Intergovernmental
Oceanographic
Commission

1

Training Course Reports

IOC Indian Ocean Region Training Course in Petroleum Monitoring

Held at the Australian Department of Science and the Environment

Perth, 18 February-1 March 1980

Unesco

PREFACE

To enhance the participation of Member States, especially developing countries, in IOC's programmes, the IOC, with the co-operation of the interested Member States and of their marine science institutes, organizes training courses in the framework of the IOC programme of Training Education and Mutual Assistance in the Marine Sciences (TEMA).

The present report is on a training course in petroleum monitoring organized by the Australian Department of Science and the Environment on behalf of IOC as a contribution to IOC's Global Investigation of Pollution in the Marine Environment (GIPME). Mr T. McKay of the Department of Science and the Environment was responsible for the organization of the course, and prepared this Report.

IOC is greatly indebted to the Australian Government and the local organizer, the Australian Development Assistance Bureau, for this excellent course, as well as to the United Nations Environment Programme for supporting the course financially.

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INTRODUCTION

In response to a request from the Intergovernmental Oceanographic Commission (IOC) of the United Nations Educational Scientific and Cultural Organisation UNESCO the Australian Department of Science and the Environment conducted a training course in Perth for marine technicians from the Indian Ocean region, South East Asia and China, from February 18 to March 1 1980. Eight trainees from six countries attended under the sponsorship of the IOC.

The course dealt with methods of sampling and analysis of petroleum residues in marine samples and followed guidelines for the operational procedures of the IOC/WMO Marine Pollution (Petroleum) Monitoring Pilot Project (MAPMOPP), given in IOC Manuals and Guides No. 7.

A major emphasis within the course programme was on field exercises based on MAPMOPP procedures for sampling ocean water and beach sands for tar balls, the observation of oil slicks and the measurement of dissolved and dispersed hydrocarbons at one metre depth in sea water.

The course was conducted at the Australian Government Analytical Laboratories at Cottesloe, near Perth, Western Australia. Field sampling exercises were undertaken off Garden Island and through Cockburn Sound on board a coastal survey vessel of the Western Australian Harbour and Light Department.Some analytical chemical work was carried out at the Western Australian Government Chemical Laboratories in Perth.

Financial support from the Australian Development Assistance Bureau (ADAB) provided local maintenance for the trainees and enabled kits of MAPMOPP samplers for dissolved and dispersed hydrocarbons as well as neuston nets to be supplied to participants. These were used during the course and subsequently retained by participants on behalf of their home institutions for use in their own regional projects.

The course was prepared and directed by Mr Terry McKay, Marine Programs Section of the Australian Department of Science and the Environment. Liaison with Western Australian Government groups, local financial arrangements and media contacts were organized through Mr David Brown, Regional Administrative Officer for the Department of Science and the Environment in Western Australia. Mr John Armstead, Marine Programs Section, Canberra, assisted with routine arrangements for purchase of equipment, printing of course documentation and dispatch of materials to Perth.

Special thanks are due to Mr Keith Chambers of ADAB's Perth Office, who met each participant at the airport and took each to his hotel, and to ADAB for its induction programme giving background information on Australia (and Perth in particular) during the first day of the course; these efforts were an important component of the success of the course and the enjoyment of each participant's visit to Australia.

OBJECTIVES

The course was designed to meet the following objectives:

- to train marine technicians from IOC Member States in procedures for sampling, measurement and reporting of petroleum pollution in marine environmental samples;
- to carry out operational exercises using IOC Manuals and Guides No. 7. and Supplements, in a technical workshop setting;
- to review briefly other chemical analytical methods applied to measurement and identification of petroleum in marine samples, such as gas chromatography, infra-red spectrophotometry;
- to develop participants' skills in training so as to assist them to pass on instruction in the techniques on return to their home institutions;
- to establish working contacts between the groups implementing MAPMOPP in their respective regions.

These objectives were met by dealing with each of the MAPMOPP project components along the following lines;

(i) Procedures were outlined in detail;

(ii) Participants discussed the procedures and exchanged experiences;

(iii) Field equipment sets were assembled and transported to sampling sites;

(iv) Field sampling and measurements were carried out in small groups, each participant demonstrating procedures to others in turn;

(v) The samples were analysed in a laboratory, the results were assessed, log forms were completed and findings were discussed; Some laboratory assignments on related activities were carried out;

(vi) Details of operations were reviewed. Each participant prepared and presented a brief summary of developments in the techniques used in the four MAPMOPP observational components, as outlined in IOC Manuals and Guides No. 7 and subsequent literature.

PARTICIPANTS

Eight trainees attended. They were from Kenya, Thailand (2), Malaysia, Indonesia, Phillipines and the The Peoples Republic of China (2). A list of names of the participants is included as Annex I.

The participants were selected by IOC from nominees of IOC Member States in the region. Some broad selection criteria were requested by Australia in preliminary correspondence. These were mainly based on the recommendations made at the IOC/WMO ad hoc Meeting on the Implementation of the IOC/WMO Marine Pollution (Petroleum) Pilot Project (MAPMOPP) in the Indian Ocean Region in New Delhi, September 1978.

Each participant was scientifically qualified and experienced in some aspects of marine chemistry. Several were engaged in routine analysis. All had reasonably good command of English. Each one was in a position to apply the procedures covered in the course on their return to their home institutions.

Arrangements for the welfare of overseas visitors were made through the ADAB Perth Office.

COURSE OUTLINE

The course provided training in field sampling, laboratory measurement and log recording procedures for the measurement of petroleum hydrocarbons in marine samples, as outlined in the Guide to Operational Procedures for the Integrated Global Ocean Station System Pilot Project on Marine Pollution (Petroleum) Monitoring (IOC Manuals and Guides No. 7, and 7 Supplement).

The four components monitored under MAPMOPP are

(i) oil slicks and other floating pollutants;

(ii) particulate petroleum residues (tar balls) in ocean surface water;

(iii) tar balls on beaches;

(iv) dissolved and dispersed hydrocarbons at one metre depth.

Besides the methods of measurement specified in IOC Manuals and Guides No. 7, other specialised techniques for the analysis of petroleum hydrocarbons in marine samples were included in this course. Participants were given basic outlines for the application of gas-liquid chromatography, thin-layer chromatography, infra-red and ultra-violet spectrophotometry. Selected samples were analyzed by gas-liquid chromatography by each participant as an extra laboratory exercise.

Sets of equipment for sampling dissolved and dispersed hydrocarbons at one metre depth were constructed along the lines specified in IOC Manuals and Guides No. 7. Details of float dimensions and clips, as well as photographs of similar equipment used by the Institut fur Meereskunde an der Universitat Kiel were provided by Dr Manfred Erhardt. These were used to prepare specifications for a local manufacturer. A sufficient number of sets were purchased to enable the participants to export one to each of their home institutions at the conclusion of the training course. The design of the sampling kit is shown in Fig. 1.

An experimental floating frame for the neuston net was designed and constructed by participants during the course using low-cost materials. As a result of the successful towing trials on the first ocean cruise, five more nets were ordered from a local manufacturer. These arrived in time to be included with the other sampling kits exported at the end of the course to the participants' home institutions. Details of the floating frame neuston net are shown in Fig. 2.

Other items given to the trainees were sets of tar ball test sieves (3 mm and 6 mm) and a standard sample of chrysene (1g) for intercalibration of fluorimetric measurements of dissolved and dispersed hydrocarbons.

Field trips were made to two beach areas for comparison of sand sampling and measurement of tar balls. An ocean-going coastal survey vessel (MV. *Vigilant*) operated by the Western Australian and Harbour

and Light Department was chartered for two ocean sampling cruises off Fremantle. On both occasions, equipment kits for sampling dissolved and dispersed hydrocarbons in water and the experimental neuston net for tar-ball collection were operated by the participants. Samples collected were returned to the laboratory for subsequent analysis of hydrocarbon levels.

A short seminar was arranged at which invited speakers from Western Australian State Government organizations discussed applications of petroleum pollution measurements in Western Australia. Aspects considered included characterization techniques for source identification, regional strategies and criteria for oil pollution controls and local marine environmental studies.

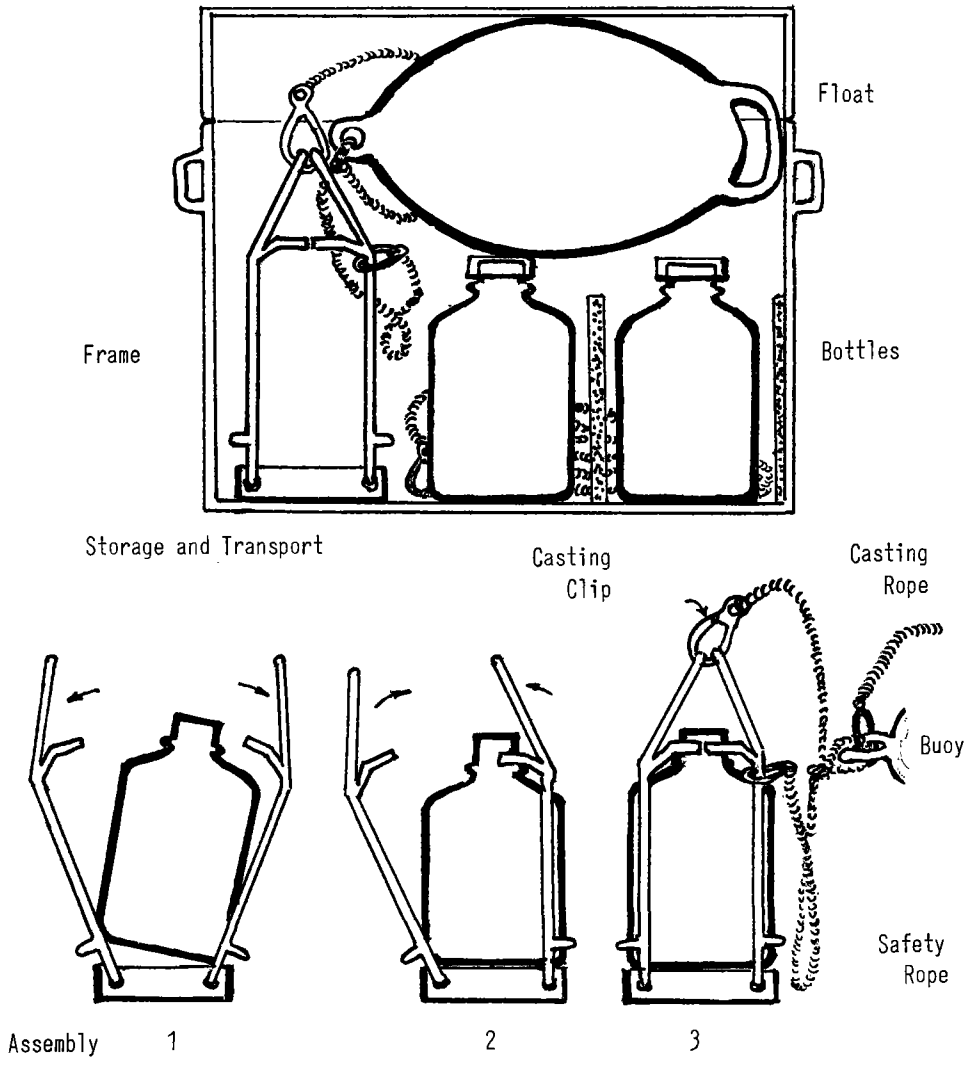
The group also visited the Western Australian Marine Research Laboratories at North Beach to inspect their fishery development activities, test aquariums and analytical laboratories.

A detailed timetable of the course programme is included as Annex II. Other participating organisations and administrative contact arrangements are set out in Annex III.

A list of the documents and literature extracts produced for the course and provided to participants is given in Annex IV. These provided the basic references for the course.

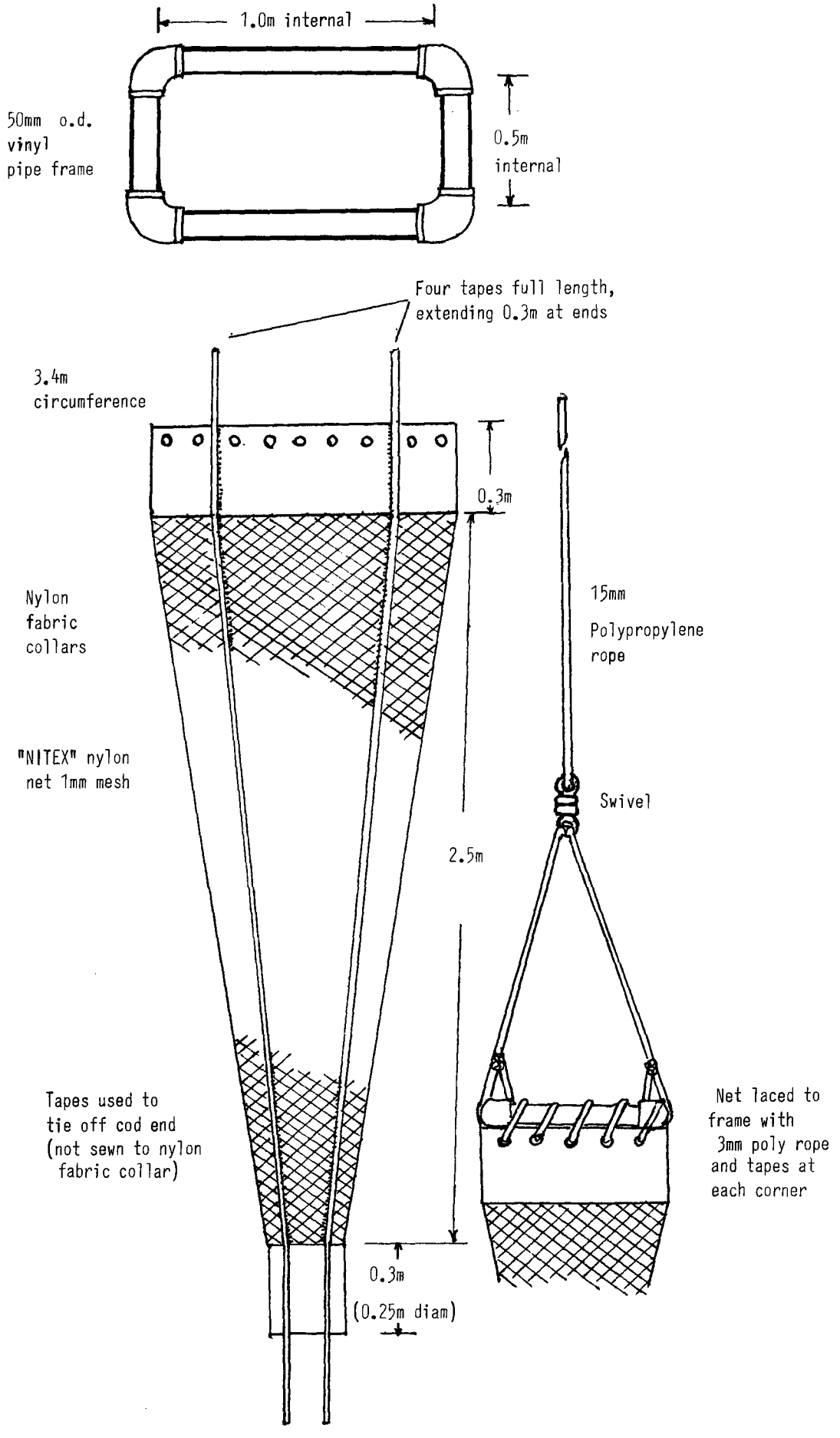
An outline of the curriculum covered by the training course, details of laboratory work undertaken and a selection of experimental results obtained by the participants is included in Annex V.

A certificate was presented to each participant at the end of the course. This certificate described the scope of the course and associated laboratory work. A copy of this is included in Annex VI.



MAPMOPP SAMPLING KIT FOR
DISSOLVED/DISPERSED HYDROCARBONS

FIGURE 2



FLOATING FRAME NEUSTON NET

GENERAL COMMENTS

General

The course was regarded as a highly successful operation and the participants expressed their appreciation of the amount and depth of detail covered . Although the lead time for preparation was somewhat short, the combined efforts and extremely helpful co-operation of other involved organizations resulted in adequate coverage of the course topics through formal discussions, field sampling trips, laboratory analytical exercises and the mutual exchange of experience.

Use of Course Measurements and Test Results

The ocean test stations for dissolved and dispersed hydrocarbon measurements were selected in consultation with officers of the Western Australian Department of Conservation and Environment. Consequently the data obtained during the course has provided useful baseline measurements for further marine pollution studies of a similar nature in this area.

Scope and Duration

The content of the course was covered within the two-week period although participants felt that they might have been able to carry out a larger range of laboratory assignments if the course had run for three weeks. Four weeks would have been too long to spend on fairly basic procedural exercises by technicians with the scientific qualifications and experience of those who attended this course.

Numbers of Participants

Eight was an ideal number; perhaps ten could have been accommodated with the same attention to personal welfare and supervision. A smaller number would have been less cost effective in terms of organizational outlay and commitment.

Media Coverage

A Departmental press release issued on the first day of the course was published in Canberra (Canberra Times-19/2/80) and subsequent contact in Perth by ABC News resulted in a four-minute film report on ABW2 evening television news of Thursday 21st February showing the group collecting sea water samples with their new kits on the first ocean cruise.

Gifts of Equipment

The sampling kits, neuston nets, test sieves and standard chrysene samples taken back by participants for their home institutions were extremely well received. These should promote a considerable increase in petroleum pollution measurements relevant to IOC marine pollution monitoring programmes in the Indian Ocean and regional seas. The part played by ADAB in providing the funds for this equipment has been fully acknowledged and the practical and goodwill value of this venture is assured. Advice from the Customs in Perth on the export of the goods was helpful.

Local Transport

A self-drive fourteen-seat minibus, provided through the Department of Administrative Services, allowed considerable flexibility in the travel arrangements.

Conference Room/Laboratory Facilities

The facilities of AGAL, at Cottesloe made an excellent location for the conference. The provision of a laboratory with fume hoods, evaporation equipment and access to solvent distillation facilities was invaluable. A gas chromatograph fitted with dual packed columns for petroleum hydrocarbon analysis was made available for the training course. The assistance of the Acting Director and the gas chromatography officer in preparing this equipment for operation was particularly welcome. Consumable supplies were obtained through this laboratory. The Laboratory Manager, Administrative Assistant and typing staff also provided valuable help.

Fluorimeter Facilities

Visits were made to the Western Australian Government Chemical Laboratories to measure standard and sample extracts of dissolved and dispersed hydrocarbons by spectrofluorimetric techniques, as prescribed in IOC Manuals and Guides No. 7. The staff in the Agricultural Division of the laboratories provided helpful assistance and advice on the operation of their fluorimeter, as well as demonstrating precautions necessary to be observed to avoid contamination of working solutions and measuring cells.

RECOMMENDATIONS

As a result of the experience gained in this venture, it is recommended that consideration be given to the preparation of a similar training course in 1981.

This would be a means of consolidating the Australian contribution to the IOC Marine Pollution Monitoring Programme (MARPOLMON). This would reinforce also the regional capability for effectively developing MARPOLMON.

Given adequate lead time, the support of the Australian Government might extend to further assistance in addition to the type of support given for the training course reported here.

Such an involvement on Australia's part would be a most effective way of contributing to the IOC programme. This type of support, which is greatly valued by the governing bodies of IOC would also add much in terms of goodwill between the participating Member States.

ANNEX I

NAMES OF PARTICIPANTS AND ORGANIZATIONS.

Mrs Puengjai Limchareon
Dept. of Mineral Resources
Mineral Fuels Division
Rama VI Road,
BANGKOK 4, THAILAND.

Chaiyong Yuangthong
Dept. of Marine Science
Faculty of Science
Chulalongkorn University
Phayathai Road,
BANGKOK, THAILAND

Liong Pit Chong
Fisheries Research Institute
Glugor, PENANG,
MALAYSIA

Qu Chuan Yu
Institute of Marine Environment Protection
National Bureau of Oceanography,
P.O. Box 303,
DALIAN
The Peoples Republic of China.

Terry McKay
(Course Director),
Dept. of Science and the Environment,*
P.O. Box 449,
WODEN, A.C.T. 2606
AUSTRALIA.

Su Xian-gong
Institute of Marine Environment Protection,
National Bureau of Oceanography
P.O. Box 303,
DALIAN
The Peoples Republic of China

Daniel Munga
Kenya Marine Fisheries Research Institute,
P.O. Box 81651,
MOMBASA, KENYA

Lt (j.g.) Isidro T. Velasco
National Operation Centre for Oil Pollution
Phillipines Coast Guard
Farola Compound
BINONDO, MANILA

Mulyono
Oil and Gas Technology Development Centre,
(PPTMGB Lemigas)
P.O. Box 89 JKT
JAKARTA, INDONESIA

* New address since Commonwealth Government re-arrangements, November 1980:

Marine Programs Section,
Department of Home Affairs and Environment,
P.O. Box 1252,
CANBERRA CITY A.C.T. 2601
AUSTRALIA

ANNEX II

COURSE PROGRAM

Date	Location	Activity
February		
Monday 18	ADAB	Welcome and orientation program arranged by ADAB (all day).
Tuesday 19	AGAL	Introduction, background of IOC oil pollution monitoring programme - Historical development. Preliminary discussion of IOC Manuals and Guides No. 7. Techniques for observation of oil-slicks. Sampling procedures for tar on beaches.
	(Lab)	Inspection of dissolved/dispersed hydrocarbon sampling kits.
Wednesday 20	AGAL (Lab)	Prepare sampling equipment for field trip.
	B.P.	Sample beach for particulates, tar balls and residues.
	AGAL (Lab)	Analysis of field samples from beach. Construct towing frame for neuston net. Prepare sampling bottles for dissolved/dispersed hydrocarbon kits.
Thursday 21	MV *"Vigilant"*	Ocean cruise - Sampling procedures for dissolved/dispersed hydrocarbons. Operation of neuston net with floating frame. Log details for oil-slick reports.
	AGAL (Lab)	Preliminary treatment of samples collected.
Friday 22	AGAL	Discussion - Techniques for sampling and analysis of dissolved/dispersed hydrocarbons. Introduction to fluorimetry, principles, instrumentation, precautions.
	(Lab)	Distillation of solvents. Preparation of solutions from extracts.
	WAGCL	Measurements by spectrofluorimeter, chrysene standards.
Saturday 23 and Sunday 24		Free time, informal tours.

Date	Location	Activity
Monday 25	AGAL	Discussion - Other methods of analysis for dissolved/dispersed hydrocarbons and comparison with fluorimetry: gas - liquid chromatography, thin-layer chromatography, infra-red and ultra-violet spectrophotometry - source characterization.
	WAGCL	Fluorimetric measurement of test sets of hydrocarbon ampoules (Workshop reference samples provided by the Department of Science and the Environment).
Tuesday 26	AGAL	Discussion - Intercalibration and standardization. Review of results of test ampoules for "chrysene equivalent" values.
	(Lab)	Preparation of test solutions and bottles for dissolved/dispersed hydrocarbons; pack kits for ocean cruise on the next day.
	Port Beach	Sample beach for particulates and tar balls.
	WAGCL (Minerals House)	Seminar - Application of marine petroleum pollution studies in Western Australia - (invited speakers).
Wednesday 27	MV *"Vigilant"*	Ocean cruise - sampling procedures for dissolved/dispersed hydrocarbons. Operation of neuston net with floating frame. Log details for oil-slick reports.
	AGAL (Lab)	Preparation of samples for analysis. Introductory gas chromatography experiments.
Thursday 28	AGAL	Continuation of sample preparation, rotary film evaporator techniques. Further gas chromatography experiments.
	WAGCL	Analysis of field samples - manual scan of sample and chrysene fluorescence spectra - measurement of spiked recovery samples.
Friday 29	WAMRL	Inspection tour of fishery research, aquariums and analytical laboratories.
	AGAL	Review of analytical results. Discussion and presentation of individual assignments on developments and revisions to IOC Manuals and Guides No.7 for each of the four measurement components of petroleum monitoring.
	(Lab)	Pack sampling kits, neuston nets for export.

Date	Location	Activity
	AGAL	Closing session, award of certificates, expressions of thanks to AGAL and the Department's Regional Administrative Office for assistance.
March		
Saturday 1		Free time, informal discussion on likely involvement in local regional monitoring activities.

Key to Locations

ADAB	Australian Development Assistance Bureau, Perth city
AGAL	Australian Government Analytical Laboratories Conference Room at Cottesloe
(Lab)	Laboratory area
B.P.	B.P. Refinery (Kwinana) Pty Ltd., at Kwinana Beach-front facilities in Cockburn Sound
MV *"Vigilant"*	Survey vessel, stationed at Fremantle complex, Western Australian Harbour and Light Department
Port Beach	(Near AGAL) Public beach open to Indian Ocean.
WAGCL	Western Australian Government Chemical Laboratories, Perth city
Minerals House	Conference Room adjoining WAGCL, Perth city
WAMRL	Western Australian Marine Research Laboratories, North Beach.

ANNEX III

OTHER PARTICIPATING ORGANIZATIONS AND ADMINISTRATIVE ARRANGEMENTS

Sponsors

Intergovernmental Oceanographic Commission (UNESCO), Paris

Australian Development Assistance Bureau, Canberra

Australian Department of Science and the Environment, Canberra.

Course Director

Mr Terry McKay
Marine Programs Section,
Department of Science and the Environment,
Canberra

Administrative Assistance

Mr David Brown, Regional Administrative Officer,
Department of Science and the Environment, Perth.
Mr John Armstead, Marine Programs Section, Canberra.

Overseas Visitors' Welfare

Mr Keith Chambers,
Australian Development Assistance Bureau, Perth

Date and Venue

February 18 to March 1
at the Department of Science and the Environment,
Australian Government Analytical Laboratory,
Clive Road,
Cottesloe, W.A. 6011.

Accommodation

The Railton Hotel,
70 Pier Street,
Perth, W.A. 7000.

Laboratory facilities

Australian Government Analytical Laboratories, W.A.

Mr E.G. Miller,
Western Australian Regional Director,
Mr J. Weaver, Acting Director,

Mr M. Carruthers, Laboratory Manager,
Mr M. Baird, Admin. Assistant
Mr K. Manning, Gas Chromatography

Western Australian Government Chemical Laboratories

Mr R. Gorman, Director,
Mr J. Jago, Head, Agricultural Division,
Miss N. Wilson,
Mrs L. Plues-Foster, Agricultural Division.
Fluorimeter used: Hitachi/Perkin Elmer Model 203.

Invited Speakers, Local Petroleum Studies Session

Dr J. Challinor, Western Australian Government Chemical Laboratories:
"Characterisation of Petroleum involved in Oil Spills"

A. Chegwidden, Western Australian Department of Conservation and Environment:
"Petroleum Monitoring and the Cockburn Sound Study".

Dr R. Field, Western Australian Department of Conservation and Environment:
"Development of a Map of Environmentally Sensitive areas of the W.A. Coast and Criteria for Petroleum Pollution Controls".

Survey Vessel

MV *"Vigilant"*, Western Australian Harbour and Light Department,
Commander Mr Jim Fletcher.
Assisting:
Mr Adrian Chegwidden and Mr Chris Simpson, Western Australian Department of Conservation and Environment,
Mrs Lorraine Plues-Foster, Western Australia Government Chemical Laboratories.

Sampling Equipment

Kits for Dissolved/Dispersed Hydrocarbons
Rimco Analite Pty. Ltd.
Mitcham, Victoria,
Mr W. Rauchfuss,

Neuston Nets for Tarballs:-
Henry Simon (Aust) Ltd.,
Glebe, Sydney NSW
Mr Hilder.

Chrysene for fluorimetry standards:-
1.0g Chrysene, EGA-CHEMIE,
D7924 Steinheim/Albuch, Germany.

Other Organizations Visited

Beach Sampling:-
B.P. Refinery (Kwinana) Pty Ltd
Kwinana W.A.
Mr M. Hyde, Services Officer.

Laboratory Inspection:-
Western Australian Marine Research Laboratories
North Beach, W.A.
Dr D. Hancock, Chief Research Officer.

ANNEX IV

DOCUMENTATION AND LITERATURE EXTRACTS
PROVIDED TO PARTICIPANTS

1. Guide to Operational Procedures for the IGOSS Pilot Project on Marine Pollution (Petroleum) Monitoring, IOC/WMO Manuals and Guides No. 7, UNESCO 1976.

2. Manual for Monitoring of Oil and Petroleum Hydrocarbons in Marine Water and on Beaches, IOC/WMO/UNEP Supplement to IOC Manuals and Guides No. 7, UNESCO 1977.

3. Joint IOC/WMO Sub group of Experts on the IGOSS Marine Pollution (Petroleum) Monitoring Pilot Project, Second Session, Washington DC, February 1978 (IOC-WMO/MAPMOPP-II/3, April 1978). (Sections relating to modification of Manuals and Guides No.7).

4. *Ad hoc* Meeting on Implementation of IOC/WMO Marine Pollution (Petroleum) Pilot Project (MAPMOPP) in the Indian Ocean Region, New Delhi, September 1978. (IOC-WMO/MAPMOPP - Ad hoc - I/3, Sept. 1978). (Sections relating to modification of Manuals & Guides No.7).

5. *Ad hoc* Group of Experts on Evaluation of MAPMOPP Project, Tokyo, July 1979 (IOC-WMO/MAPMOPP - Ad hoc - II/3, December 1979). (Sections relating to modification of Manuals & Guides No. 7).

6. E.M. Levy, "The IGOSS Pilot project on Marine Pollution (Petroleum) Monitoring: Its evolution and a personal viewpoint", Marine Pollution Bulletin, 10, 5-11, (1979).

7. D.P. Kohnke, "Results of MAPMOPP : Visual observations and tar balls", IOC-WMO/MPM-1/7, Third IOC/WMO Workshop on Marine Pollution Monitoring, New Delhi, February 1980.

8. E.J. Carpenter, "Plastics, Pelagic Tar and Other Litter". Chapter 5, in Strategies for Marine Pollution Monitoring, (E.D. Goldberg, ed.), John Wiley and Sons, New York 1976.

9. P.M. David, "The neuston net - a device for sampling the surface fauna of the ocean", J. Mar. Biol. Assoc. U.K., 45, 313-320, (1965).

10. M. Erhardt and F. Bouchertall, "Dissolved/dispersed hydrocarbons - What is the nature of the substances being measured?" IOC-WMO/MPM-1/6, Third IOC/WMO Workshop on Marine Pollution Monitoring New Delhi, February 1980.

11. M. Erhardt and M. Blumer, "The source identification of marine hydrocarbons by gas chromatography", Environ. Pollut. 3 179-194, (1972).

12. M. Erhardt and J. Heinemann, "Hydrocarbons in blue mussels from the Kiel Bight", Environ. Pollut. 9, 263-282, (1975).

13. A. Zsolnay, "Intercalibration within the framework of MAPMOPP and MARPOLMON", IOC-WMO/MPM-1/12, Third IOC/WMO Workshop on Marine Pollution Monitoring, New Delhi, February 1980.

14. W.J. Cretney and C.S. Wong, "Fluorescence monitoring study at Ocean Weather Station 'P'", NBS Spec. Publ. 409, Marine Pollution Monitoring (Petroleum) - Symposium and Workshop, Gaithersburg M.D., May 1974, 175-177, (Issued December 1974.)

15. Table - Properties of Oil Slicks Related to Appearance Characteristics, adapted from "Manual on Disposal of Refinery Wastes, Part 1, Waste Water Containing Oil", 7th ed., American Petroleum Institute, New York, 1963.

Test Books issued:-

16. Introduction to Ultraviolet and Visible Spectrophotometry, J.E. Steward, ed., 24pp, figures and tables, First edition September 1975, reprinted July 1976, Pye Unicam Ltd, York Street, Cambridge, CB1 2PX, England.

17. An Introduction to Gas Chromatography, J.D. Ashby. 32 pp, figures and tables, Second edition August 1977, Pye Unicam Ltd, York Street, Cambridge CB1 2PX, England.

Log Forms:
(supplied courtesy of NOAA Data and Information Service, National Oceanographic Data Center, Washington D.C.)

18. 72/8 Log for Observation and Reporting Oil Slicks and Other Floating Pollutants.

19. 72/9 Log for Sampling and Reporting Particulate Petroleum Residue (Tar Balls)

20. 72/10 Log for Sampling, Analysis and Reporting Dissolved/Dispersed Hydrocarbons

21. 72/10A Data Documentation Form (for use with 72/10).

ANNEX V

CURRICULUM DETAILS, ASSIGNMENTS AND EXPERIMENTAL RESULTS

1. CURRICULUM DETAILS

The curriculum for the Training Course was based on the following topics. These were dealt with in informal discussion sessions.

Introduction

Background of oil pollution monitoring program activities within IOC - historical outline.
References: 1, 3, 4, 5, 6.

Observation of Oil Slicks

Discussion of procedures, use of observers from various maritime organisations, differences between slicks from petroleum and natural causes, use of polarizing glasses, completing log forms and dispatching reports to appropriate Oceanographic Data Centre.
References: 1(14-20), 2(1-5), 3(Annex V), 5(3, 6, 20-22), 6(7), 15.

Observation of Particulate Petroleum Residues (Tar Balls)

Discussion of procedures, operation of neuston nets, sample collection and measurement, completing log forms and dispatching reports to appropriate Oceanographic Data Centres.
References: 1(9, 21-24), 2(6-8), 3(Annex V, VI).

Sampling Tar on Beaches

Characteristics of sampling zones, collecting samples, measurement techniques using 1 and 2 measuring cylinders, completing log forms and dispatching reports to appropriate Oceanographic Data Centres.
References: 1(9, 25-27), 2(9-11), 3(Annex VI)

Petroleum Hydrocarbons Dissolved and Dispersed in Sea Water

Discussion of sampling equipment, preparation of samples, importance of avoiding contamination, transfer of samples to laboratory (see Laboratory Techniques section for fluorimetry, distillation of solvents, rotary evaporator, calibration and quality control), completing log forms and dispatching data to appropriate Oceanographic Data Centre, application of other methods of analysis (see Laboratory Techniques section for gas chromatography, infra-red and ultra-violet spectrophotometry)
References: 1(10, 28-38), 2(12-20), 3(Annex VI), 4(5), 5(8, 9), 10, 11, 12, 13, 14, 16(4), 17.

2. PRESENTATION ASSIGNMENTS

The participants prepared assignment topics during the course and, each one presented a brief talk on

- General outline of work related to oil pollution monitoring in home institutions or countries.
- Summary of developments and variations in the methods for each of the components of MAPMOPP as outlined in IOC Manuals and Guides No. 7 and subsequent literature.

3. FIELD ASSIGNMENTS

The following field activities were undertaken by the participants working in small groups.

Cruises:

- Neuston net sampling for floating tar balls
- Sampling sea water for dissolved/dispersed hydrocarbons
- Navigational details necessary for preparation of log reports on oil slick observations, floating tar balls and dissolved/dispersed hydrocarbons.

Beaches:

- Setting out sample zones, identification of tar balls, sweeping the surface, collecting sand samples for solvent extraction.

4. FIELD ASSIGNMENTS

The following laboratory techniques were considered in group discussion periods.

- Quality control Importance of preparation of samplers, sample collection, storage, transfer, extraction methods, measurement and calculations, tests for variability and recovery.
- Rotary evaporation Assembling apparatus, optimising vacuum bleed rate, controlling conditions.
- Solvent distillation Assembling apparatus, controlling distillation rates, safety aspects.
- Calibration Preparation of standards, advantages and disadvantages of chrysene, linearity, working range, standard curves, standard additions, limits of detection, sensitivity.
- Fluorimetry Theory, molecular structure, principles of instrumentation, manual and automatic scan of spectra, sample handling and precautions.

- Infra-red and ultra-violet spectrophotometry Molecular energy absorption, principles of instrumentation, preparation of samples and limitations, interpretation of spectra, fingerprinting and characterisation of samples.

- Gas chromatography Principles of operation, qualitative and quantitative aspects, column selection for hydrocarbons, optimising gas flow and temperature program conditions, use with mass spectrometry, reproducible injection techniques.

5. LABORATORY ASSIGNMENTS

Several laboratory assignments were carried out by the participants.

- Prepare sets of equipment for beach sampling
- Measure tar balls by volume difference
- Extract sand samples for tarry residues
- Construct floating frame for neuston net
- Prepare solvents by distillation
- Prepare sample bottles for dissolved/dispersed hydrocarbon samplers by
  - open evaporation
  - rotary evaporator
- Calibrate fluorimeter with chrysene
- Measure dissolved/dispersed hydrocarbons by fluorimetry
- Measure extracts from "spiked" test samples to determine efficiency of recovery.
- Measure chrysene equivalent values of hydrocarbon reference samples to determine intercomparison ratios
- Prepare fluorescence spectrum of chrysene and field samples
- Measure fluorescence quenching effects of added traces of carbon tetrachloride
- Compare extraction efficiency of carbon tetrachloride and Freon TF for sea water samples.
- Analyse hydrocarbon reference samples by gas chromatography.

6. EXPERIMENTAL RESULTS

A selection of results of the field and laboratory assignments are included as an indication of the scope of the work undertaken by the participants.

IOC/WMO IGOSS MARINE POLLUTION MONITORING PILOT PROJECT

OBSERVATION/PLATFORM HEIGHT ABOVE SEA LEVEL _____ Meters

NOAA FORM 72-8 (1-75)

U. S. DEPARTMENT OF COMMERCE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

Form Approved
O.M.B. No.
41R2835
Expires
December, 1979

LOG FOR OBSERVATION AND REPORTING OF OIL SLICKS AND OTHER FLOATING POLLUTANTS

PLATFORM/SHIP				INSTITUTE/ORGANIZATION
TYPE	NAME	FLAG	RADIO CALL	
1	VIGILANT			DEPARTMENT OF SCIENCE AND THE ENVIRONMENT

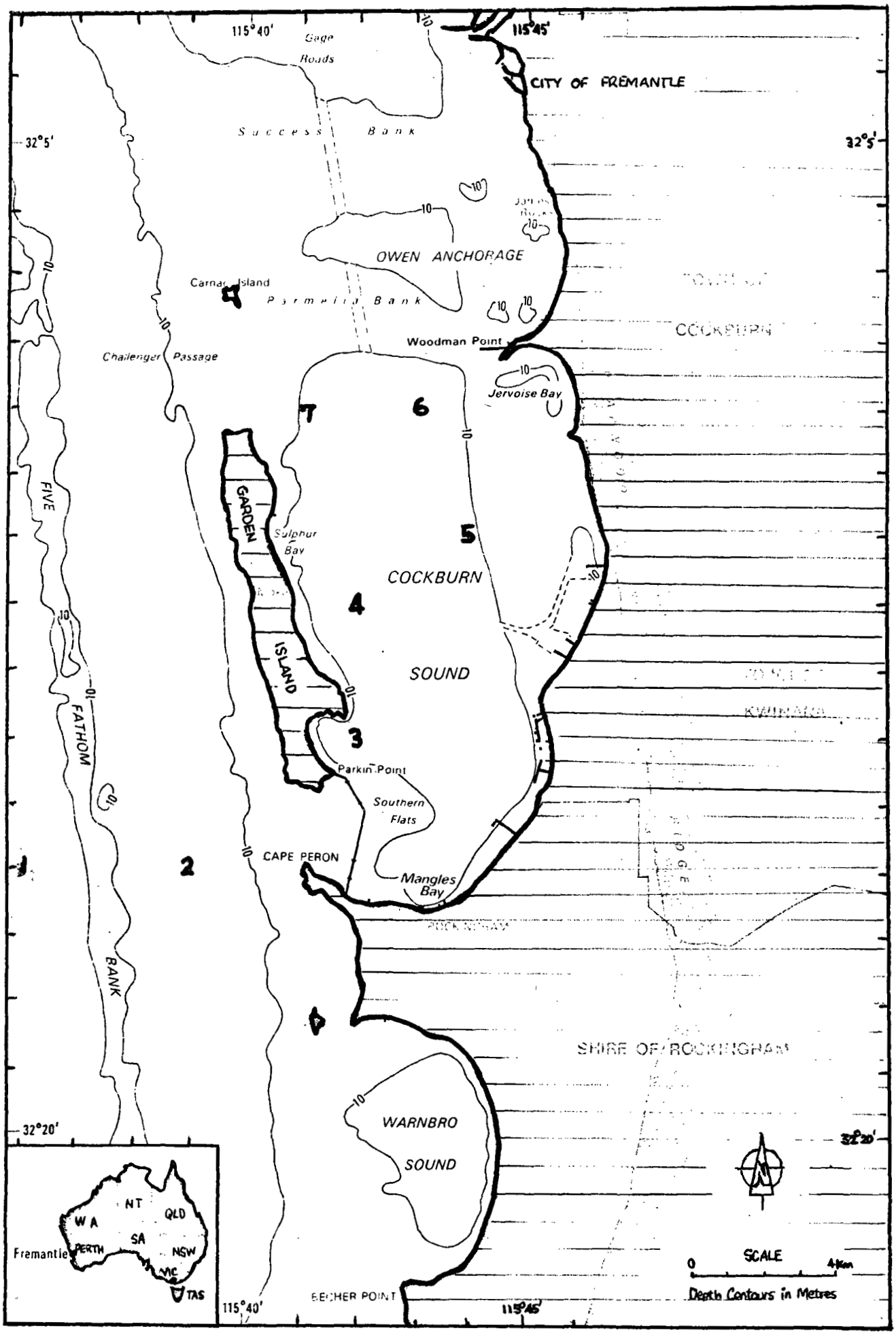
DATE/TIME G.M.T.										LOCATION										POLLUTION DATA				COVERAGE (1/10 N. Miles)				ENVIRONMENTAL DATA									REMARKS
DAY		MO.		YEAR		HR.		MIN.		QUAD	LAT. DEG.		LAT. MIN.		LONG. DEG.			LONG. MIN.							ALONG TRACK			ACROSS TRACK			WIND UNIT	WIND DIR.		WIND SPEED		WAVE PER.		WAVE HT.		
Y	Y	M	M	J	J	G	G	g	g	Q_c	L_a	L_a	L_a	L_a	L_o	L_o	L_o	L_o	L_o	A	B	C	D								d	d	f	f	P_w	P_w	H_w	H_w	
2	7	0	2	8	0	0	4	0	0	3	3	2	0	9	1	1	5	4	1	0	-	-	-	-	-	-	-	-	-	3	1	2	1	5	0	0	0	0	Cockburn Sound

- 24 -

FIGURE 3

SAMPLING STATIONS, DISSOLVED/DISPERSED HYDROCARBONS

FIGURE 4



IOC/WMO IGOSS MARINE POLLUTION MONITORING PILOT PROJECT

NOAA FORM 72-10 (1-75)

U. S. DEPARTMENT OF COMMERCE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

Form Approved O.M.B. No. 41R2837 Expires December, 1979

(1)

LOG FOR SAMPLING, ANALYSIS AND REPORTING DISSOLVED/DISPERSED HYDROCARBONS

PLATFORM/SHIP TYPE	PLATFORM/SHIP NAME *	PLATFORM/SHIP CALL SIGN *
	VIGILANT	

COUNTRY: AUSTRALIA

INSTITUTE: DEPARTMENT OF SCIENCE AND THE ENVIRONMENT

CRUISE NUMBER *: MAP9/1

STATION NUMBER	SAMPLE NUMBER *	CONCENTRATION (2) µg/kg	DATE * (GMT) DAY	DATE * (GMT) MO.	DATE * (GMT) YR.	TIME * (GMT) HR.	TIME * (GMT) MIN.	QUAL	POSITION * LAT. DEG.	POSITION * LAT. MIN.	POSITION * LONG. DEG.	POSITION * LONG. MIN.	OPTIONAL ENVIRONMENTAL INFORMATION WIND DIR.	WIND SP.	WAVE PER	WAVE HT.	TEMP. °C AIR	TEMP. °C WATER	REMARKS
			YY	MM	JJ	GG	gg	Q_c	L_a L_a	L_a L_a	L_o L_o	L_o L_o	i_u ddd	ff	P_w P_w	H_w H_w	s_n TTT	T_w T_w T_w	
00000 1	0031	0.13	27 02 80	01	45	3	32	16	11	53	36	430	10	07	02	020	220	220	DCE outer buoy
00000 2	0041	0.42	27 02 80	02	15	3	32	16	11	53	39	430	10	07	02	020	220	220	DCE inner buoy
00003 0	0051	0.04	27 02 80	02	40	3	32	14	11	54	23	310	21	50	00	002	230	220	Cockburn Sd.
00003 0	0052	0.08	27 02 80	02	40	3	32	14	11	54	23	310	21	50	00	002	230	220	" "
00004 0	0062	0.22	27 02 80	03	00	3	32	12	11	54	23	310	21	50	00	002	230	220	" "
00005 0	0042	0.42	27 02 80	03	36	3	32	11	11	54	23	410	21	50	00	002	230	220	" "
00006 0	0061	0.61	27 02 80	03	45	3	32	09	11	54	23	310	21	50	00	002	230	220	" "
00007 0	0032	0.13	27 02 80	04	00	3	32	09	11	54	23	410	21	50	00	002	230	220	" "

NAME AND ADDRESS *(Individual/Office to contact reference this report.)*

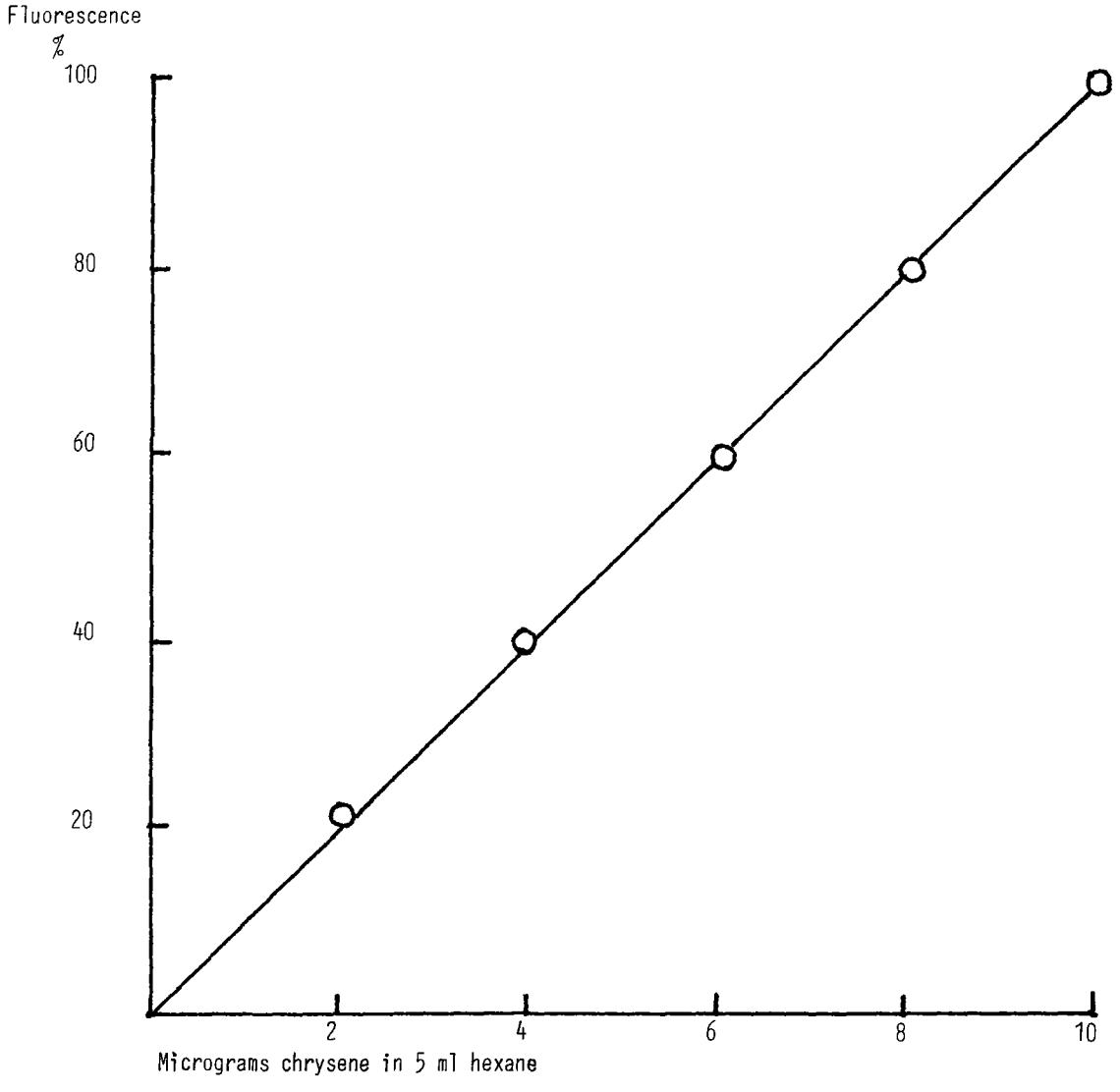
*NOTE: – *Include items marked with an asterisk on bottle label.*

(1) This form should be accompanied by NOAA Form 72-10A Data Documentation Form.

(2) Concentration to be determined by Analysis Laboratory.

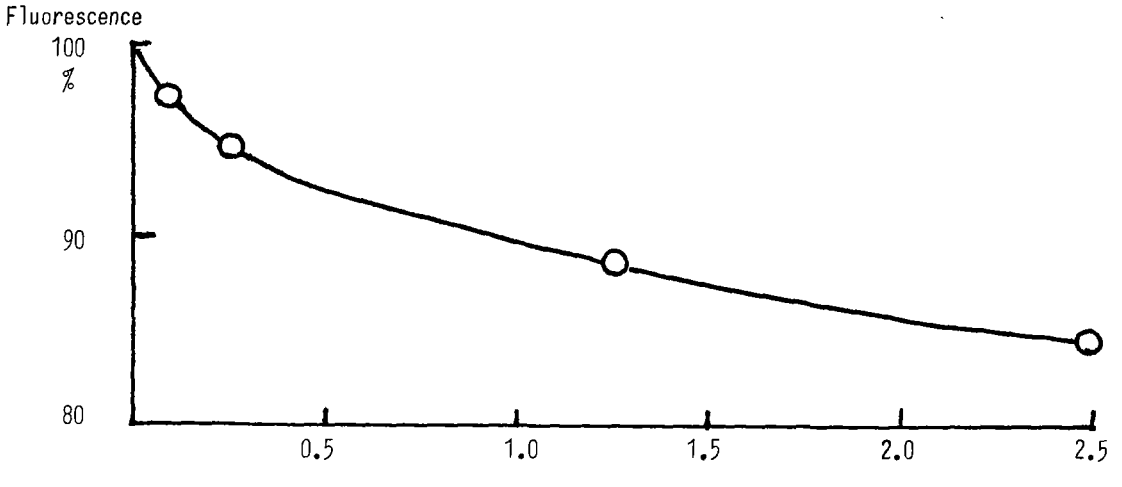
FIGURE 5

FIGURE 6



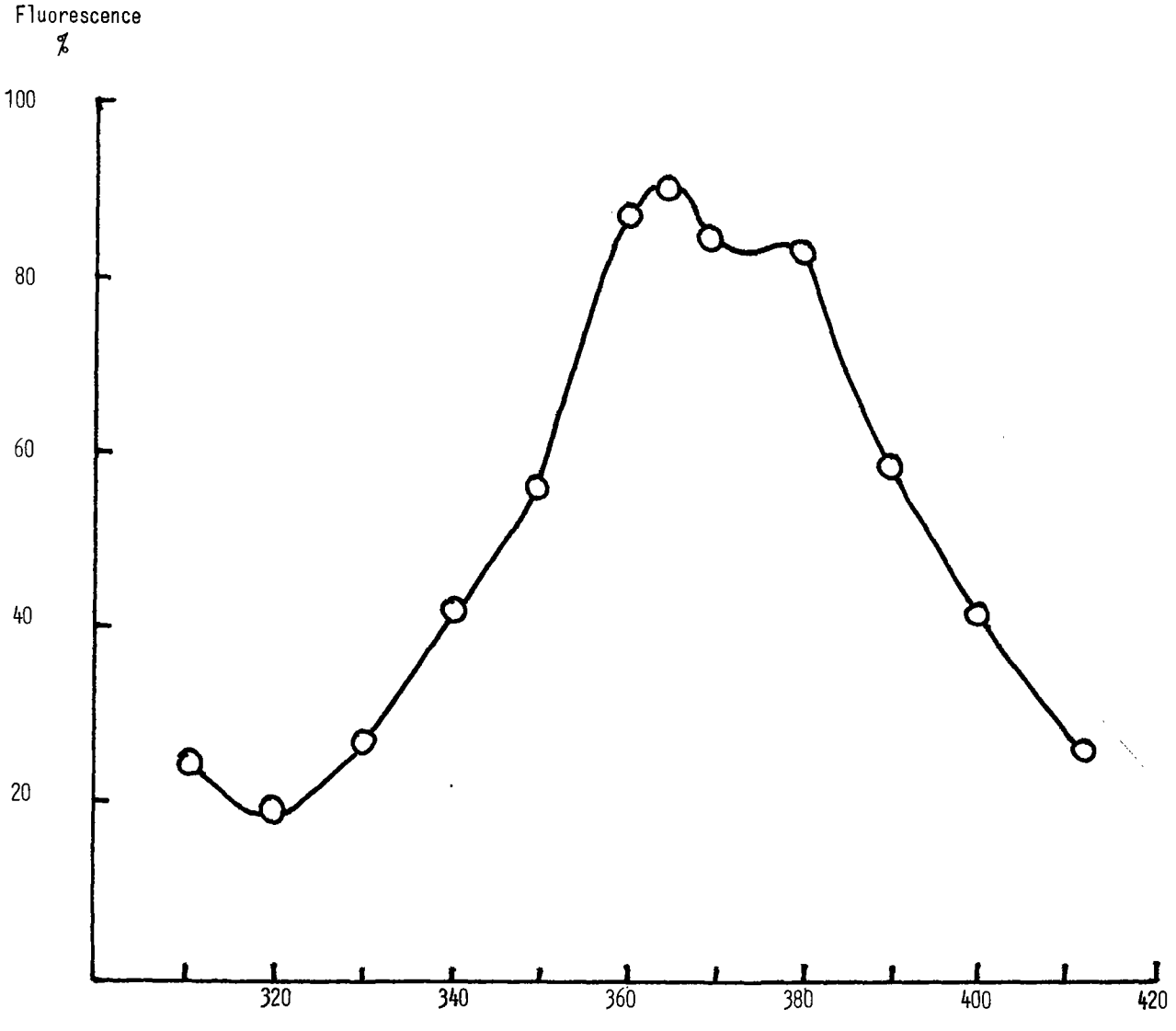
CALIBRATION GRAPH FOR EXTRACT MEASUREMENTS

FIGURE 7



"QUENCHING" EFFECT OF CCL_4 CONTAMINATION

FIGURE 8



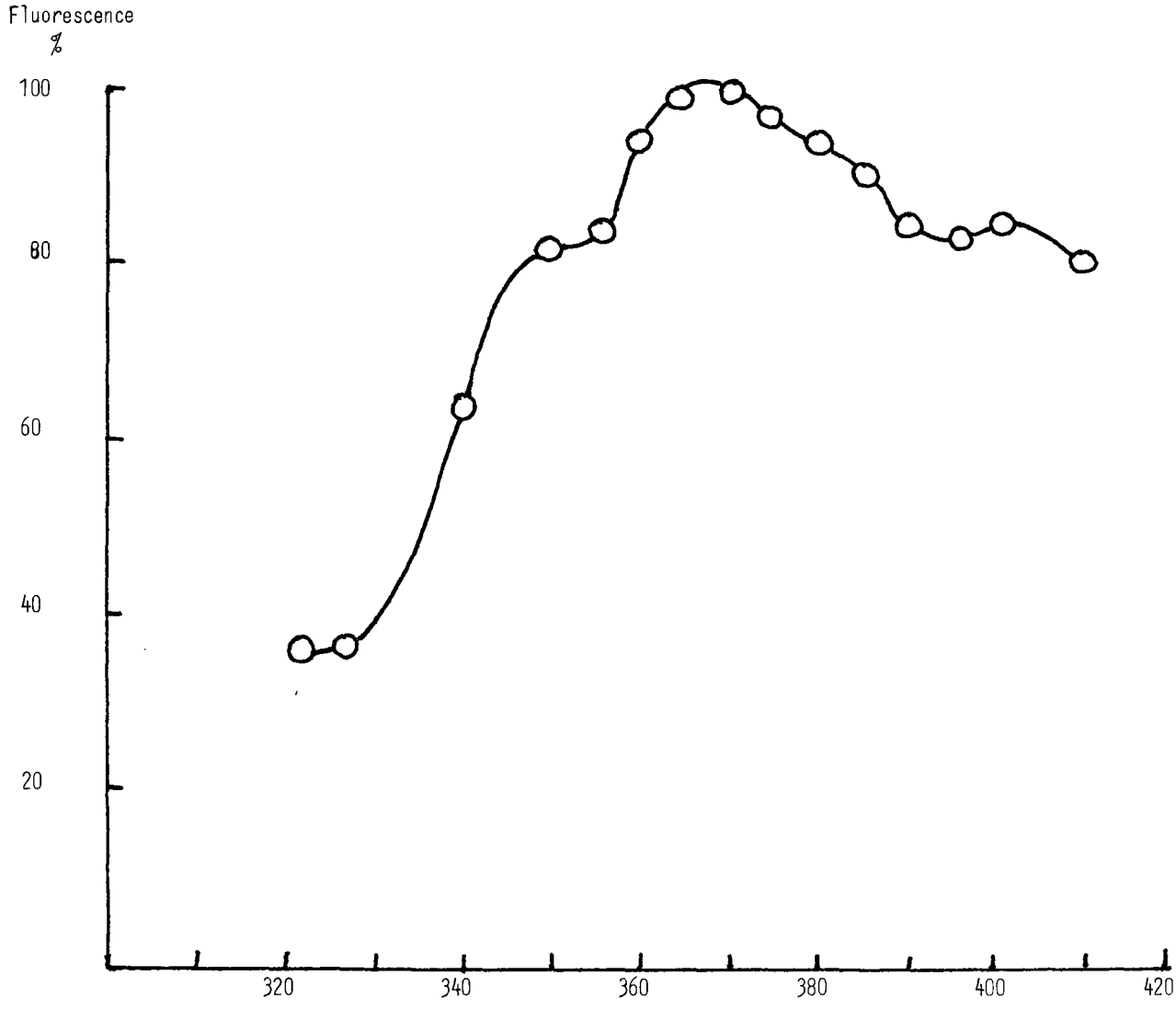
Wavelength nm

Manual scan of 10 micrograms chrysene in 5 ml hexane

Excitation wavelength 310nm, 10 mm cell

FLUORESCENCE SPECTRUM OF CHRYSENE SOLUTION

FIGURE 9

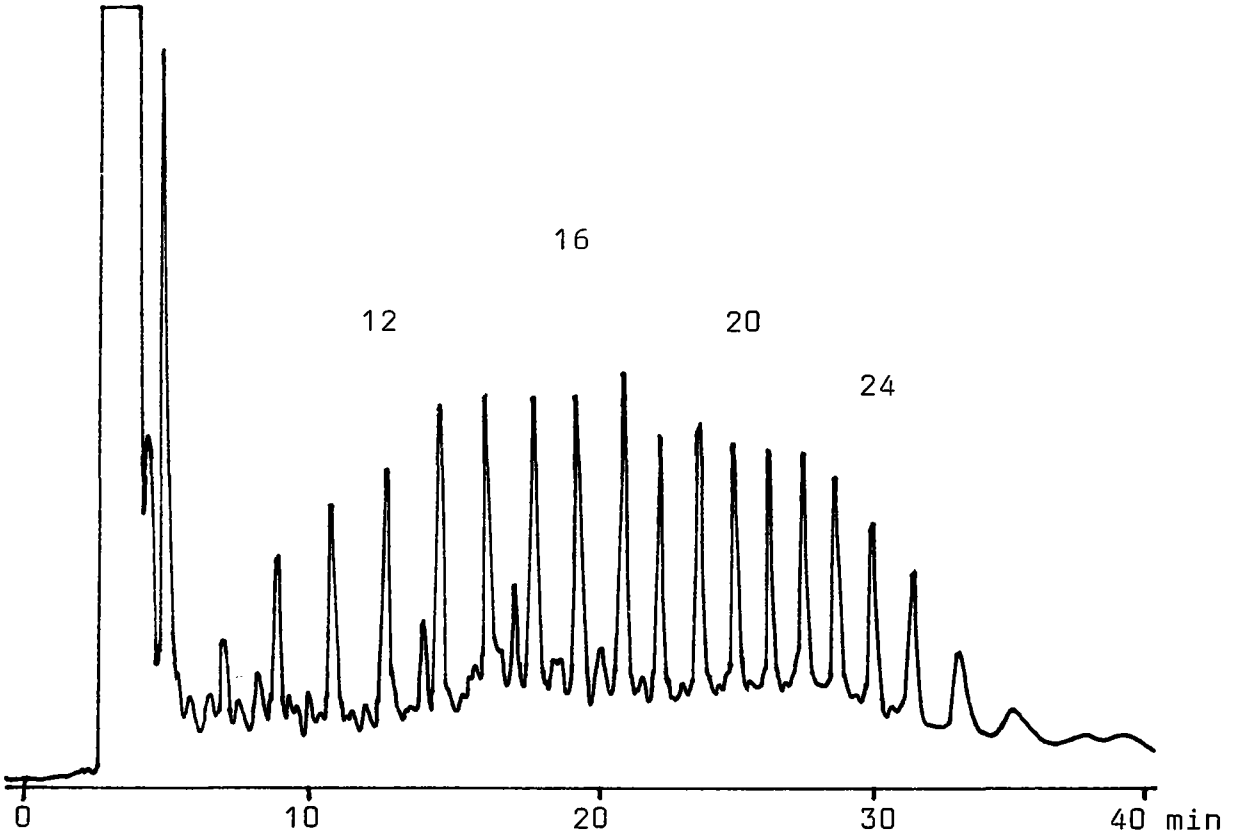


Fluorimeter sensitivity adjusted to 100% at maximum emission (367nm)

FLUORESCENCE SPECTRUM OF HIGH-READING SAMPLE
OF PETROLEUM EXTRACT FROM STATION No 5, 27/2/80

FIGURE 10

Gas chromatogram of crude oil reference sample.



"Weathered" Gippsland Crude, from petroleum hydrocarbon reference set used in Australian inter-laboratory surveys.

Sample: 10 micrograms crude oil in 1.0 microlitres hexane.

Column: 3% OV101 on 100-120 mesh, 4m x 4mm dual s/steel.

Temperature programmed: 80^{o} - 300^{o} at 8^{o} per minute.

Note: Although resolution of n-heptadecane/pristane and n-octadecane/phytane has not been achieved under these column conditions, good quantitative agreement between different operators was achieved with manual injection techniques.

Calculations of column features: for nC_{16}, $t_1 = 102$, $t_{w1} = 2.5$

for nC_{17}, $t_2 = 110$, $t_{w2} = 2.8$

$\therefore \Delta t = 8.0$

$$\text{Resolution} = \frac{2 \quad \Delta t}{t_{w1} + t_{w2}} = \frac{16}{4.8} = 3.3 \text{ (for } nC_{16}/nC_{17})$$

$$\text{Theoretical Plate Number} = 16 \left(\frac{t}{t_w}\right)^2 = 16. \left(\frac{102}{2.5}\right)^2 = 26\,000 \text{ (for } nC_{16})$$

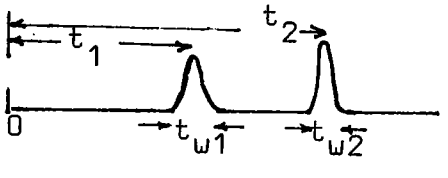


TABLE 1

PROPERTIES OF OIL SLICKS RELATED TO APPEARANCE CHARACTERISTICS

APPEARANCE OF OIL SLICK	APPROXIMATE THICKNESS		QUANTITY PER UNIT AREA		
	10^{-6} in	μm	$USgal.mi^{-2}$	$L.km^{-2}$	$ton.mi^{-2}$
Barely visible under most favourable light conditions	1.5	0.4	25	36	0.08
Visible as a silvery sheen on the surface of the water	3	0.8	50	73	0.16
First trace of colour	6	1.6	100	146	0.33
Bright bands of colour visible	12	3.1	200	292	0.65
Colour beings to turn dull	40	1.0	666	973	2.2
Colour much darker	80	2.0	1332	1946	4.3

Adapted from "Manual on Disposal of Refinery Wastes, Part 1, Waste Water Containing Oil". 7th Edition American Petroleum Institute, New York, 1963.

TABLE 2

Chrysene Equivalent Values of Petroleum Hydrocarbon Samples in Inter-laboratory Test Set

Ampoule No. and hydrocarbon type	Duplicate results from different analysts (chrysene equiv. mg/ampoule)		Mean	Target Conc. mg.	Inter-comparison ratio
1 Blank	0	0	0	0	-
2 Gippsland	0.054	0.058	0.056	1.0	17.9
3 Lube oil	0.115	0.090	0.103	1.0	9.7
4 Gippsland	0.450	0.440	0.445	5.0	11.2
5 Kuwait	1.76	1.76	1.76	5.0	2.8
6 Gippsland	0.56	0.83	0.70	10.0	14.3
7 Kuwait	3.70	4.00	3.85	10.0	2.6
8 Diesel	0.35	0.30	0.33	10.0	30.3

TABLE 3

Intercomparison Ratios (R) of Petroleum Types

Target Concentrations	1mg	5mg	10mg
Gippsland crude	17.9	11.2	14.3
Kuwait crude	-	2.8	2.6
Lube oil	9.7	-	-
Diesel	-	-	30.3

$$R = \frac{\text{Fluorescence of chrysene solution}}{\text{Fluorescence of petroleum soln.}} \times \frac{\text{wt. petroleum}}{\text{wt. chrysene}}$$

TABLE 4

Repeatability of gas chromatography injection technique*

Operator	nC_8 peak height
1	97
2	108
3	109
4	103
5	101
Mean	103.6
Standard deviation (s.d)	4.97
Relative s.d.	4.8%

* Procedure for 1.0 microlitre injection:

(1) Slowly draw solution into a five microlitre syringe and expel by gently tapping the plunger, keeping below solution surface.

(2) Repeat several times to clear air bubbles.

(3) Slowly draw solution into syringe to around 2 microlitre mark.

(4) Return plunger to 1.0 microlitre mark and carefully wipe excess solution from needle tip.

(5) Draw the measured column of solution slowly back from the needle into the syringe barrel until an air meniscus just appears above the needle at the zero mark. Note up-scale reading of the end of the plunger.

(6) Inject solution through chromatograph septum, wait for 3-4 seconds before withdrawing needle.

(7) Draw residual solution back into the syringe and re-locate end of plunger at scale reading noted in (5). The air space from zero to the solution meniscus indicates the volume of sample actually injected.

Notes: (1) This technique avoids unpredictable losses of solution from the needle in the proximity of heated injection septum surfaces.

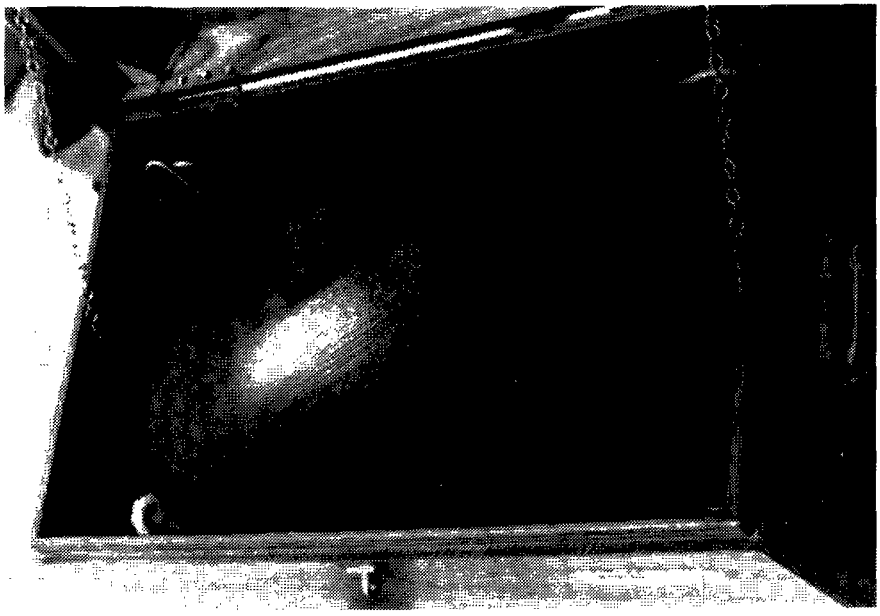
(2) Step (6) minimises sample vapour loss back through septum if needle withdrawn too rapidly after injection.

7. PHOTOGRAPHS

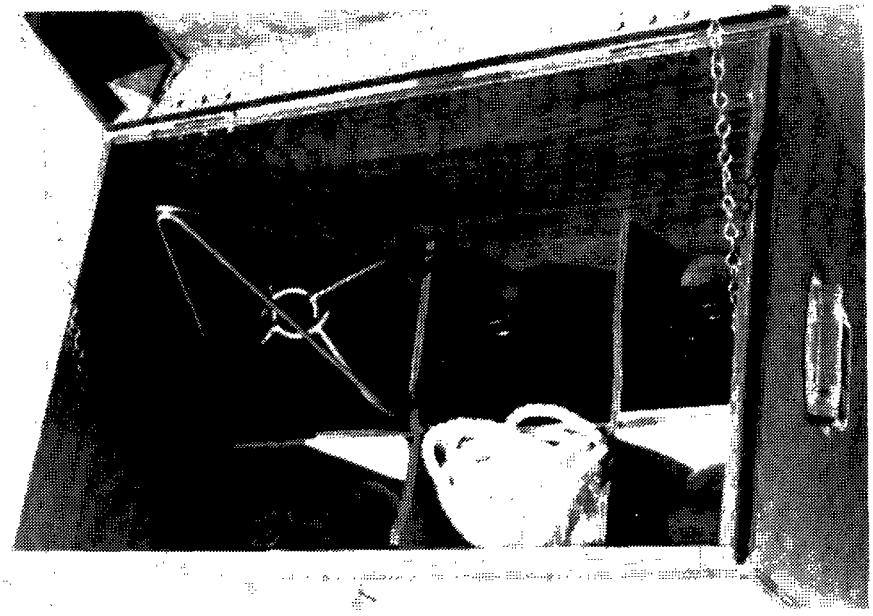
Details of field sampling equipment, laboratory exercises and the way in which the participants were involved in many aspects of this training course are illustrated by these photographs:

Sampling kit for dissolved/ Dispersed hydrocarbons	(1) Float storage
	(2) Four bottles, frame and rope
	(3) Assembled
Operating the samplers	(4) Assembly
	(5) Casting
	(6) Coming ashore
Surface sampler	(7) Low-cost float frame
	(8) The group with net in tow
	(9) Hauling aboard
Beach sampling for tar-balls	(10) Setting out sample zone
	(11) Discovery
	(12) Finer details
On board	(13) Plotting the course
	(14) Casting the sampler
	(15) Calculations
Sample preparation	(16) Rotary evaporation
	(17) Sand extracts
	(18) Distilling solvents
Fluorimetry - dissolved/ dispersed hydrocarbons	(19) Setting-up
	(20) Samples in cells
	(21) Measuring

SAMPLING KIT FOR DISSOLVED/DISPERSED HYDROCARBONS

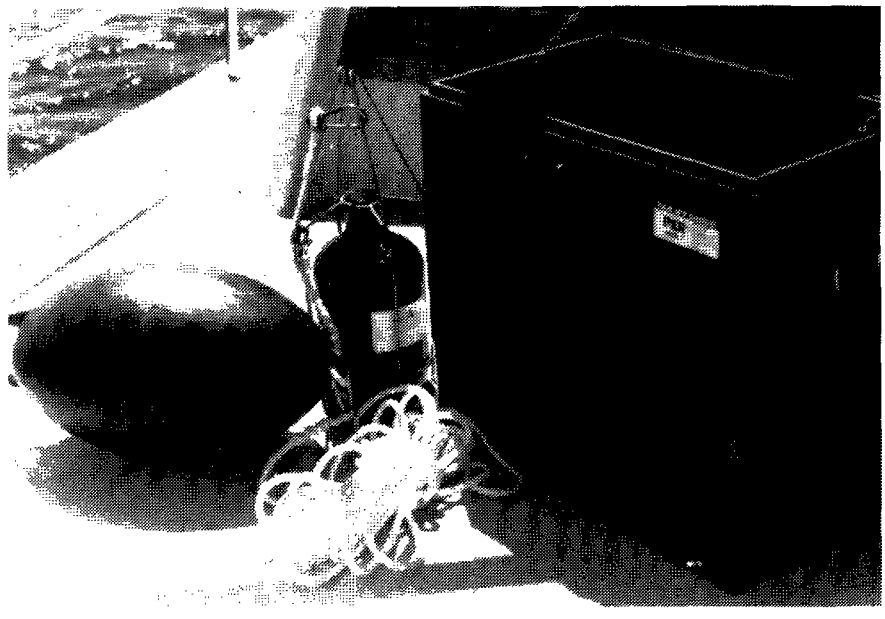


(1) Float storage



(2) Four bottles, frame and rope

(3) Assembled



OPERATING THE SAMPLERS

(5) Casting

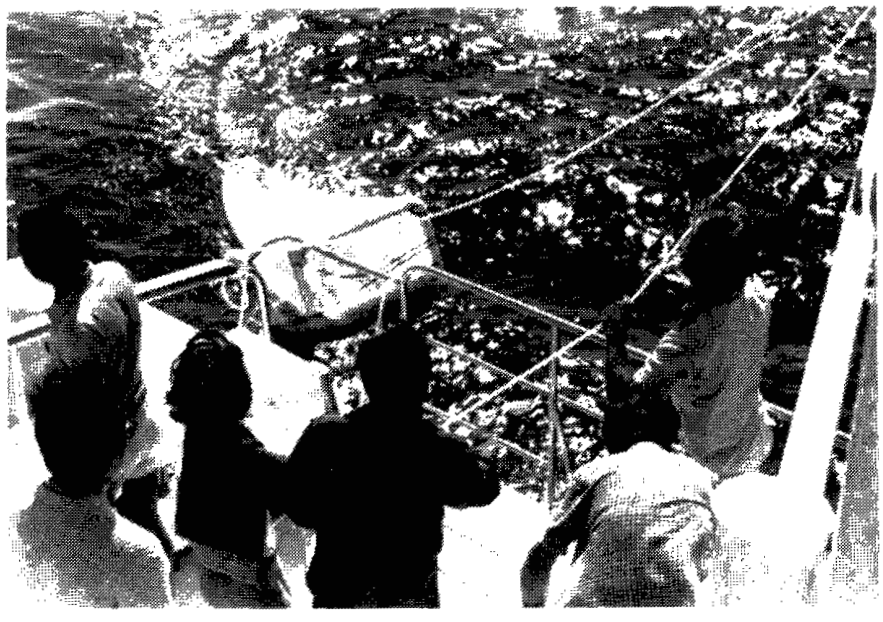
(4) Assembly

(6) Coming ashore

SURFACE SAMPLER

(7) Low-cost float frame

(8) The group with net in tow



(9) Hauling aboard

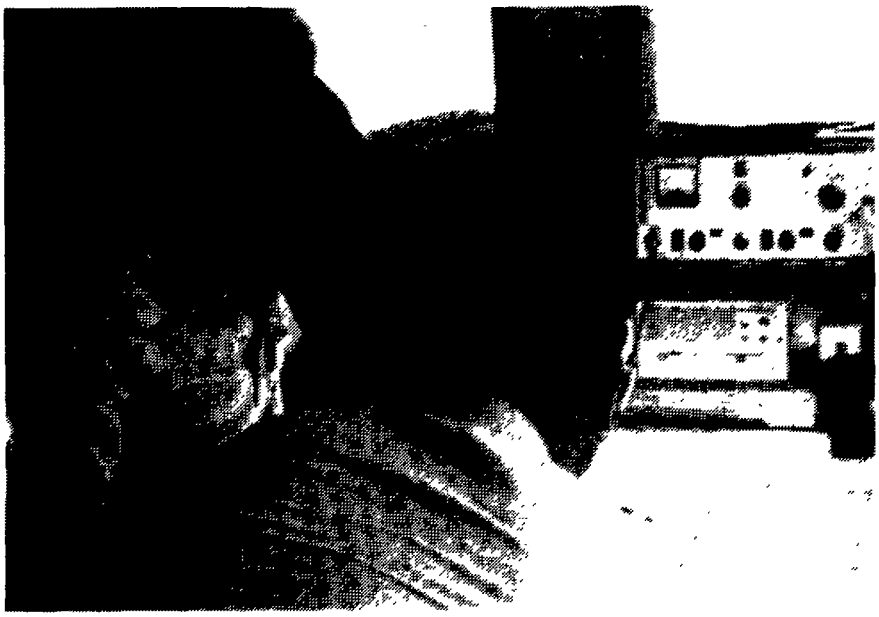
BEACH SAMPLING FOR TAR-BALLS

(10) Setting out sample zone

(11) Discovery

(12) Finer details

ON BOARD

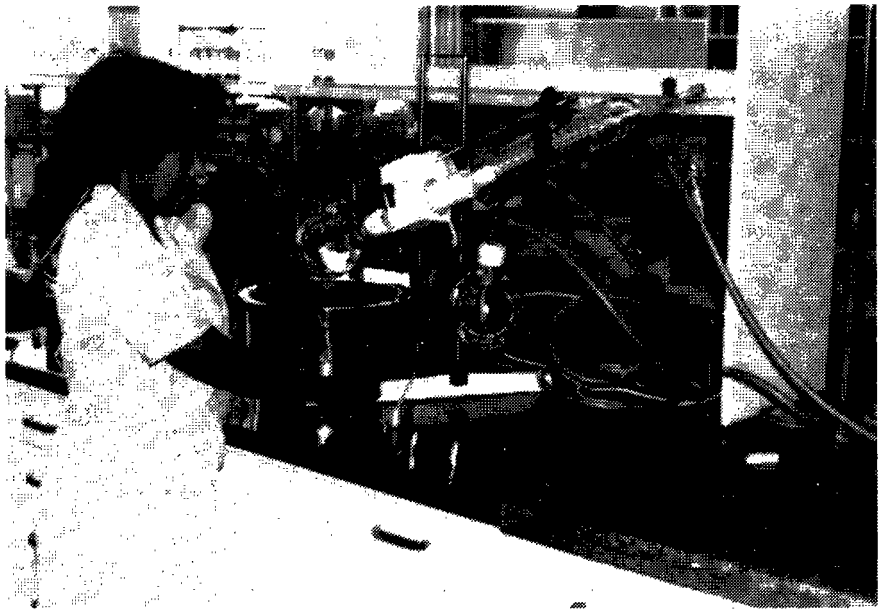


(13) Plotting the course

(14) Casting the sampler

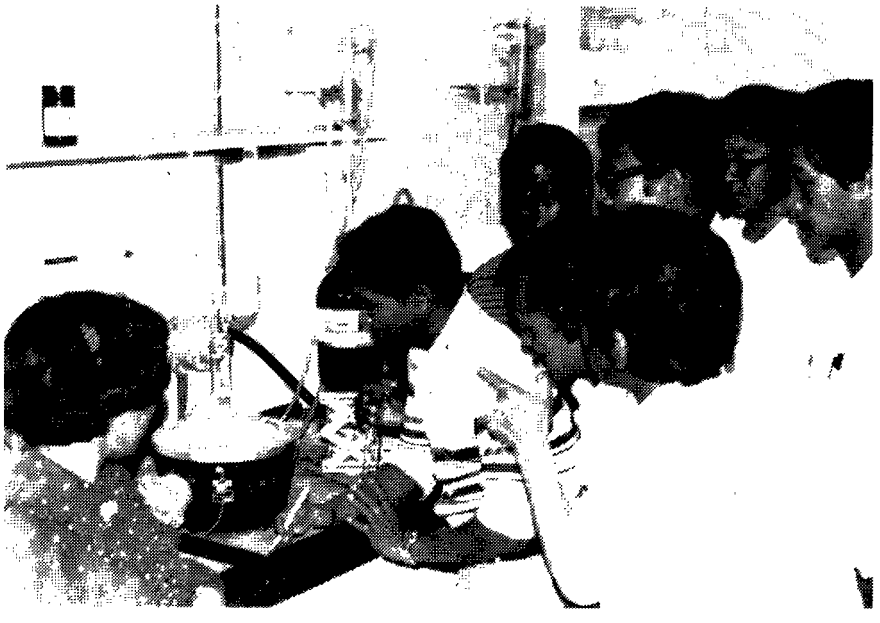
(15) Calculations

SAMPLE PREPARATION



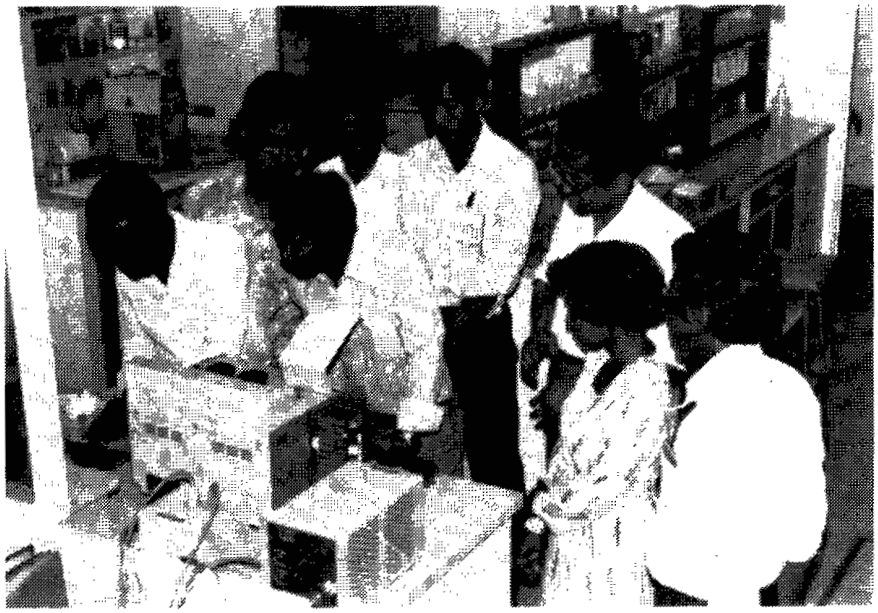
(16) Rotary evaporation

(17) Sand extracts



(18) Distilling solvents

FLUORIMETRY - DISSOLVED/
DISPERSED HYDROCARBONS



(19) Setting-up

(20) Samples in cells

(21) Measuring

DEPARTMENT OF SCIENCE AND THE ENVIRONMENT

CENTRAL OFFICE
SCARBOROUGH HOUSE, PHILLIP,
P.O. BOX 449, WODEN, A.C.T. 2606.
Telegrams: CONSCIENCE Telex: AA62484

SPECIMEN OF COURSE CERTIFICATE

This is to certify that 29 FEB 1980

(Name and Organisation of Participant)

attended the United Nations Educational Scientific and Cultural Organisation/Intergovernmental Oceanographic Commission - Indian Ocean Region petroleum monitoring training course in Perth, Western Australia from 18 February 1980 to 1 March 1980.

The course was conducted by the Commonwealth Department of Science and the Environment with the assistance of the Australian Development Assistance Bureau and the Western Australian Government Chemical Laboratories and the Harbour and Light Department. The course covered the Intergovernmental Oceanographic Commission/World Meteorological Organisation "Guide to Operational Procedures for the Integration Global Ocean Station System Pilot Project on Marine Pollution (Petroleum) Monitoring".

Participants were instructed in:

- field and laboratory techniques for measurement of tar-balls in ocean water samples and beach sand
- the technique for observation of oil-slicks
- the measurement of dissolved/dispersed hydrocarbon in sea water.

The course members also conducted assignments on basic gas chromatographic analytical techniques as applied to petroleum in sea water.

(T.R. McKay)
Marine Programs Section
Course Director

(G.R. Mills)
Assistant Secretary,
Environment Programs Branch

for (John L. Farrands)
Secretary