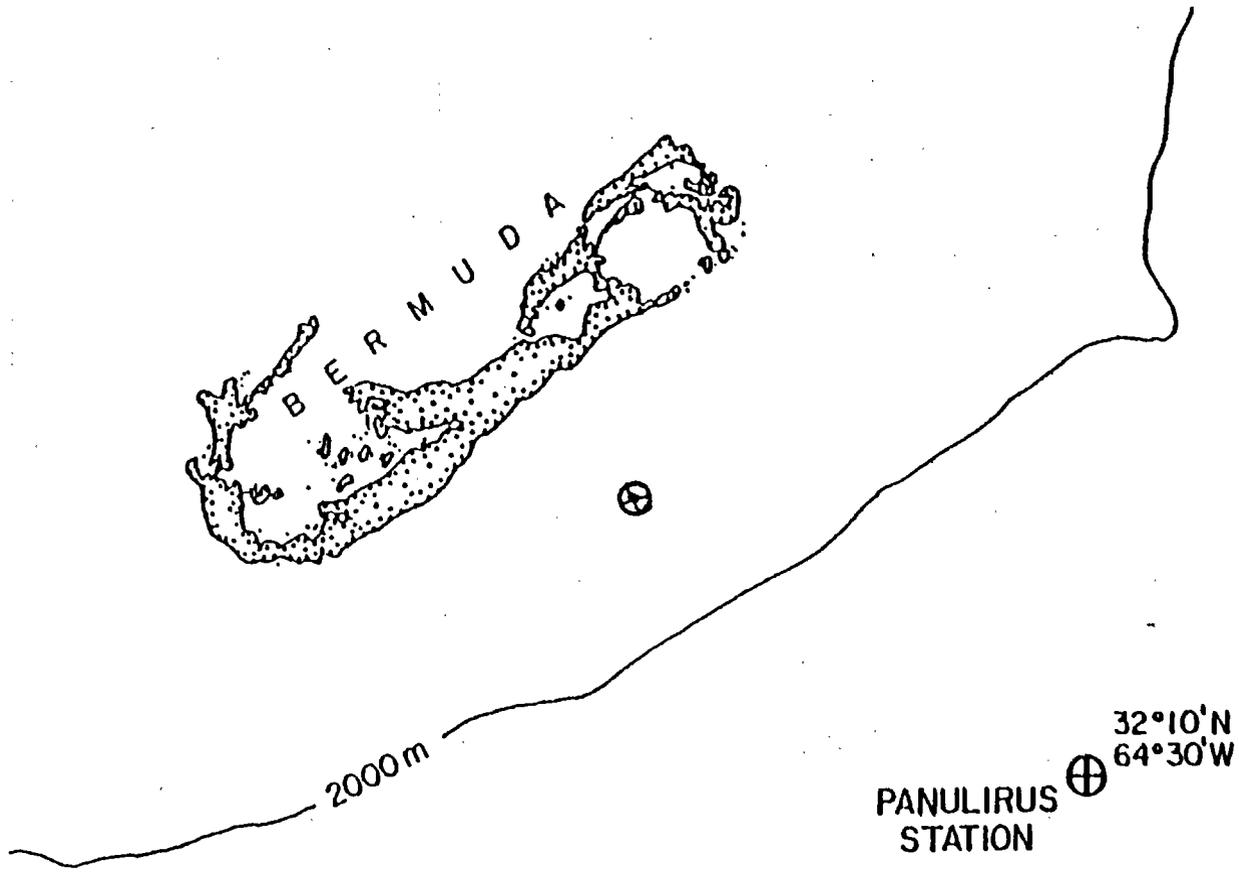
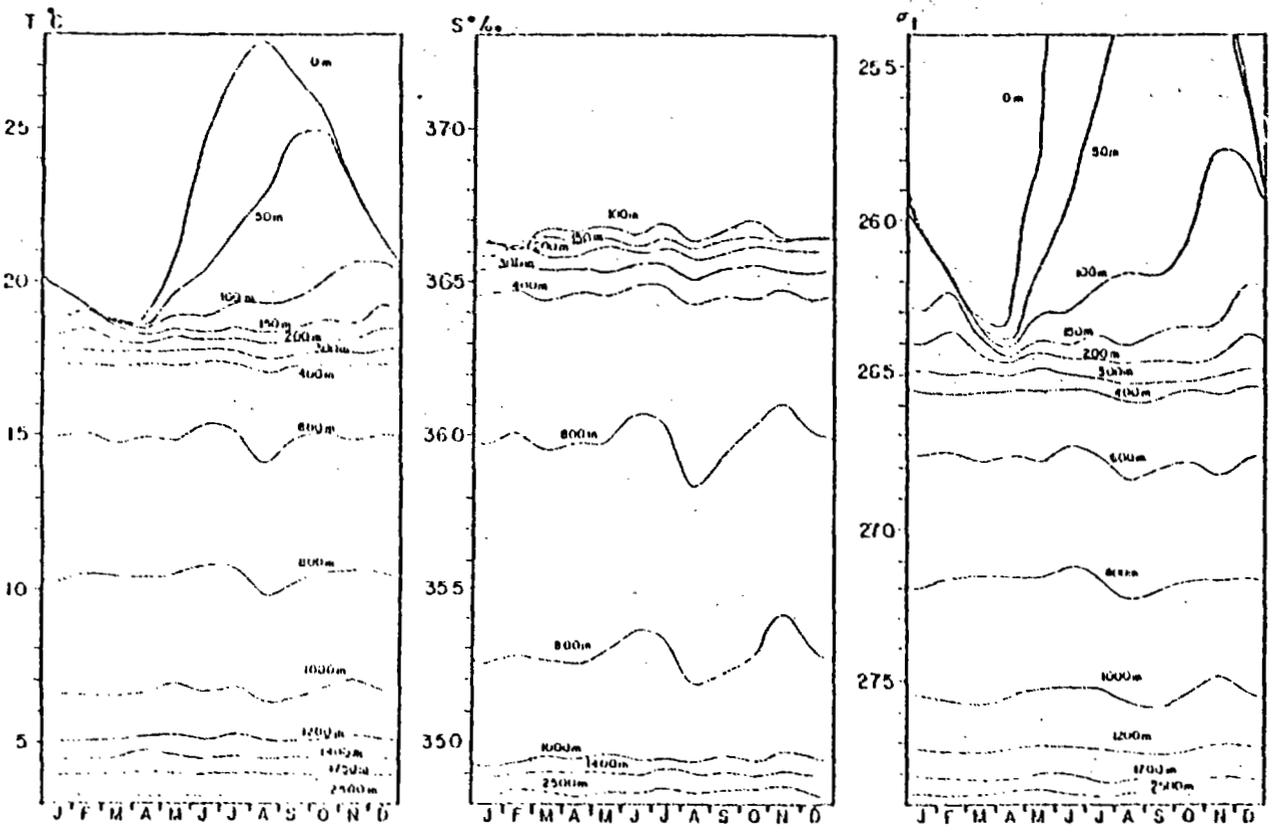


FIGURE 1: *Panulirus* Station Location



Depth-time of Temperature, Salinity and Sigma-T at the Kaulbar Station

OPERATION OF R/V "KELEZ" FOR THE INTERCALIBRATION EXPERIMENT

January 13-21 1980

Presently, the R/V GEORGE B KELEZ (R-441) will operate out of St. GEORGES from the period 13-21 January 1980. In-port and docking assistance will be provided through MEYERS SHIPPING AGENCY (attention Capt. J. Willard Moore).

The vessel will arrive equipped with 3 vans:

- a clean van located athwartships on the main deck;
- a chemistry van located on the port side of the main deck;
- a geology van located on the starboard side of the main deck.

Two winches, a hydraulic hydro-winch with 2000 m of 3/16" stainless cable and an electric hydro-winch with KEVLAR cable, provided by NOAA's Atlantic Ocean Marine Laboratory, will be mounted on the main deck, for operation through the starboard A-frame. A crane and a Rowe oceanographic winch will also be available if operations require. The Rowe winch is equipped with 3000 of 1/2" galvanized cable.

Navigation will be by radar and LORAN C.

Primary vessel operations are planned for 6 days (14-20 January (a.m.)) according to the following schedule:

- (1) Departure to the Panulirus station will be in the late morning or the early afternoon;
- (2) Work will be round the clock with sampling for either trace metals or chlorinated hydrocarbons on alternative days;
- (3) Sampling operations will be suspended in time to arrive at the Bermuda pilot's station at sunrise;
- (4) Docking will follow with turn-around time allowed for off-loading personnel and equipment;
- (5) Ship will then return to sea to follow a similar schedule.

Weather may cause delays in arrival, loss of operational time and/or may necessitate early departure.

After four days of full operation, activities will be suspended so that the ship may re-fuel and take on water and provisions at the Naval Station Annex at Hamilton. Staging will occur probably during the normal working day. However, these tasks will be completed in the least possible amount of time.

Because of the round-the-clock operations, the ship will be able to provide accommodation for only 6 scientists, including women, in a 2-berth and a 4-berth cabins.

Scientific personnel are reminded that weather and safety are critical factors in winter operations. The following equipment is recommended for all personnel:

- (1) Warm clothing including coat or sweater
- (2) Close-toed shoes
- (3) Foul-weather gear -Jacket necessary, boots and pants optional.
- (4) Gloves for heavy work
- (5) Sea-sickness pills.

The R/V KELEZ will be docked at Norfolk, Va., from 15 November to 10 January, with staging planned for 2-9 January. All equipment to be transported by the KELEZ should be delivered and ready for loading by 31 December 1979. All items should be identified as being for use in the Intercalibration Experiment at the Bermuda Biological Station, and should be shipped to:

NOAA Ship GEORGE B KELEZ  
Atlantic Marine Center,  
439 W. York St.,  
Norfolk, Va. 23510.

A list of items should also be sent to the same address. It is hoped that any customs formalities can be handled between station personnel and local officials.

Cruise and project instructions should be sent to the ship as soon as possible. Instructions should be prepared in accordance with standard NOAA-NO 5 procedures.

A final note:

In completing a standard cast, the vessel will generally work with its stern into the winds and seas, favoring the starboard quarter. This enables straight wire angle and a level platform to be maintained, as well as protecting all personnel.

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LIST OF FACILITIES PROVIDED FOR THE WORKSHOP

The Bermuda Biological Station for Research

1. Clean laboratory with the positive pressure inside, for trace-metal analyses
2. Two ceramic-tiled laboratories for pre-treatment of the sea-water samples for chlorinated hydrocarbon analyses
3. Three laboratories for gas chromatographs and atomic-absorption spectrophotometers
4. Laboratory for storage of special sampling equipment and containers for sea-water samples
5. Two conference rooms
6. Equipment and glassware for sea-water analyses
7. Solvents, other chemicals and standards for chlorinated-hydrocarbon analyses
8. Containers for collection of sea water
9. Copying machine
10. Transportation facilities (car, motor-boats)
11. Accommodation and full board for participants

The US National Oceanic and Atmospheric Administration

1. R.V. GEORGE B. KELEZ
2. Clean van for preparation of sea water samples for trace-metal analyses
3. Chemistry van
4. Geology van
5. Hydraulic hydro-winch with 2000 meters of 3/16" stainless-steel cable
6. Electric hydro-winch with Kevlar cable
7. Crane and a Rowe oceanographic winch with 3000 meters of 1/2" galvanized cable
8. Gas-lift pumping system
9. Installation for extraction of sea-water samples for chlorinated-hydrocarbon analyses
10. Stainless-steel drums for collection of sea-water samples
11. Two BODMAN bottles
12. Concrete hydroweight set on polyethylene
13. Meter wheel assembly
14. Modified 10 l GO-FLO bottles
15. Two satellites NOAA-6 and NIMBUS-7

Bedford Institute of Oceanography

1. 600-litre plastic tank for storage experiments
2. Modified and unmodified 12-litre GO-FLO bottles
3. 12-litre NISKIN bottles
4. 3000 metres of Type 302 stainless-steel hydro-wire

Deutsches Hydrographisches Institut

1. 4000 metres plastic-coated galvanized-steel hydro-wire
2. 12 HYDRO-BIOS bottles

Skidaway Institute of Oceanography

1. 1500 metres of Kevlar hydro-wire
2. High-purity pumping system

Apparatus and accessories

Gas Chromatographs

1. Hewlett-Packard  
5340 A Gas Chromatograph equipped with Electron Capture Detector (ECD) and 30 m fused-silica capillary columns covered by SE-54  
  
Accessories: 18835 B Capillary Inlet System  
5840 A GC Terminal
2. Perkin-Elmer  
Two Sigma 3 B GC Gas Chromatographs equipped with Electron Capture Detector (ECD) and 2 m glass-packed columns (liquid phase 1,95% OV-17 + 1,5 OV-101)  
  
Accessories: Sigma 10B GC Data Station  
Recorders  
Battery Backup Pack 332-2400
3. Varian  
Gas Chromatograph Model 3700 equipped with Electron Capture Detector (ECD) and 30 m fused silica capillary columns covered by SE-54  
  
Accessories: Chromatographic Data Systems CDS 111  
9176 Recorder

Atomic Absorption Spectrophotometers

1. Perkin-Elmer  
5000 Atomic Absorption Spectrophotometer  
  
Accessories: Graphite Furnace  
HGA 500 Programmer  
Printer Sequencer PRS-10  
Recorder 56
  
2. Varian  
AA 775 Series Atomic Absorption Spectrophotometer  
  
Accessories: CRA 90 Carbon Rod Atomizer  
Model 65 Vapour Generation Accessory  
ASD-53 Atomic Sample Dispenser

Additional equipment and chemicals provided by participants

1. Sampling set for immediate liquid-liquid extraction of chlorinated hydrocarbons (Dr. H. Gaul)
2. XAD-2 columns for preparation of sea-water extracts of chlorinated hydrocarbons (Dr. Villeneuve)
3. XAD-2 columns for in situ extraction of chlorinated hydrocarbons
4. Equipment for sampling of microlayer (Dr. Pellenbarg)
5. Standard solutions of PCB compounds (Dr. Duinker)
6. Standard solutions of chlorinated hydrocarbons (Dr. Villeneuve)
7. Some chemicals for trace-metal analyses (Dr. Lee)

COMPOSITION OF THE TEAMS

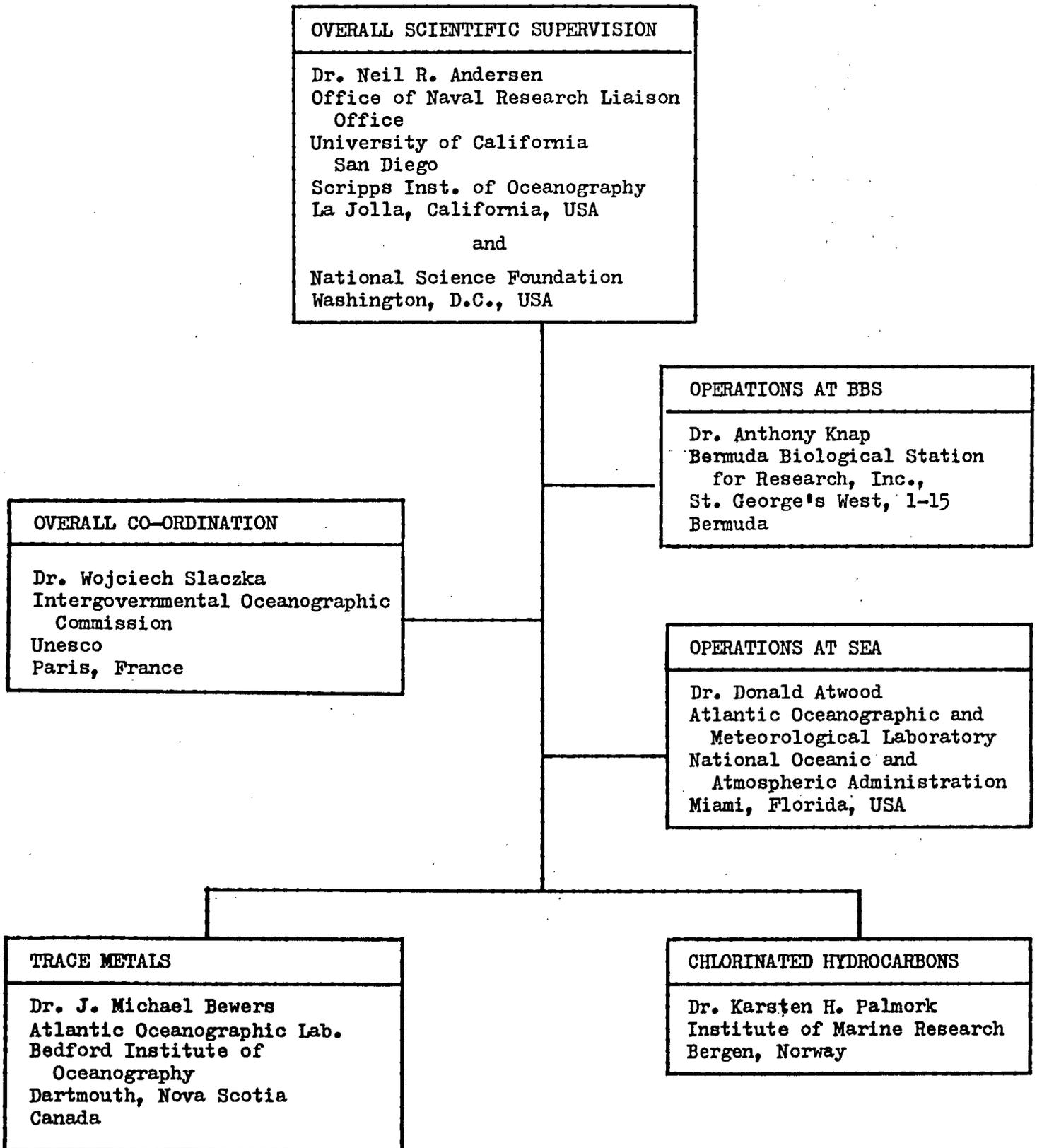
Chlorinated-hydrocarbon Team

J. Duinker  
H. Gaul  
M. Hillebrand  
J. Leonard  
K. Palmork  
K. Sullivan  
J.P. Villeneuve  
S. Wilhelmsen  
A. Knap  
D. Elder (observer)

Trace-metal Team

M. Ambe  
D. Atwood  
M. Bowers  
L. Brüggemann  
T. Church  
J. Duinker  
K. Lee  
C. McLeod  
J. Olafsson  
R. Pellenbarg  
S. Piotrowicz  
R. Presley  
D. Schmidt  
M. Sivalingam  
R. Smith  
F. Storti  
G. Topping  
J. Tramontano  
D. Waslenchuk  
H. Windom  
P. Yeats  
A. Orlando (observer)  
M. Bernhard (observer)

COMPOSITION OF THE WORKSHOP STEERING COMMITTEE



CHLORINATED-HYDROCARBON SAMPLING PROGRAMME

Planned Shipboard Operation - First Day

Sequence of shipboard operations

1. Eight 90-1 BODMAN-bottles to 5-10 metres  
to fill:           2       210-1   Stainless steel drums  
                  2       50-1   Glass carboys  
                  1       90-1   Bodman-bottle  
  
TOTAL                   610-1  
  
Time =                   3 hours
  
2. Start extractions immediately, using glass columns with XAD-2 resin.
  
3. 1 BODMAN-bottle to 1200 m  
to fill:           2       50-1   Glass carboys (~ 90-1 actually taken)  
  
Time =                   1 hour
  
4. Return to Bermuda  
  
TOTAL TIME =       8 hours, port to port

Planned Shipboard Operation - Second Day

The aim was to intercalibrate both sampling and analytical methods. The following samplers were used:

- (1) one 90-litre anodized aluminium BODMAN bottle
- (2) a stainless steel gas-lift pumping system
- (3) an in-situ XAD-2 extraction system
- (4) three 10-litre glass sampling/extraction flasks

The following samples were to be obtained:

- 1) 50 litre samples from gas-lift, BODMAN bottle and glass sampling/extraction flasks, to be extracted and analyzed by Gaul at Bermuda, to compare the three sampling methods.

The gas-lift and BODMAN bottle samples are to be stored in two stainless steel drums. Transfer from drums to Gaul's flasks will be through stainless steel piping.

- 2) One 50-litre sample from BODMAN bottle and one 50-litre sample from gas-lift pumping system (columns for both to be supplied by Villeneuve) and two 50-litre samples from in-situ XAD-2 extraction system (one column each to be supplied by Villeneuve and Sullivan), to compare the three sampling methods and to compare (by combining the results with those of the preceding exercise) the extraction by solvents and XAD-2 columns, including a comparison between the two types of columns.

Samples to be analyzed at Bermuda.

The BODMAN and gas-lift samples to be transferred from the stainless steel drums as in the preceding exercise. The samples obtained in the exercises 1) and 2) are to be analyzed by one person, or a small team, consisting of Villeneuve, Gaul, Sullivan, Hillebrand and Wilhelmsen. Determination of blanks is included.

- 3) Fourteen 50-litre samples in separate glass carboys will be obtained from the gas-lift pumping system. XAD-2 resin columns and transfer systems to be supplied by Villeneuve. Two XAD-2 columns will be supplied to each participant, one of which must be analyzed at Bermuda by him; the second one is to be analyzed in the home laboratory. The analytical procedure to be used at the home laboratory is left to the analyst's discretion. However, full details of the modifications of the procedures suggested at Bermuda will be supplied by each participant along with his results.

Inter-laboratory differences should become apparent from these results.

To analyze any temporal variation in homogeneity in respect of organochlorines, one of these fourteen carboys will be specifically designed for sampling and analyzing water at regular intervals during the entire sampling period. Individual 50-litre samples will be transferred to individual XAD-2 columns (transfer system and columns to be supplied by Villeneuve). The carboy will be refilled when empty to allow the extraction of the next 50-litre sample by the next column.

The analysis is to be performed at Bermuda preferably by the same person or a small group of persons.

The activities on board were scheduled as follows:

Start with filling three Gaul flasks (1 hour)

Start filling glass carboy no. 1 as soon as possible. This carboy should be the one designated for the study of time variation. Continue operation with the gas-lift pumping system so as to fill 13 carboys and one stainless-

steel drum with at least 100 litres (two BODMAN casts will be required).

The designated carboy will be used for extraction with XAD-2 resin columns repeatedly during the whole sampling period. The other samples to be extracted are next in priority; the remaining samples will be extracted in the laboratory.

Gaul will require 4 hours to extract his first samples and prepare the flasks for the next cast. If three flasks are available, two casts will be sufficient to obtain at least 50 litres. The extracts of 5 samples (each 10 litres) will be combined for analysis.

TRACE-METAL SAMPLING PROGRAMME

In view of restrictions on ship time imposed by the adverse weather conditions, the following contingency plans were devised to meet probable cuts in total ship time originally required for the completion of the trace-metal exercise.

If the time available is

- 3 days Stay with original design.  
Planned shipboard operations for each day remain unaltered.
- 2 days Reduce redundancy in the original design  
Plans for first day remain unaltered.  
On the second day 2 modified and 2 unmodified GO-FLO samplers will be deployed on the remaining 2 hydro-wires.  
Each participant will receive 16 samples in addition to the 12 collected on the first day.
- 1 day Restrict experiment to a comparison of sampling bottles bottles using only a single hydro-wire type.
- 0 day Use the large-volume container to collect a subsurface sea-water sample with the Biological Station's work boat (Mic Mac).  
Sub-sample this water to provide each participant with up to 8 samples for analysis in the Station and in home laboratories.

PARTICIPANTS INSTRUCTIONS FOR SAMPLE COLLECTION

SCIENTIST	BOTTLE TYPE	FILLING	PRESERVATION
AMBE	1 litre Plastic	Leave small air gap	None
	5 litres Poly.	Leave small air gap	None
	500 ml Glass	Leave small air gap	Bottles contains acid
BEWERS/YEATS	2 litres CPE	Remove Red Flash Drain to waste Shake out drops Fill to shoulder	5 ml ULTREX HCl using dispenser provided. Cap and tighten with plastic spanner
BRUGMANN	500 ml Silica with Poly. Stopper (bagged)	Leave small air gap	1 ml conc HNO <sub>3</sub> with pipette provided. Wash tip in HNO <sub>3</sub> once before use. Cap and reseal bottles in plastic bags.
CHURCH		Rinse twice. Fill to 800 ml.	2 ml HNO <sub>3</sub> with pipette provided.

SCIENTIST	BOTTLE TYPE	FILLING	PRESERVATION
DUINKER	1 litre CPE	Rinse twice. Fill to 2 cm below neck.	2 ml MERCK HCl
LEE	1 litre Poly.	Rinse once. Fill to line on bottle neck.	5 ml redistilled HNO <sub>3</sub> with dispenser provided. Replace double caps.
MCLEOD	1 litre Poly.	Rinse once. Leave small air gap.	Bottle contains 1 ml ULTREX HNO <sub>3</sub> .
OLAFSSON	500 ml Pyrex (bagged)	Rinse three times. Fill to 400 ml level.	8 ml HNO <sub>3</sub> (MERCK 456) using dispenser provided. Rinse dispenser twice with acid before use. Seal tight and replace in plastic bag.
	1 litre CPE	Rinse three times. Leave air gap.	5 ml redistilled HCl using dispenser provided. Rinse dispenser twice with acid before use. Seal tight and replace in plastic bag.
PELLENBARG	500 ml CPE	Rinse twice with 10 ml S.W. sample. Fill to 1 cm below shoulder.	250 µl conc. HNO <sub>3</sub> with Eppendorf pipette provided. Place sample in refrigerator.
PIOTROWICZ	1 litre Teflon		1 ml ULTREX HNO <sub>3</sub> with pipette provided.
	250 ml Teflon		250 µl ULTREX HNO <sub>3</sub> with pipette provided.
PRESLEY		Do not rinse.	1 ml ULTREX HNO <sub>3</sub>
SCHMIDT	500 ml Teflon	Rinse with 100 ml SW sample.	1 ml redistilled HCl with dispenser provided.
SIVALINGAM	300 ml Glass	Rinse three times.	500 µl MERCK HCl
WASLENUK	1 litre CPE (bagged)	Rinse twice. Fill to shoulder.	500 µl conc. HNO <sub>3</sub> with Eppendorf pipette provided. Use new pipette tip each time. Replace bottle in zip-lock bag and reseal.
WINDOM/SMITH	250 ml Teflon (bagged)	Drain. Rinse twice	200 µl NBS HNO <sub>3</sub> with Eppendorf pipette provided. Tip must be rinsed with 10% HCl before dispensing NBS acid. Replace bottle in plastic bag and seal.

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Poly = Polyethylene

TRACE-METAL SAMPLING PROGRAMME

Planned Shipboard Operations - First Day

Sequence of shipboard operations

1. Swing weight over side and lower to sea surface.
2. Zero meter block.
3. Lower to 50 M.
4. Attach Reversing Bottle to wire. (No. 10) (KNUDSEN)
5. Lower to 55 M.
6. Attach No. 9. (HYDRO-BIOS)
7. Lower to 60 M.
8. Attach No. 8 (HYDRO-BIOS)
9. Lower to 65 M.
10. Attach No. 7. (HYDRO-BIOS)
11. Lower to 70 M.
12. Attach No. 6 (HYDRO-BIOS)
13. Lower to 75 M.
14. Attach No. 5. (HYDRO-BIOS)
15. Lower to 80 M.
16. Attach No. 4. (HYDRO-BIOS)
17. Lower to 85 M.
18. Attach No. 3. (GO-FLO)
19. Lower to 90 M.
20. Attach No. 2. (NISKIN)
21. Lower to 95 M.
22. Attach No. 1 (HYDRO-BIOS)
23. Lower to 1300 M.

Prior to the following series of hydrocasts the bottles will be deployed in sequence, tripped and recovered. The water from this preliminary cast will be discarded to waste. This cast is intended to provide a messenger and bottle trip test as well as some sampling bottle acclimatization.

- CAST 1. Cast consists of 1 NISKIN, 1 modified GO-FLO and 7 HYDRO-BIOS bottles on hydro-wire.  
Samples taken for Lee and Pellenbarg. Additional homogeneity check samples collected.
- CAST 2. Cast consists of 1 NISKIN, 1 modified GO-FLO and 7 HYDRO-BIOS\*) bottles on KEVLAR hydro-wire.  
\*) One HYDRO-BIOS bottle malfunctioned.
- CAST 3. Cast consists of 1 NISKIN and 2 modified GO-FLO bottles on KEVLAR hydro-wire.  
Samples taken for Church, Duinker, Schmidt and Sivalingam.
- CAST 4. Cast consists of 1 NISKIN and 2 modified GO-FLO bottles on KEVLAR hydro-wire.  
Samples taken for Bowers/Yeats, Brugmann and Windom/Smith.

- CAST 5. Cast consists of 1 NISKIN and 2 modified GO-FLO bottles on KEVLAR hydro-wire.  
Samples taken for McLeod, Piotrowicz and Presley.
- CAST 6. Cast consists of 1 NISKIN and 2 modified GO-FLO bottles on KEVLAR hydro-wire.  
Samples taken for Ambe.
- CAST 7. Cast consists of 2 modified and 2 unmodified GO-FLO bottles on STAINLESS STEEL hydro-wire.  
Samples taken for Duinker, Lee, Olafsson, Pellenbarg, Schmidt and Sivalingam.
- CAST 8. Cast consists of 2 modified and 2 unmodified GO-FLO bottles on STAINLESS STEEL hydro-wire.  
Samples taken for Bewers/Yeats, Church and Windom/Smith.
- CAST 9. Cast consists of 2 modified and 2 unmodified GO-FLO bottles on STAINLESS STEEL hydro-wire.  
Samples taken for Brugmann, McLeod, Piotrowicz and Presley.

Planned Shipboard Operations - Second Day

Sequence of shipboard operations

1. Swing weight over side and lower to sea surface. Zero meter wheel.
2. Lower to 50 M.
3. Attach bottle No. 11 (NANSEN)
4. Lower to 58 M.
5. Attach bottle No. 10 (GO-FLO)
6. Lower to 66 M.
7. Attach bottle No. 9 (HYDRO-BIOS)
8. Lower to 74 M.
9. Attach bottle No. 8 (HYDRO-BIOS)
10. Lower to 82 M.
11. Attach bottle No. 7 (HYDRO-BIOS)
12. Lower to 90 M.
13. Attach bottle No. 6 (HYDRO-BIOS)
14. Lower to 98 M.
15. Attach bottle No. 5 (HYDRO-BIOS)
16. Lower to 106 M.
17. Attach bottle No. 4 (HYDRO-BIOS)
18. Lower to 114 M.
19. Attach bottle No. 3 (HYDRO-BIOS)
20. Lower to 122 M.
21. Attach bottle No. 2 (HYDRO-BIOS)
22. Lower to 130 M.
23. Attach bottle No. 1 (GO-FLO)
24. Lower to 1300 M.

- CAST 1. Cast consists of 2 modified GO-FLO and 8 HYDRO-BIOS bottles on PLASTIC-COATED GALVANIZED STEEL hydro-wire. Samples taken for Bowers/Yeats, Brugmann and Windom/Smith. Additional homogeneity check samples collected.
- CAST 2. Cast consists of 2 modified GO-FLO and 8 HYDRO-BIOS bottles on PLASTIC-COATED GALVANIZED STEEL hydro-wire. Samples taken for Ambe, Olafsson and Piotrowicz.
- CAST 3. Cast consists of 2 modified GO-FLO and 8 HYDRO-BIOS<sup>\*)</sup> bottles on PLASTIC-COATED GALVANIZED STEEL hydro-wire. Samples taken for Church, Duinker, Pellenberg and Schmidt.  
\*) One HYDRO-BIOS bottle malfunctioned.
- CAST 4. Cast consists of 2 modified GO-FLO and 8 HYDRO-BIOS<sup>\*)</sup> bottles on PLASTIC-COATED GALVANIZED STEEL hydro-wire. Samples taken for Presley, Waslenchuk and Sivalingam.  
\*) One HYDRO-BIOS bottle malfunctioned.
- CAST 5. Cast consists of 2 modified GO-FLO and 8 HYDRO-BIOS<sup>\*)</sup> bottles on PLASTIC-COATED GALVANIZED STEEL hydro-wire. Samples taken for Bowers/Yeats, Lee, McLeod and Windom/Smith. Additional homogeneity check samples collected.  
\*) One HYDRO-BIOS bottle malfunctioned.

Contingency cast sequence using 6 HYDRO-BIOS Bottles

1. Swing weight over side and lower to sea surface.
2. Zero meter wheel.
3. Lower to 50 M.
4. Attach reversing bottle to wire.
5. Lower to 58 M.
6. Attach No. 8 GO-FLO bottle to wire.
7. Lower to 66 M.
8. Attach No. 7 HYDRO-BIOS bottle to wire.
9. Lower to 74 M.
10. Attach No. 6 HYDRO-BIOS bottle to wire.
11. Lower to 82 M.
12. Attach No. 5 HYDRO-BIOS bottle to wire.
13. Lower to 90 M.
14. Attach No. 4 HYDRO-BIOS bottle to wire.
15. Lower to 98 M.
16. Attach No. 3 HYDRO-BIOS bottle to wire.
17. Lower to 106 M.
18. Attach No. 2 HYDRO-BIOS bottle to wire.
19. Lower to 114 M.
20. Attach No. 1 GO-FLO bottle to wire.
21. Lower to 1300 M.

SAMPLING BOTTLE

<u>Type</u>	<u>No.</u>	<u>Scientist</u>	<u>Sample</u>
GO-FLO	1	Yeats	3 x 2
		Windom	3 x 0.25 1
HYDRO-BIOS	2	Yeats	1 x 1.7 1 etc.
HYDRO-BIOS	3	Yeats	1 x 1.7 1 etc.
HYDRO-BIOS	4	Yeats	1 x 1.7 1 etc.
HYDRO-BIOS	5	Yeats	1 x 1.7 1 etc.
HYDRO-BIOS	6	Windom	3 x 0.25 1 etc.
HYDRO-BIOS	7	Windom	3 x 0.25 1 etc.
GO-FLO	8	Yeats	3 x 2 1 etc.
		Windom	3 x 0.25 1 etc.
NANSEN	9	-	Salinity

SAMPLING BOTTLE

CAST 2

CAST 3

<u>Type</u>	<u>No.</u>	<u>Scientist</u>	<u>Sample</u>	<u>Scientist</u>	<u>Sample</u>
GO-FLO	1	Olafsson	4 x 1 1	Duinker	4 x 1 1
		Olafsson	4 x 0.5 1	Saving --	4 x 0.25 1
HYDRO-BIOS	2	Olafsson	1 x 1 1	Duinker	1 x 1 1
		Olafsson	1 x 0.5 1	Saving --	1 x 0.25 1
HYDRO-BIOS	3	Olafsson	1 x 1 1	Duinker	1 x 1 1
		Olafsson	1 x 0.5 1	Saving --	1 x 0.25 1
HYDRO-BIOS	4	Olafsson	1 x 1 1	Duinker	1 x 1 1
		Olafsson	1 x 0.5 1	Saving --	1 x 0.25 1
HYDRO-BIOS	5	Olafsson	1 x 1 1	Duinker	1 x 1 1
		Olafsson	1 x 0.5 1	Saving --	1 x 0.25 1
HYDRO-BIOS	6	McLeod	1 x 1 1	Ambe	+ ) combine excess
		Ambe-Glass	1 x 0.5 1		1 x 1 1
HYDRO-BIOS	7	McLeod	1 x 1 1	Ambe	1 x 1 1
		McLeod	2 x 1 1	Ambe	3 x 1 1
NANSEN	9	-	Salinity	-	Salinity

\*) Ambe received one sample from HYDRO-BIOS bottle No. 6, one sample from HYDRO-BIOS bottle No. 7, and one sample from HYDRO-BIOS bottles Nos. 6 and 7.

SAMPLING BOTTLE		CAST 2			CAST 3						
<u>Type</u>	<u>No.</u>	<u>Scientist</u>	<u>Sample</u>			<u>Scientist</u>	<u>Sample</u>				
GO-FLO	1	Presley	4	x	1	1	Schmidt	4	x	0.5	1
							Pellenburg	4	x	0.5	1
							Lee	4	x	1	1
HYDRO-BIOS	2	Presley	1	x	1	1	Schmidt	2	x	0.5	1
HYDRO-BIOS	3	Presley	1	x	1	1	Schmidt	2	x	0.5	1
HYDRO-BIOS	4	Presley	1	x	1	1	Church	1	x	1	1
HYDRO-BIOS	5	Presley	1	x	1	1	Church	1	x	1	1
HYDRO-BIOS	6	Brugmann	2	x	0.5	1	Church	1	x	1	1
HYDRO-BIOS	7	Brugmann	2	x	0.5	1	Church	1	x	1	1
GO-FLO	8	Brugmann	4	x	0.5	1	Church	4	x	1	1
NANSEN	9	-	Salinity			-	Salinity				

SAMPLING BOTTLE		CAST 6				
<u>Type</u>	<u>No.</u>	<u>Scientist</u>	<u>Sample</u>			
GO-FLO	1	Waslenchuk	4	x	1	1
		Yeats	3	x	2	1
		Windom	3	x	0.25	1
HYDRO-BIOS	2	Waslenchuk	1	x	1	1
HYDRO-BIOS	3	Waslenchuk	1	x	1	1
HYDRO-BIOS	4	Waslenchuk	1	x	1	1
HYDRO-BIOS	5	Waslenchuk	1	x	1	1
HYDRO-BIOS	6	Piotrowicz	1	x	1	1
		Piotrowicz	2	x	0.25	1
HYDRO-BIOS	7	Piotrowicz	1	x	1	1
		Piotrowicz	2	x	0.25	1
GO-FLO	8	Piotrowicz	2	x	1	1
		Piotrowicz	4	x	0.25	1
		Yeats	3	x	2	1
		Windom	3	x	0.25	1
NANSEN		-	Salinity			

TRACE-METAL ANCILLARY EXPERIMENT

TEST OF SAMPLING-BOTTLE STORAGE EFFECTS

- Pump 200 litres at CSS site +), return to dock.

Monday (later, when sampling bottles are available)

- Set peristaltic pump to pull water from tank.
- Secure 2 GO-FLO bottles in vertical position, with valves open.
- Secure 6-8 HYDRO-BIOS bottles, having disconnected trip mechanism so as to open top of bottle only.
- Secure 1 NISKIN bottle, top open.
- Level sample bottles prior to filling.
- Fill each participant's "time-zero" bottles (in duplicate)
- Fill GO-FLOS (requires 5 minutes/bottle), record time when starting and finishing filling.
- Immediately begin filling sample bottles, starting from the GO-FLO that was filled first. Take half of sample from each GO-FLO to make composite sample. Record time for sample when full.
- Continue for all early GO-FLO time-series samples.
- Once the early GO-FLO samples are done, fill the HYDRO-BIOS, record time of filling (start/finish).
- Begin filling sample bottles immediately, starting from the HYDRO-BIOS filled first. Fill bottle 1/6 or 1/8 from each HYDRO-BIOS. Participants should provide a scale for each sample bottle type. Do all early HYDRO-BIOS samples.
- Fill NISKIN, take a sample 5 minutes after NISKIN is full (for Olafsson only); record actual time. (Done in duplicate, of course).
- Take the 2-hour and 10-hour samples approximately 2 and 10 hours after the sampling bottles were initially filled. Record actual times.

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+) Contingency Surface Sample

Manpower requirements

<u>Minimum No.</u>	<u>Purpose</u>
6	One person per sampling bottle, to fill sample bottles (but only 2 required while GO-FLOS are done).
1	One person to "feed" sample bottles to the filling people.
1	One person to receive, acidify, cap, and bag filled bottles.
1	One person to observe and record time at which each sample bottle becomes full.

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9 people (minimum);

11 people if HYDRO-BIOS bottles are used.

Bottle requirements

Each participant needs 6 bottles for each sampling-bottle type sampled; i.e.,

- Church, Brugmann, Waslenchuk (mercury), Waslenchuk and Schmidt (other metals), all need 6 bottles for timed-samples, plus 2 bottles for "time-zero" sample, for 8 bottles total.
- Windom needs 12 bottles for timed-samples, plus 2 for time-zero, for 14 bottles total.
- Olafsson needs 6 bottles for metals from HYDRO-BIOS, 6 bottles for mercury from HYDRO-BIOS, and 6 bottles for NISKIN samples, plus 2 for time-zero, for 20 bottles total.

QUESTIONNAIRE FOR PARTICIPANTS IN THE TRACE-METAL PROGRAMME

Name:

Institution  
and address:

A. Please specify the procedures employed during the PANCAL-80 Exercise.

1. Elements to be determined

2. Type of sample storage bottle

- material
- size/volume
- method of pre-cleaning

3. Sample storage conditions

- condition of sample storage bottle prior to sampling (e.g. Super Q filled)

- conditions of sample storage

Temperature (e.g. ambient)  
Additive      Type  
                  Strength  
                  Source  
                  Volume per sample

- any other special conditions

B. Please describe the equipment and methods of sample collection and analysis which you commonly use under the following headings:

1. Shipboard sampling

- hydro-wire type
- hydroweight construction/material
- samplers type/material
- describe any special sampler modifications
- messenger type (indicate whether of commercial origin or specially made; and construction materials, if known)

- describe any other special conditions which you employ in deploying samplers, e.g., teflon-lined winch drum.

2. Other shipboard operations:

- do you filter samples on board ship?
- pressure or vacuum filtration?
- directly from the sampler or after sample transfer to another vessel?
- filter type
- filter size
- filter holder type (if locally constructed - i.e., custom-made - indicate materials used)
- type of tubing used
- precleaning of filters, filter holders, tubes, etc.
- use of clean rooms or clean benches facilities on board ship

Please also specify any other sample handling/pre-treatment or analytical steps normally conducted on board ship.

3. Normal sample storage procedures.

Do you normally use different sample storage bottles and preservation/storage conditions than those used during PANCAL-80 (as specified in section A). If so, please describe these differences.

4. Laboratory analysis procedures.

Please describe the following:

- preconcentration technique
- analytical instrument used
- laboratory conditions under which preconcentration and analytical steps are conducted; e.g., laminar-flow hood, clean room.

How many independent analyses for each element do you normally conduct on each sample?

What elements in seawater do you believe you are equipped to determine on a routine basis?

C. Reasons for foregoing choices.

Please describe briefly ( $\leq$  1 page) the reasons for which you chose the particular methods/equipment described above.

## Suggestions for Monitoring the Marine Surface Micro-layer

(by Robert Pellenbarg, Naval Research Laboratory)

### The Significance of the Marine Micro-layer

The sea-surface micro-layer, as the boundary between the oceans and atmosphere, offers a unique opportunity to monitor environmental changes. The uniqueness arises in part because the micro-layer becomes a first repository for a great many of the materials released by industrial activity. The materials of interest are, for example, petroleum hydrocarbons from tanker operations, pesticide aerosols from agricultural activities, and metallic species from heavy industrial processes. The micro-layer acts as a catchment and concentrator for these and other cast-offs from human activities which can be and are easily transported by atmospheric motion. Knowledge of the contents of pollutants in the micro-layer will aid in understanding the mass balance of synthetic materials in the marine environment.

The relative enrichments in both organic and inorganic species seen in the micro-layer make the analyses of a variety of synthetic materials easier in the sense that a concentrated sample is usually more easily analyzed than is a dilute one, such as sea water.

Thus, in summary, the special qualities of the sea surface micro-layer which enhance its potential usefulness as an environmental monitor are: 1) the rapidity with which the micro-layer can collect and concentrate pollutants generated by man, and 2) the fact that materials to be monitored in the micro-layer are present in concentrations high relative to bulk sea water, thus facilitating the measurement of such materials.

### Sampling the Micro-layer

It is desirable that any standardized method for sampling the micro-layer be simple in construction for required equipment, and in the use of such equipment. Simplicity will aid in enlisting world-wide assistance in monitoring the micro-layer. It is precisely the simplicity of the Screen which strongly suggests it as a standardized device to be used for sampling the sea surface micro-layer on an international scale. The Screen was demonstrated to the participants of the IOC/WMO/UNEP Intercalibration Exercise in Bermuda, January 1980, whose comments were positive. The scientists who attended the IOC Workshop could easily serve as a core of researchers who would be interested in assisting in developing a co-ordinated international effort for monitoring the micro-layer. It is strongly suggested that the IOC/WMO/UNEP participants be contacted directly with regard to joining the micro-layer monitoring effort. However, final decisions as to the ultimate type of sampler to be used for the micro-layer monitoring are beyond the scope of this document. It may prove desirable to conduct a screen sampler intercomparison exercise in which screens of different materials could be compared as to their ability to collect non-contaminated samples.

### Standardization of the Screen

The Screen sampler demonstrated in Bermuda is constructed of aluminium. For hydrocarbon work it is probable that stainless steel would be a more durable material for the Screen to be used in sea water. A plastic screen is imperative for work involving the measurement of trace metals in the micro-layer. In any case, it is required that recommendations for a standard Screen be promulgated. Some points of feasibility to be resolved are:

1. Materials of construction:
  - (a) which materials for organic work - stainless steel, monel or aluminium?
  - (b) which plastics for trace metal work - acrylic, nylon or fiberglass?
2. Overall size for the Screen - 0.75 m x 0.75 m appears to be a convenient size.
3. Recommended Screen mesh size as a function of Screen material - 1 mm x 1 mm from wire centre to wire centre appears to be a useful average size.
4. Shape of the Screen - square or triangular. Both shapes have advantages, but a square Screen collects a larger sample per dip.
5. Accepted methods for cleaning each type of Screen.
6. Accepted methods for storing each type of Screen.
7. Accepted methods for using the Screen; i.e., from a small boat away from major surface vessels, or from major surface vessels using a bridle to tether a triangular Screen, for example.

Many of the above points are covered in the context of suggestions in a paper detailing the version of the Screen used at the Naval Research Laboratory, Washington, D.C. All participants in Bermuda received a copy of this paper.

#### Intercalibration for Micro-layer Monitoring

Once details for a standardized screen and its use have been developed, these instructions should be forwarded to those laboratories expressing interest in participating in an intercalibration exercise. The laboratories could be assembled at a central sampling location to collect samples simultaneously for analysis at their laboratories, or one group could collect sufficient samples to be distributed among participating laboratories. In either case, prior to sampling, the following points must be decided:

1. Parameters to be measured should be those monitored during the Workshop on Intercalibration of Sampling Procedures (Bermuda, 11-26 January 1980): chlorinated hydrocarbons, and the trace metals, copper, zinc, cadmium, and nickel. This approach will emphasize the relationships between surface micro-layers and underlying waters.
2. Techniques for sample treatment such as whether to filter or not, whether to use centrifugation, or solvent extraction, or digestion, or other sample treatments.
3. Acceptable methods for sample preservation, such as cooling, immediate extraction, pickling with acids, or organic solvents, and so forth.
4. Accepted methods to be used for sample analyses.

It is strongly suggested that any sample collection take place in a region of the world that has predictably low winds for an extended period of time for intercalibration work. Bermuda in the summer is proposed as a suitable location, with calm waters readily accessible from shore in the summer, and such regions as the Mediterranean, and waters of the Equator should also be considered in this content.

S Y M P O S I U M  
OF THE WORKSHOP ON INTERCALIBRATION OF SAMPLING PROCEDURES

Bermuda, 22 January 1980

Summary Report

Introduction

The meeting was opened by the Chairman, Dr. Neil R. Andersen, at 1400 hours, 22 January 1980; the Agenda is attached hereto. He briefly outlined the development of the project and noted relationships with other programmes, particularly the intercalibration activities of ICES. Recognition was given to the major sources of support external to IOC, in particular UNEP, and the U.S. NOAA who provided the vessel R.V. GEORGE B. KELEZ for the exercise. Special note was made of the contribution of the Bermuda Biological Station, without which the intercalibration experiment could not have been carried out. It was pointed out that Dr. Antony Knap deserved particular recognition in this regard.

Results (to date) of the Analyses of Chlorinated Hydrocarbon Standards

Dr. J.-P. Villeneuve reported on the distribution of standards and samples for organochlorine analyses. High-level standards had been sent to 40 laboratories, of which 5 had replied. A second set had been sent to 14 laboratories, of which 1 had replied. The organic standards were supplied free of charge by the IAEA Laboratory in Monaco. Since the total cost of preparation and distribution was less than \$2,000, samples were sent to any laboratory that might do the analyses. Several people reported that this led to some confusion because samples without identification were received in laboratories where organochlorine analyses are not carried out.

It was agreed that more direct contact with the scientists who do the analyses is necessary so that samples are not sent to people who do not conduct such analyses. This is particularly true for the trace-metal standards, for which costs are higher.

Several suggestions were made as to how to get information to the scientists in various countries and how to get their responses. One suggestion (Dr. G. Topping) was to name a lead person in each country who can distribute the samples to the appropriate person in his country. Another suggestion (Dr. M. Bowers) was to circulate a questionnaire, as ICES does, asking people what they want and what they can do. Yet another (Dr. M. Bernhard) was to mention the programme either in Unesco bulletins or in the Marine Pollution Bulletin and let the scientists clear channels. Dr. Slaczka stated that, with respect to some of its Member States, IOC is not allowed to deal with scientists without the permission of their governments, and that in some cases the scientists are not granted permission to participate even when they are interested. It was generally agreed that it would be useful to get an expert to visit laboratories and estimate capabilities and solicit participation in intercalibration exercises.

### Plans for Trace-Metal Standards Analyses

Dr. Slaczka reported that there had been some difficulty in providing enough funds to cover the costs of the analyses of trace-metal standards. He pointed out that \$20,000 would be required for 30 participants. It was indicated that funds would be sought, perhaps from UNEP, for the analyses. Dr. Andersen pointed out that without the analyses of standards, the total sampling intercalibration for trace metals would be seriously compromised.

The Sagami Chemical Research Center can supply many of the standards for distribution in May, but the cost will be ~\$20,000. It may be possible that the IAEA Laboratory in Monaco can supply some of the standards. The remainder could be purchased from Sagami. This matter will be discussed by Drs. Fukai, Bewers, and Slaczka in Monaco in February 1980. It was agreed that the standards programme was of most use to laboratories that had not taken part in previous intercalibrations.

### Sampling Programme Results

#### (a) Ship operations

Dr. Andersen noted that the officers and crew of the R.V. GEORGE B. KELEZ did an outstanding job in assisting in the sampling programme, under adverse weather conditions. He indicated that special recognition was in order. He also pointed out that the efforts expended by the scientists who went to sea equally deserve special mention, particularly Drs. Atwood, Harvey, Yeats and Mr. Smith, who served as chief scientist on board at various times during the period of sampling. Dr. Andersen suggested that a letter of recognition from IOC would be in order, which was unanimously agreed to by those attending the seminar.

#### (b) Chlorinated Hydrocarbons

Dr. K. Palmork reported that there were no direct results from the organic analyses yet. On the first day, owing to adverse weather conditions, not all samples were obtained. However, on the second day all was completed as planned in the operational plan, which had to be progressively modified during the experiment to take into account the adverse weather. Because other equipment, such as the gas-lift system, was available and many extra sample bottles were supplied, additional work could be done. Two samples were obtained for each participant and all the results should be in by April. Dr. Palmork pointed out that much of the credit should go to Dr. Knap and the Bermuda Biological Station for obtaining the instruments, standards, and much other equipment, which considerably enhanced the experiment.

It was considered important to continue the analysis of the large number of complex chromatograms obtained from samples collected on the second cruise, after the completion of the work anticipated. It was concluded that it would be worthwhile to investigate the feasibility of composing a mixture of individual components that would represent the patterns obtained by application of temperature-programmed capillary column chromatography. It was therefore agreed that the following participants would remain in Bermuda for several additional days and undertake this task: Drs. K. Palmork, J.-P. Villeneuve, J.C. Duinker and Mr. T.J. Hillebrand.

(c) Trace metals

Dr. M. Bowers reported that the original design of the trace-metal work remained intact although the sea conditions modified the plans. His only concern was the validity of the homogeneity assumption since shallower depths were taken than intended. Dr. Church reported that the values he has obtained at the Biological Station from three different bottles in Leg I suggest that homogeneity was maintained. The bottles were within analytical precision, which he stated was superior to that which he achieves in his own laboratory. He stressed that it was good to get values here, so one could see problems right away. The surface-sample values compare well with those given in the scientific literature. It was agreed that it was indispensable to have instrument people here as well as instruments, since different laboratories have different machines and there was very little time for accustoming oneself to the instruments.

Dr. Bowers stated that all the trace-metal results should reach him at the Bedford Institute by 31 May. He also reported that the additional storage experiment devised by Drs. Bernhard, Waslenchuk and Brugmann appeared to have worked satisfactorily.

(d) Surface films

Drs. Pellenburg and Smagin stressed the importance of having sea-surface micro-layer sampling included in any ocean monitoring plan. In this experiment, because of the short lead time and the rough seas, only a demonstration of a sampling screen was possible. Annex X is a report provided by Dr. Pellenburg on suggestions for monitoring the surface micro-layer.

Dr. Smagin was asked if WMO would support the ocean monitoring project when and if sea-surface sampling is included. He replied that no funds are presently available but that funds, if necessary, would be sought from UNEP. Some discussion followed as to whether the screen was the best sampling technique but no consensus was reached.

Disposition/Results of Analyses of Samples

Dr. N. Andersen suggested that any comments with regard to problems in general, which could be addressed if a similar effort were repeated, should be compiled by the sub-groups together with their reports. The two sub-reports should reach Dr. Andersen by 1 August 1980, and he would distribute the integrated report by 1 September. The report would then be submitted to GEMSI-III for approval and forwarding to GIPME-IV and IOC.

It was agreed that participants should receive the appropriate sub-group reports before they are sent to Dr. N. Andersen, to ensure accuracy.

Dr. M. Bowers asked about funding of travel etc. for sub-group leaders to get together for writing the reports. Dr. Slaczka said that IOC will pay this under its consultants programme. UNEP is to receive two reports: the first, a report of what happened in Bermuda, activities, problems, etc., is required by April 1980; the second, the final report, is to include all results obtained in Bermuda and those obtained in the home laboratories (including all intercalibration results), and is required by September 1980. This second report will be drafted by three consultants paid under the IOC/UNEP Project.

Dr. Slaczka stated that when the report is ready, GEMSI-III will meet to discuss the feasibility of monitoring. Is it possible to do baseline studies, followed by monitoring, or not? GEMSI will also discuss training, education etc., in trace metal and organochlorine analysis for developing countries.

Dr. N. Andersen thanked the representatives of the Hewlett Packard, Perkin Elmer and Varian Companies for their helpfulness. Purcell (Perkin Elmer) replied that they were quite pleased with the experiment although more notice to get instruments here would have made it easier for all concerned.

Dr. Slaczka thanked everybody for their hard work, both on land and sea, and especially Drs. Andersen, Bowers and Palmork for organizing the work so well, and the Bermuda Biological Station for Research for having everything available when it was needed.

Dr. Andersen adjourned the meeting at 1700 hours, 22 January 1980.

SEMINAR ON THE CHLORINATED-HYDROCARBON AND  
TRACE-METAL INTERCALIBRATION EXPERIMENT

Bermuda, 22 January 1980

A G E N D A

1. Introduction
  - (a) Project development
  - (b) Relationships to other programmes
  - (c) Sources of support
  - (d) Involvement of Bermuda Biological Station
2. Results (to date) of Analysis of Chlorinated-hydrocarbon Standards
3. Plans for Trace-metal Standard Analyses
  - (a) Distribution
  - (b) Reporting format and timetable
4. Sampling Programme Results
  - (a) Ship operations
  - (b) Halogenated hydrocarbons
  - (c) Trace metals
  - (d) Surface films
5. Disposition/Results of Analyses of Samples
  - (a) Halogenated hydrocarbons
  - (b) Trace metals
6. Analytical Aspects of Instrumentation Present at BBS and Application to a Monitoring Activity
7. Preliminary Discussion on Feasibility of a Monitoring Operation for Halogenated Hydrocarbons and Trace Metals
8. Future Activities (e.g., TEMA; other pollutants)