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SUMMARY OF RESULTS OF THE FIRST ICES INTERCOMPARISON EXERCISE ON PETROLEUM HYDROCARBONS

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ABSTRACT

An intercomparison of petroleum hydrocarbon analyses has been conducted for samples of crude oil, marine sediment, and a mussel homogenate. Thirty-six sets of samples were distributed, and at the time of preparing this report, 25 sets of results had been received from analysts in ten countries. No specific analytical methods were specified for the exercise, and analyses using fluorescence spectroscopy, gravimetry, infrared and ultraviolet spectrophotometry, gas and liquid chromatography, and combined gas chromatography/mass spectrometry were reported. The results are considered briefly in this preliminary report.

INTRODUCTION

At the meeting of the Marine Chemistry Working Group in May 1979 it was proposed that an intercalibration of methods for the analyses of petroleum hydrocarbons in marine samples should be conducted under the auspices of ICES. This proposal was approved by the Council at the 67th Statutory Meeting in October, and its form was agreed. It was decided that the exercise should be in three parts consisting of the examination of samples of crude oil and oil fractions, tissue samples and sediment samples.

AIMS

The aim of the intercomparison was twofold:

1. to discover the range of methods in general use for the analysis of petroleum hydrocarbons in marine samples;
2. to compare the analytical results obtained both between laboratories and between methods.

For this first exercise it was not thought possible to stipulate any particular methods; participants were encouraged to analyse samples by a number of techniques, from broad fraction analysis to the analysis of individual hydrocarbons if possible. Results were to be reported relative to a standard oil so as to facilitate comparison of the results. Samples were distributed to the first participants in late December 1979. The deadline for submission of results was set at 30 June 1980.

PREPARATION OF SAMPLES

In all, four samples were made available to participants. These were a crude oil, an aliphatic fraction of the same oil, a naturally contaminated marine sediment, and a mussel homogenate. The second and fourth samples were supplied only to those who especially requested them.

Sample No. 1: Crude oil standard

Ekofisk crude oil supplied by the Warren Spring Laboratory (Stevenage, U.K.) was lightly air-weathered to remove the most volatile fractions. The oil was sealed under nitrogen into 2 ml glass ampoules.

Sample No. 2: Aliphatic fraction

This sample was in two parts each sealed into an ampoule, consisting of:

a. a standard comprising the normal alkanes from n-C12 to n-C32, pristane and phytane, all at known concentrations;

b. the aliphatic fraction of the standard crude oil.

As noted above, this sample was not distributed to all participants, but was available on request.

Sample No. 3: Marine sediment

A fine sandy sediment was collected from the intertidal flats of the Isle of Grain (Thames Estuary), close to shipping routes and oil refineries. It was oven-dried at 105°C and passed through a 1.4 mm sieve. Aliquots (ca 200 g) of that fraction which passed through the sieve were placed in glass jars. Analyses of several replicates from both a single aliquot and several different aliquots suggested homogeneity was good to at least ±10%.

Sample No. 4: Mussel homogenate

This was prepared from mussels collected in Narragansett Bay, U.S.A. and was originally prepared for an intercalibration between participants in the E.P.A. mussel watch programme. Aliquots of ca 20 g were sealed in teflon containers. Homogeneity of the sample was assured by the E.P.A. source laboratory. This sample was supplied by the Rhode Island Laboratory (Dr Phelps). Requests for the samples were however routed via the Coordinator (Dr Portmann).

All samples were stored in a freezer at -20°C prior to distribution.

DISTRIBUTION OF SAMPLES

This was by British Rail (Express) parcels service wherever possible within the U.K., and by air to Europe or North America. Mussel samples were shipped by air packed in dry ice to prevent spoilage. Strict regulations govern the transport by air of crude oil because of its extreme flammability. These regulations apply to 2 ml quantities as well as to larger quantities. For this reason samples of oil and sediment were professionally packed to meet the regulations. All of the oil and sediment samples, and approximately one-third of the mussel samples, were despatched from the Coordinator's laboratory at a cost of ca £1800 (packing

£400, transport £1400) or ca £50 per participant. In addition the preparation of samples and organisation of despatch took about 1 man month.

RESULTS

The original estimate of the number of participants was 15-20, in fact 36 sets of samples were distributed and 25 sets of results had been returned by the 30 June deadline. (A list of these participants is appended to this report.) One further set of results was received after completion of this report; the results from this laboratory will be included in the final report. Although the exercise received some critical comments, generally either expressing concern over the likely homogeneity of samples or the feeling that the use of widely differing methods may make comparison of results difficult, the general level of interest and commitment was high. One set of results from an overseas laboratory was even delivered in person to the Coordinator's laboratory, in order that the analyst could discuss the results of his analyses! The results of the analyses are given in Tables 1-7.

Mussel homogenate

Total hydrocarbon analyses of the mussel homogenate showed a wide variation by all methods, and a number of laboratories using fluorescence spectroscopy (UVF) reported quenching of the mussel extracts, necessitating dilution to constant fluorescence.

Sediment sample

Results of analyses of the sediment sample by UVF using the IGOSS wavelengths (excitation 310 nm, emission 360 nm) (IOC/WMO, 1976) showed the best agreement. The range of concentrations was from 13.6 to 42μg g^{-1} Ekofisk crude oil equivalents (mean = 32.1μg g^{-1}, SD = 7.6, n = 29). Infrared spectrophotometry (IR), the second most common quantitative technique, showed a range of values for sediment samples of 11 to 93.6μg g^{-1} (mean = 41.0μg g^{-1}, SD = 25, n = 25). Most of the laboratories involved in the intercalibration used either IR or UVF in conjunction with capillary gas chromatography to generate hydrocarbon profiles.

Aliphatic and aromatic hydrocarbons

Individual hydrocarbon determinations of both aliphatic and aromatic compounds were carried out by a number of laboratories on the crude oil, sediment and mussel samples, although one laboratory reported difficulty obtaining a clean aromatic extract from the mussels. Considerable variation was found in reported concentrations for both aliphatic and aromatic compounds, sometimes greater than an order of magnitude, particularly in the sediment and mussel samples. Hydrocarbon profiles also differed from laboratory to laboratory, nC18/Ph ratios (for instance) ranging from 0.26 to 1.49 in sediment samples and from 0.83 to 4.21 in mussels. Agreement on the analyses of the standard oil was however rather better, e.g. nC18/Ph ratio ranged from 2.07 to 2.90 and was also better for the nC17/Pr ratio.

A more detailed study of the results, including a comparison of the extraction methods used and the authors' interpretation of some of the reasons for the differences observed, will appear in a later report.

CONCLUSION

The response to this intercalibration exercise was very good, 25 of 36 possible sets of results being returned within six months of the start of the exercise. Preliminary assessment of the results for total hydrocarbon analyses suggest that UVF analyses using the IGOSS wavelengths yield the most comparable results, even for laboratories which have only recently begun to use this method (10, 13). Individual hydrocarbon hydrocarbon analyses by gas chromatography and combined gas chromatography/mass spectrometry show great variation for both aliphatic and aromatic compounds.

REFERENCE

INTERNATIONAL OCEANOGRAPHIC COMMISSION/WORLD METEOROLOGICAL OFFICE, 1976. Guide to operational procedures for the IGOSS project on marine pollution (petroleum) monitoring. UNESCO Manuals and Guides (7), 50 pp.

LIST OF PARTICIPANTS RETURNING RESULTS

Laboratory No.	Country	
1	U.K.	Mr R J Law Ministry of Agriculture, Fisheries and Food Fisheries Laboratory Remembrance Avenue Burnham on Crouch Essex, CM0 8HA
2	U.K.	Mr P R Mackie Ministry of Agriculture, Fisheries and Food Torry Research Station PO Box 31 135 Abbey Road Aberdeen, AB9 8DG
3	U.K.	Dr J M Davies Department of Agriculture & Fisheries for Scotland Marine Laboratory PO Box 101 Victoria Road Torry Aberdeen, AB9 8DB
4	U.K.	Dr K B Pugh North East River Purification Board Woodside House Persley Aberdeen, AB2 2UQ
5	U.K.	Mr D Hammerton Clyde River Purification Board Rivers House Murray Road East Kilbride Glasgow, G75 OLA
6	U.K.	Mr D Buchanan Highland River Purification Board Strathpfeffer Road Dingwall, IV15 9QY
7	F.R.G.	Dr M Ehrhardt Institut fur Meereskunde Dürstenbrooker Weg 20 D 2300 Kiel 1
8	F.R.G.	Dr G Dahlmann Deutsches Hydrographisches Institut Postfach 2 20 2000 Hamburg 4
9	France	Dr P Michel ISTPM Rue de L'Ile-D'Yeu BP 1049 44037 Nantes Cedex

Laboratory No.	Country	
10	France	Dr J C Roussel Institut Francais du Petrole BP 311 92506 Rueil-Malmaison Cedex
11	France	Mr G Bodennec Centre Oceanologique de Bretagne CNEXO BP 337 29273 Brest Cedex
12	France	Mr F Berthou Faculte de Medecine de Brest BP 815 29279 Brest Cedex
13	Portugal	Mr J L Biscaya Instituto Hidrografico Rua Das Trinas 49 1296 Lisboa Codex
14	Norway	Dr K H Palmork Institute of Marine Research PO Box 1870 N5011 Nordnes Bergen
15	Norway	Dr R G Lichtenthaler Central Institute for Industrial Research PB 350 Blindern Oslo 3
16	Eire	Dr D O'Sullivan Fisheries Research Centre Abbotstown Castleknock County Dublin
17	Denmark	Dr V B Jensen Water Quality Institute 11 Agern Alle DK-2970 Horsholm
18	Canada	Dr G R Sirota Fisheries and Oceans Halifax Laboratory PO Box 550 Halifax Nova Scotia, BJ3 2S7
19	Canada	Dr J W Kiceniuk Fisheries and Oceans PO Box 5667 St Johns Newfoundland, A1C 5X1

Laboratory No.	Country	
20	Canada	Dr E M Levy Atlantic Oceanography Laboratory Bedford Institute of Oceanography Dartmouth Nova Scotia, B2Y 4A2
21	Netherlands	Dr W A M den Tonkelaar Research Institute for Environmental Hygiene Schoemakerstraat 97 2600 AE Delft
22	Netherlands	Dr M A T Kerkhoff Rijksinstituut voor Visserijonderzoek 1 Haringkade 1970 AB Ijmuiden
23	Netherlands	Dr P Hoogweg Governmental Institute for Sewage Purification Maerlant 4-6 8224 AC Lelystad
24	Finland	Dr F Koroleff Institute of Marine Research PO Box 166 SF-00141 Helsinki 14
25	Finland	Dr K Haapala National Board of Waters PB 250 00101 Helsinki 10

Table 1. Results of total hydrocarbon analyses of mussel homogenate ($\mu g\ g^{-1}$ wet weight Ekofisk oil equivalents)

a) Fluorescence spectroscopy

Laboratory number	Exλ	Emλ	Results	Mean
1	310	360	55	55
3	310	360	124,135	130
10	340		96	96
	420		74	74
11	310		32,32	32
16	340	460	130	130
20	310	460	86,90	88

Overall Mean 85.6 (SD = 36, n = 10)

b) Infrared spectrophotometry

Laboratory number	Results
5	< 620
10	270
16	6011

c) Gas chromatography

Laboratory number	Results	Mean
15	28	28
17	39,53	46

Overall mean 40

d) Gravimetry

Laboratory number	Result
10	256

Table 2. Results of total hydrocarbon analyses of sediment samples ($\mu g\ g^{-1}$ Ekofisk oil equivalents)

a) Fluorescence spectroscopy

Laboratory number	Exλ	Emλ	Results	Mean	SD'
1	310	360	36,37,39,42	38.5	2.3
2	310	360	36,37	36.5	
3	310	360	35.8,36.4	36.1	
6	310	360	13.6,14.8	14.2	
7	310	360	33.8,33.9,34.5,38.4	35.2	1.9
8	310	360	29.5,32.8	31.2	
10	310	360	38.0	38.0	
	340		56.0	56.0	*
	420		70.8	70.8	*
13	310	360	30,30,30,36	31.5	2.6
	310	360	33,35,35,41	36.0	3.0
16	340	460	22.0	22.0	*
19				29.5	4.5
20	310	360	16.3,16.8	16.5	

Overall mean 32.1 (SD = 7.6, n = 29)

b) Infrared spectrophotometry

Laboratory number	Results	Mean	SD'
4	15.0	15.0	
10	16.2	16.2	
11	63.0,73.0	68.0	
13	22,22,23,24	22.8	0.8
15	23	23.0	
16	93.6	93.6	
21	39,44,53,54,56,57,79,85	58.0	16
23	54,59	56.5	
25	11,11,12,16,20	14.0	4.0

Overall mean 41.0 (SD = 25, n = 25)

c) Gas chromatography

Laboratory number	Results	Mean	SD'
15	19	19.0	
17	26,27,27,28,33,36	29.5	3.7
24	10.1	10.1	

Overall mean 25.8 (SD = 7.6, n = 8)

d) Gravimetry

Laboratory number	Results	Mean
4	130,170,190	165
10	15.6	15.6

Overall mean 126 (SD = 68, n = 4)

' SD quoted only for four or more replicate measurements

* Results not included in calculation of mean as longer excitation wavelengths would be expected to give higher results

Table 3. Aliphatic hydrocarbons in Ekofisk oil ($\mu g\ g^{-1}$)

Laboratory number	1	2		3		8	17	24
nC7								22 900
8								19 200
9								14 200
10								11 700
11	7 540							10 200
12	7 190					7 070		10 200
13	6 740					6 260		8 100
14	6 070					9 290		7 500
15	5 790	2 139	2 313	7 614	6 972	7 680		7 100
16	4 920	2 062	2 188	7 400	6 388	6 870		6 200
17	5 330	1 867	1 964	5 550	6 611	6 570		5 300
Pristane	1 770	949	961	3 203	3 408	2 830		
18	4 530	1 453	1 516	4 946	4 489	5 450		4 800
Phytane	1 560	656	668	2 385	2 103	2 420		
19	3 300	1 323	1 371	4 391	3 223	5 350		4 100
20	2 950	1 199	1 251	4 129	2 425	5 050		3 400
21	2 630	1 089	1 135	3 661	2 337	3 540		3 000
22	2 570	1 008	1 189	3 116	1 947	3 540		2 200
23	2 330	924	998	2 999	1 840	3 130		1 400
24	2 090	747	774	2 609	1 685	2 530		1 000
25	1 950	680	667	2 171	1 441	2 530		720
26		482	448	1 685	1 159	2 220		510
27		318	326	1 568	1 022	1 720		300
28		256	250	1 402	847	1 620		200
29		224	217	1 392	779	1 620		120
30		179	171	1 285	643	1 520		70
31		173	168	1 158	565	1 210		
32		169	164	867	438	1 920		
33		147	140	711	467			
17/Pr	3.01	1.97	2.04	1.73	1.94	2.32	2.17	
18/Ph	2.90	2.21	2.27	2.07	2.13	2.25	2.57	
Pr/Ph	1.13	1.45	1.44	1.34	1.62	1.17	1.45	

Table 5. Aliphatic hydrocarbons in sediment and mussel samples (ng g^{-1} wet weight)

	Sediment									Mussels			
Lab No	1	2		3		8	12	17	22	24	2		3*	
nC_{12}						8				11				
nC_{13}	4.7					3				16				
nC_{14}	7.9					12				26				
nC_{15}	16	35	40	9	26	10	1.9			33	71	48	49	67
nC_{16}	17	38	38	14	34	15	7.4		10	35	38	24	42	54
nC_{17}	46	68	73	48	84	20	18.3			35	37	28	51	73
PRISTANE	32	100	106	95	39	15	10.4			41	36	26	14	32
nC_{18}	23	42	41	35	61	25	15.5		80	31	16	14	32	39
PHYTANE	38	57	59	134	41	31	13.2				16	10	7.6	11
nC_{19}	19	42	44	36	55	18	16.5			52	16	12	19	31
nC_{20}		51	47	44	46	15	18.5		140	50	14	9	45	61
nC_{21}		45	43	59	58	15	21.5			68	26	19	147	218
nC_{22}		42	36	102	124	15	17.7		110	107	29	28	410	356
nC_{23}		41	41	241	304	13	21.6			151	29	26	723	515
nC_{24}		49	46	458	623	15	20.1		70	192	27	26	928	1330
nC_{25}		59	65	605	752	15	32.4			214	32	30	962	1360
nC_{26}		66	71	718	896	14	38.2			190	36	32	976	1270
nC_{27}		84	93	611	819	20	74.3			131	38	37	911	1190
nC_{28}		62	69	501	738	14	44.9		40	92	38	46	687	972
nC_{29}		98	111	471	576	26	74.5			41	53	63	532	755
nC_{30}		59	66	235	367	15	48.8			26	33	34	357	501
nC_{31}		68	80	232	260		32.9			9	38	41	214	302
nC_{32}		30	35	98	142				30	4	26	25	116	202
nC_{33}		29	35	82	104						24	23	64	97

Table 5 (contd)

Lab No	Sediment									Mussels			
	1	2		3		8	12	17	22	24	2		3*	
17/Pr	1.44	0.68	0.69	0.51	2.15	1.33	1.76	1.13		0.85	1.03	1.08	3.64	2.28
18/Ph	0.61	0.74	0.69	0.26	1.49	0.81	1.17	0.79			1.00	0.83	4.21	3.55
Pr/Ph	0.84	1.75	1.80	0.71	0.95	0.48	0.79	0.44			2.25	2.60	1.84	2.91

* These figures were supplied as dry weight of the mussels, and have been recalculated to wet weight assuming 14% dry matter as measured in authors' laboratory

Table 6. Aromatic hydrocarbons in sediment and mussel samples (ng g^{-1} wet weight)

	Sediment								Mussels				
Lab No	1	2	7	14	18				1	14	18		
Naphthalene	3.3	2		3.4					3.4	1.8			
C_1 N	3.3	3		8.2					8.3	1.7			
C_2 N	8.6	4		14.6					21	3.6			
C_3 N	13			14.7					51	3.2			
Phenanthrene	19	19	4	16.2	ND	ND	ND	ND	1.6	1.7	35	55	33
Anthracene	3.0			3.4					0.16				
C_1 P	20	21		18.4					3.3	4.6			
C_2 P	11			12.7					5.5	7.6			
Dibenzothiophene	1.8			ND					0.29				
C_1 D	1.9			4.1					0.71	0.8			
C_2 D	4.1			15.9					1.7	6.8			
C_3 D	2.7			18.8					1.0	7.6			
Fluoranthene			7		72	73	88	129			17	26	13
Pyrene			6		ND	ND	ND	ND			TR	TR	TR
Chrysene			16	165	162	121	206				36	40	34
Benzofluor			34										
B(a)Pyrene			31	15.8	15.5	10.5	17				0.4	0.4	0.3
B(e)Pyrene				153	144	132	178				26	26	25
Triphenylene				ND	ND	ND	ND				21	19	19
B(a)A				232	217	211	331				31	33	32
B(b)F				36.2	36.5	31	37				4.3	3.9	4
B(k)F				10.5	11	9	11				1.1	1.1	1.1
B(ghi)perylene				83	78	70	74				6	5.8	5
O-phenylene pyrene				131	127	110	100				7.7	9.6	7.1

ND : Not detected
TR : Trace

Table 7. Ring type analysis of aromatic hydrocarbons in oil, sediment and mussels ($\mu g\ g^{-1}$ chrysene equivalents)

LABORATORY NUMBER 9

Ring number	Ekofisk oil			Sediment			Mussels		
1	1900	2000	2000	0.01	0.01	0.01	0.13	0.09	0.10
2	11600	11600	11800	0.12	0.14	0.13	0.65	0.51	0.66
3	13000	13000	13400	0.18	0.23	0.25	1.05	0.76	1.03
4	6100	6200	6000	0.12	0.19	0.22	0.87	0.58	0.75
5	1915	2200	1800	0.16	0.25	0.33	0.31	0.21	0.34
Total	34800	35000	35000	0.59	0.82	0.92	3.00	2.16	2.88