PCB'S AND OTHER ORGANOCHLORINES IN BCR REFERENCE CANDIDATE FISH OILS

A Report
to
The Vrije Universiteit, Instituut voor Milieuvraagstukken, Amsterdam

by

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INTRODUCTION

The Vrije Universiteit, Instituut voor Milieuvraagstukken, Amsterdam has requested the Institute of Marine Research to take part in an extended collaborative exercise, also including organochlorine other than PCB's. The background for this is as follows:

At a BCR meeting in Bruxelles July 2. 1986, Dr. B. Griepink considered it useful if other determinants than PCB's could be included and the results be "appended to the certification report as indicative values".

Dr. D. E. Wells, of the Freshwater Fisheries Laboratory, Pitlochry, Scotland, sent a letter to all members of the PCB Group dated July 23. 1986 (APPENDIX I), where he requested us, especially those of us with a special interest in fish oils, to extend our analyses to include our usual organochlorines range for 2/3 of the replicates, if not all five.

Several laboratories agreed to do this and standards covering these extra determinants, organochlorines and PCB compounds, were sent out to the different laboratories in October 1986. A follow-up letter of December 9., 1986, with a standard result form for organochlorines and PCB compounds with extra space allocated for further determinants (APPENDIX II) were sent out.

Check out of the standards received from Dr. Wells.

The 6 ampoules received October 28., 1986 were labeled as follows:

A: is a mixture of D2-D18 (dichlorobenzylether) DCBE at 0.5 µg/ml iso-octane.

B: is a solution of D6 at 10 µg/ml iso-octane.

C: is a solution of D12 at 10 µg/ml iso-octane.

D: is a solution of D16 at 10 µg/ml iso-octane.

E: is a mixture used for $(GC)^2$ calibration.

F: is a mixture used for $(GC)^2$ calibration.

$(GC)^2$ = gas chromatography -glass capillary

Sample E and F were checked towards two standard solutions used daily in our laboratory. The Standard-SR was obtained from BCR and the Standard-A from Lars Reutergårdh, Naturvårdsverket, Special Analytiska Laboratorium, Stockholm , Sweden.

The following compounds were added to standard-A:

gamma-HCH
aldrin
dieldrin
4,4-DDE
4,4-DDD
4,4-DDT

DCBE-14, supplied from BCR in an earlier Ring Test, was used as an internal standard.

All the standard solutions were diluted with iso-octane to give approximately the same concentrations (approx. 20 ng/ml). The concentration of DCBE-14 was 455 ng/ml.

The samples were injected on-column because of severe adsorption in the inlet system when injecting splitless, especially of DDT.

MATERIAL AND METHODS

Table I. Chemicals used during the analyses of the fish oils.

Chemicals	:	Grade of purification
Pentane	:	Merck, Art. 7179, Uvasol
Sulphuric acid	:	Merck, Art. 731, pro analysis
Silica	:	Merck, Art. 7734, 63-200 µm
Iso-octane	:	Merck, Art. 4718, Uvasol
Dichloromethane	:	Distilled technical grade
Nitrogen	:	99.99% purity

Table II. Instrumental conditions.

Gas chromatograph	: HP-5880A
EC-detector	: Ni-63
Column	: Fused silica, SE-54, CB, 50 x 0.32 mm, 0.17µm.
Carrier gas	: Hydrogen, 20 cm/sec.
Oven temp. prog.	: 1 min. 90 °C-3 °C/min.-260 °C
Injection	: On-column, 3µl.

Analytical procedure

The samples - 0.2 g fish oil - were treated with concentrated sulphuric acid and the PCB's and DDT's were separated on a silica column as described in: Determination of PCB-Congeners in Candidate Reference Material (Fish Oils), by S. Wilhelmsen and K. H. Palmork, January 1987.

The PCB's were eluted with 10 ml of pentane and the DDT's with 10 ml pentane: dichloromethane (1:1). DCBE-14 was used as an internal standard.

Results and comments.

The concentrations of the standards supplied by Wells were given in µg/kg. Since we always use µg/l when dealing with liquids, the concentrations were transformed to these units. (1 l iso-octane = 0.692 kg).

Tables IV and V shows our results compared to the given concentrations both in µg/l and µg/kg. As can be seen from the tables, our results in µg/l are in agreement with the given results in µg/kg. (Is there a possibility of a misprint so that the given concentrations should be in µg/l ?).

Tables VI and VII shows the results of our analyses of the extra organochlorine components in Cod liver oil and Mackerel oil respectively.

Table III. Concentrations of the chlorinated compounds appearing in our standards (µg/ml).

Compound	Standard-SR	Standard-A
PCB-28	0.50	
PCB-52	0.50	1.18
PCB-44		1.00
PCB-95		0.82
PCB-101	0.50	1.00
PCB-110		1.00
PCB-118	0.50	1.00
PCB-153	0.50	1.00
PCB-138	0.50	1.00
PCB-128		1.00
PCB-180	0.50	1.00
PCB-170		1.00
PCB-194		1.00
gamma HCH		1.05
Aldrin		0.98
Dieldrin		1.00
4.4-DDE		1.05
4.4-DDD		1.00
4.4-DDT		1.00

Table IV. Results from the analysis of Standard-E in the order of elution from column CP Sil 5 CB and SE-54.

	Given		Found (n=3)	
Compound	µg/l	µg/kg	µg/l	RSD
HCB	66.9	97		
D6	345.0	500		
PCB 28	67.6	98	101.1	3.7
Heptachlor	66.9	97		
PCB 52	67.6	98	92.4	0.1
Aldrin	67.6	98	86.3	2.1
PCB 44	66.9	97	89.2	0.7
2.4-DDE	67.6	98		
PCB 101	67.6	98	92.4	1.4
4.4-DDE	67.6	98	89.4	2.3
PCB 118	67.6	98	92.4	2.4
PCB 153	67.6	98	87.1	2.4
PCB 137	67.6	98		
PCB 138	67.6	98	92.3	2.1
PCB 128	67.6	98		
D12	345.0	500		
PCB 180	67.6	98	97.3	2.5
Mirex	68.3	99		
PCB 195	67.6	98		
PCB 194	67.6	98	87.3	1.4
D16	345.0	500		

Table V. Result from the analysis of Standard-F in the order of elution from column CP Sil 5 CB.

	Given		Found (n=3)	
Compound	µg/l	µg/kg	µg/l	RSD
alpha HCH	67.6	98		
beta HCH	142.1	206		
gamma HCH	67.6	98	96.9	3.5
D6	345.0	500		
Heptachlor	67.6	98		
alpha chlordene	68.3	99		
gamma chlordene	66.2	96		
Heptachlor epoxide	66.9	97		
Oxychlordane	66.2	96		
gamma chlordane	66.9	97		
Endosulfan I	66.9	97		
2.4-DDE	67.6	98		
alpha chlordane	67.6	98		
trans nonachlor	67.6	98		
Dieldrin	67.6	98	97.1	2.2
2.4-DDD	66.9	97		
Endrin	67.6	98		
4.4-DDD	66.9	97	99.7	3.8
2.4-DDT	66.7	98		
4.4-DDT	66.7	98	100.1	3.2
D12	345.0	500		
PADS	174.0	252		
cis permethrin	704.0	1021		
trans permethrin	711.0	1031		
D16	345.0	500		

Table VI. Sample: Cod liver oil, individual results expressed on fat basis (ng/g).

Compound	1	2	3	x	RSD
alpha HCH	32	37	39	36	9.7
gamma HCH	78	88	88	85	7.3
4.4-DDE	285	272	327	295	9.7
4.4-DDD	161	180	182	174	6.6
4.4-DDT	63	70	68	67	5.8
PCB-44	94	85	85	88	5.6
PCB-95	207	204	205	205	0.7
PCB-110	226	222	219	222	1.6
PCB-128	241	237	240	239	0.9
PCB-170	84	77	91	84	8.3

Table VII. Sample: Mackerel oil, individual results expressed on fat basis (ng/g).

Compound	1	2	3	x	RSD
alpha HCH	23	26	22	24	7.5
gamma HCH	51	56	49	52	6.5
4.4-DDE	97	100	92	96	4.2
4.4-DDD	78	85	81	81	4.7
4.4-DDT	105	91	109	102	9.1
PCB-44	39	40	43	41	5.1
PCB-95	106	101	115	107	6.6
PCB-110	114	107	121	114	6.1
PCB-128	82	72	88	81	10.0
PCB-170	17	16	18	17	5.9

APPENDIX I

CHROMATOGRAMS

1. STANDARDS E (TABLE IV)

2. STANDARDS F (TABLE V)

3. BCR COD LIVER OIL

4. BCR MACKEREL OIL

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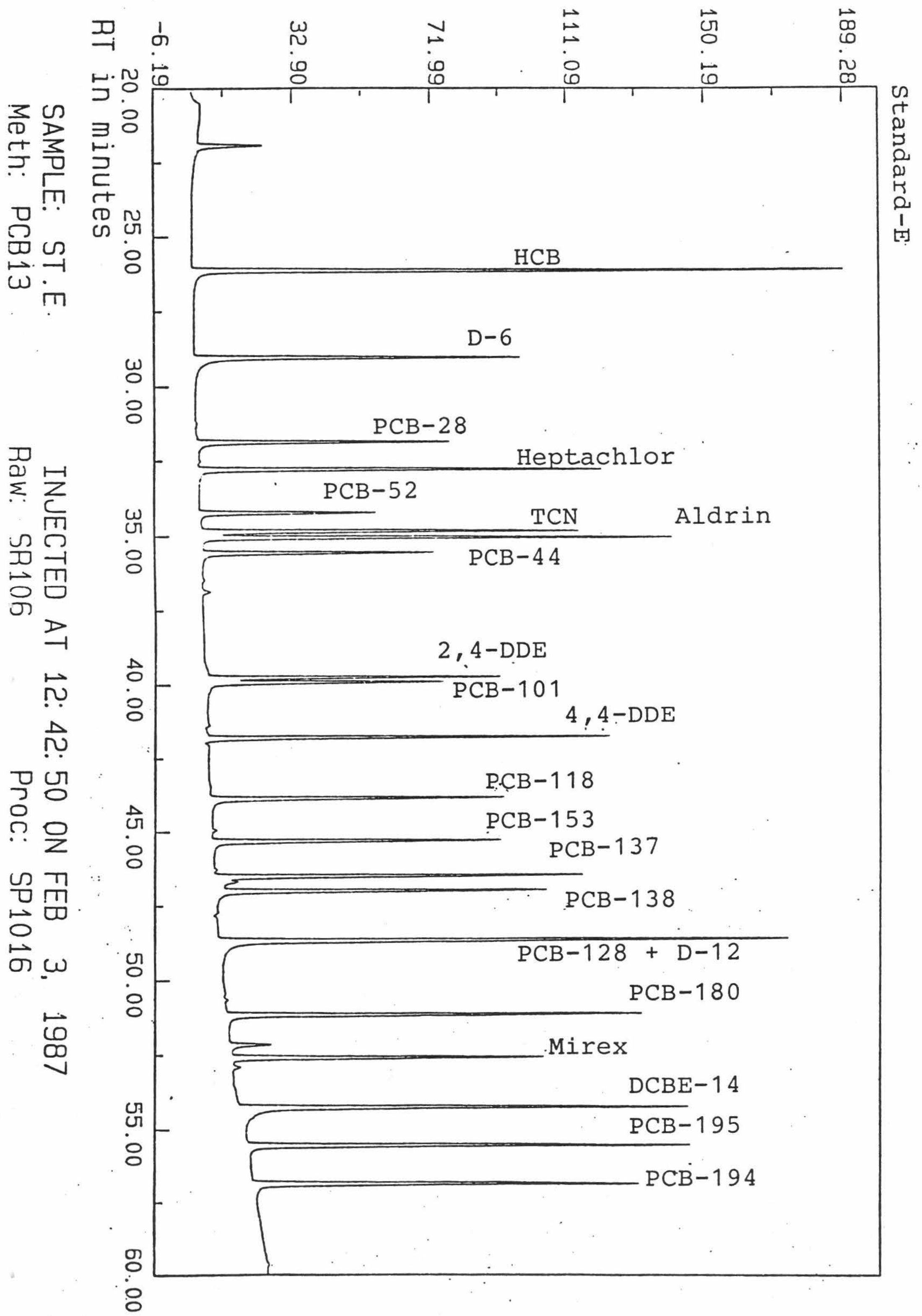
AMPLITUDE/1000
Range Normalized



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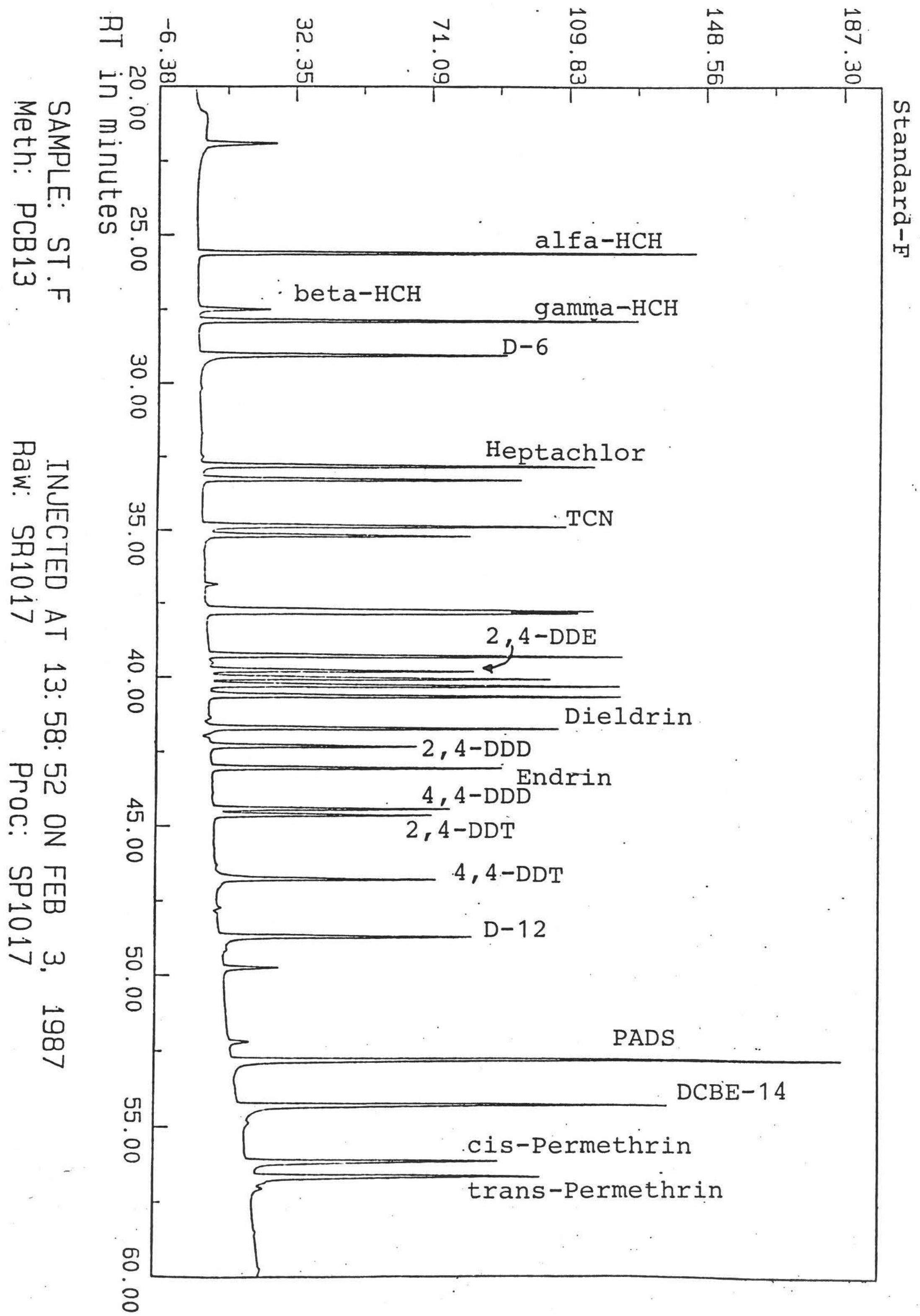

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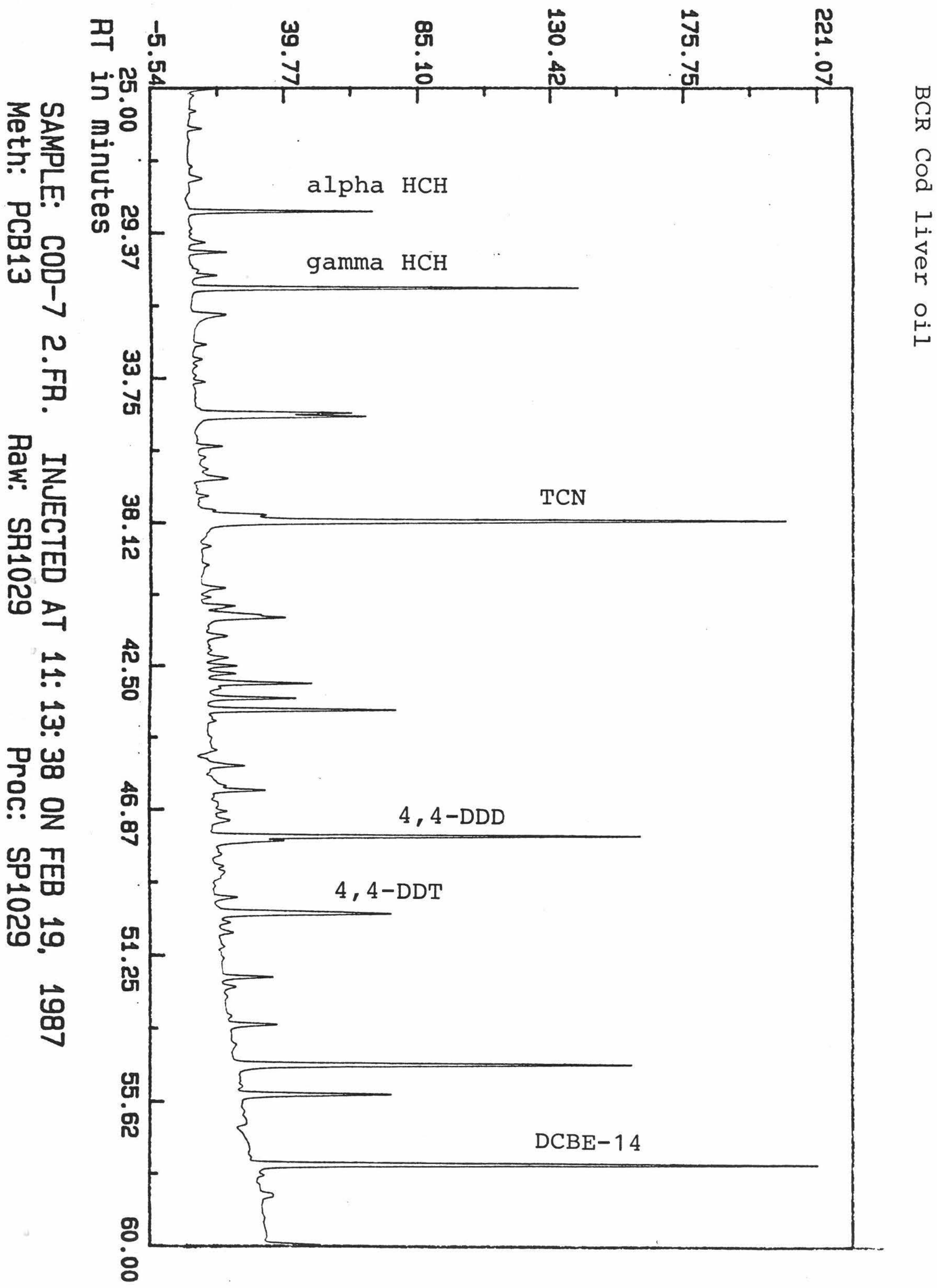

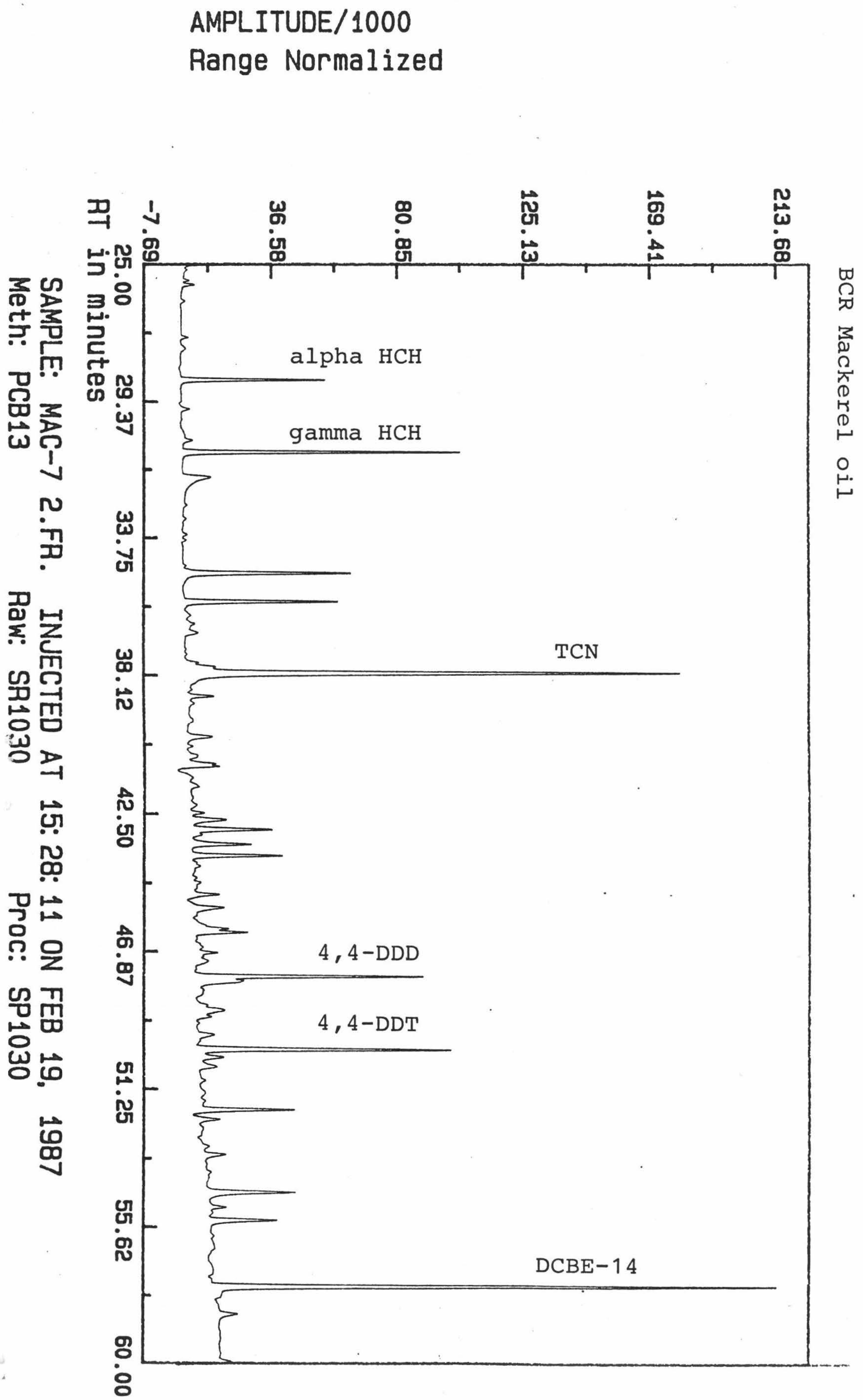
AMPLITUDE/1000
Range Normalized
BCR Mackerel oil
-7.69
36.58
80.85
125.13
169.41
213.68
25.00
29.37
33.75
38.12
42.50
46.87
51.25
55.62
60.00
RT in minutes
alpha HCH
gamma HCH
TCN
4,4-DDD
4,4-DDT
DCBE-14
SAMPLE: MAC-7 2.FR. INJECTED AT 15:28:11 ON FEB 19, 1987
Meth: PCB13 Raw: SR1030 Proc: SP1030