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US/INT/88/227 - Contract No. 92/002/VK

The Execution of Services Related to Preparatory Assistance in Clean Technology for the Recycling of Waste Oil.

DETERMINATION of PCB´s CONTENTS in WASTE OILS

Final Report

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Summary

The determinations of polychlorinated biphenyls in petroleum - based, waste oils have been carried out using gas - liquid chromatography method. A total of 34 samples of waste oils from different regions of Africa, Asia, Nord America and South America have been analyzed. The results have shown that samples from Senegal contain respectively 83, 94, 30 and 29 ppm of PCB´s. One sample from Brazil contains 93 ppm of PSB´s and two samples from Mexico contain 26 and 32 ppm of PSB´s, respectively. These are the sample with high level of PCB´s contents. The concentration of PCB´s in all other samples were below 10 ppm, but all samples from Indonesia, Singapore, Chile and Pakistan contain less than 5 ppm of PCB´s. Only 3 samples /one from Singapore, one from Pakistan and one from Mexico/ contain no PCB´s.

1. General

The presented work has been carried out within the scope of the CONTRACT NO. 92/002, dated 28 Jan., 1992 between the :

United Nations Industrial Development Organization /UNIDO/ located at Vienna International Centre, P.O.Box 30, A - 1400 Vienna, Austria

and

The Institute of Petroleum Technology /since 1st July, 1992 Central Laboratory of Petroleum/, located at Żwirki and Wigury Avenue 31, 02-091 Warsaw, Poland

for

The Execution of Services Related to Preparatory Assistance in Clean Technology for the Recycling of Waste Oil.

In accordance with the terms and conditions stated in Contract No.92/002 and Annexes previously accepted by Contractor /General Documents and Formulars of UNIDO/, the Contractor /Institute of Petroleum Technology - Central Laboratory of Petroleum/ is obliged to perform chemical analysis of petroleum - based, waste oils. The aim of these analyses was to give an answer if analyzed oils contain any polychlorinated biphenyls and if so to determine their contents in specified samples of oils.

The results of analyses performed by Contractor will be utylized by UNIDO experts in their activities within the scope of UNIDO PROJECT US/INT/88/227.

2. Introduction

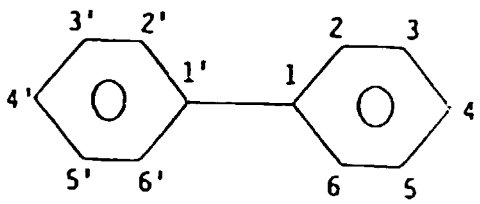
Polychlorinated biphenyls /PCB´s/ have been introduced into industry and into technical use over sixty years ago. As these compounds have appeared to be thermaly and chemicaly stable, their production and fields of application have increased substantialy. The overall world production of PCB´s since 1929 till 1980 is evaluated to be close to $2 \cdot 10^9$ kg /1,2/ although there are evidences that since 1980 the dynamic of PCB´s production has decreased. The chemistry of the polychlorinated biphenyls has been reviewed /2/ and the world wide occurence of PCB´s is well established /3/.

The problems associated with the manufacture, use and disposal of PCB´s have been summarized in the conference report compiled by the U.S. Environmental Protection Agency /4/ which seems to be the best single source of information on PCB´s. The PCB´s have appeared to be strong environmental pollutants being harmful for living organisms. The first reports on finding of PCB´s in birds and fishes were announced in 1966, and in 1968 the toxicity of PCB´s was revealed to public opinion /5/ after so called Yusho rice-oil catastrophe. This had an impact not only on production technologies, safety precautions and legal regulations but also on development of analytical methods. These methods have been continualy improved and currently with the use of modern laboratory techniques the PCB´s can be precisely determined both in technical products and in environmental smaples. Nowadays, the most frequently used techniques for analytical determinations of PCB´s are gas-liquid chromatography /GLC/ or GLC coupled with mass spectrometry /MS/. Several papers have been published on this field and the cited ones are only the examples /5, 6, 7, 8/.

As for routine determinations of any chemical species or specimens it is commonly accepted practice to develop some analytical standards, for determinations of PCB´s in petroleum - based oils such standard have been developed /9, 10/, and they are widely used and recommended.

2.1. Polychlorinated biphenyls /PCB´s/.

The chemical name - polychlorinated biphenyls, or shortly PCB´s - is used for the compounds in which some hydrogen atoms in biphenyl bone



are substituted by chlor atoms. Formally there are 209 different chemical compounds which form so called PCB-class. All of them can be derived from biphenyl. Accordingly there are 3 monochlorobiphenyls, 12 dichlorobiphenyls, 24 trichlorobiphenyls, 42 tetrachlorobiphenyls, 46 pentachlorobiphenyls, 42 hexachlorobiphenyls, 24 heptchlorobiphenyls, 12 octachlorobiphenyls, 3 nonachlorobiphenyls and 1 decachlorobiphenyl . As there is defined number of chlorinated biphenyls it is commonly accepted practice to use abbreviated forms of their names. The most popular is the method proposed by Ballschmitter and Zell /6/.

This method is based on systematic numbering of PCB compounds, then the number is used as a synonym for the corresponding PCB compound. The Table 1 presented in this paragraph is taken from the work of Ballschmitter and Zell /6/ and can serve as a Kay-table for connecting the Ballschmitter´s numbering and chemical structure of given PCB.

Table 1. Systematic numbering of PCB compounds. The number is used as a synonym for the corresponding PCB compound.

No.	Structure
Monochlorobiphenyls	
1.	2
2.	3
3.	4
Dichlorobiphenyls	
4.	2,2'
5.	2,3
6.	2,3'
7.	2,4
8.	2,4'
9.	2,5
10.	2,6
11.	3,3'
12.	3,4
13.	3,4'
14.	3,5
15.	4,4'
Trichlorobiphenyls	
16.	2,2',3
17.	2,2',4
18.	2,2',5
19.	2,2',6
20.	2,3,3'
21.	2,3,4
22.	2,3,4'
23.	2,3,5
24.	2,3,6
25.	2,3',4
26.	2,3',5
27.	2,3',6
28.	2,4,4'
29.	2,4,5
30.	2,4,6
31.	2,4',5
32.	2,4',6
33.	2',3,4
34.	2',3,5
35.	3,3',4
36.	3,3',5
37.	3,4,4'
38.	3,4,5
39.	3,4',5
Tetrachlorobiphenyls	
40.	2,2',3,3'
41.	2,2',3,4
42.	2,2',3,4'
43.	2,2',3,5
44.	2,2',3,5'
45.	2,2',3,6
46.	2,2',3,6'
47.	2,2',4,4'
48.	2,2',4,5
49.	2,2',4,5'
50.	2,2',4,6
51.	2,2',4,6'
Tetrachlorobiphenyls	
52.	2,2',5,5'
53.	2,2',5,6'
54.	2,2',6,6'
55.	2,3,3',4
56.	2,3,3',4'
57.	2,3,3',5
58.	2,3,3',5'
59.	2,3,3',6
60.	2,3,4,4'
61.	2,3,4,5
62.	2,3,4,6
63.	2,3,4',5
64.	2,3,4',6
65.	2,3,5,6
66.	2,3',4,4'
67.	2,3',4,5
68.	2,3',4,5'
69.	2,3',4,6
70.	2,3',4',5
71.	2,3',4',6
72.	2,3',5,5'
73.	2,3',5',6
74.	2,4,4',5
75.	2,4,4',6
76.	2',3,4,5
77.	3,3',4,4'
78.	3,3',4,5
79.	3,3',4,5'
80.	3,3',5,5'
81.	3,4,4',5
Pentachlorobiphenyls	
82.	2,2',3,3',4
83.	2,2',3,3',5
84.	2,2',3,3',6
85.	2,2',3,4,4'
86.	2,2',3,4,5
87.	2,2',3,4,5'
88.	2,2',3,4,6
89.	2,2',3,4,6'
90.	2,2',3,4',5
91.	2,2',3,4',6
92.	2,2',3,5,5'
93.	2,2',3,5,6
94.	2,2',3,5,6'
95.	2,2',3,5',6
96.	2,2',3,6,6'
97.	2,2',3',4,5
98.	2,2',3',4,6
99.	2,2',4,4',5
100.	2,2',4,4',6
101.	2,2',4,5,5'
102.	2,2',4,5,6'
103.	2,2',4,5',6
104.	2,2',4,6,6'

No.	Structure
Pentachlorobiphenyls	
105.	2,3,3',4,4'
106.	2,3,3',4,5
107.	2,3,3',4',5
108.	2,3,3',4,5'
109.	2,3,3',4,6
110.	2,3,3',4',6
111.	2,3,3',5,5'
112.	2,3,3',5,6
113.	2,3,3',5',6
114.	2,3,4,4',5
115.	2,3,4,4',6
116.	2,3,4,5,6
117.	2,3,4',5,6
118.	2,3',4,4',5
119.	2,3',4,4',6
120.	2,3',4,5,5'
121.	2,3',4,5',6
122.	2',3,3',4,5
123.	2',3,4,4',5
124.	2',3,4,5,5'
125.	2',3,4,5,6'
126.	3,3',4,4',5
127.	3,3',4,5,5'
Hexachlorobiphenyls	
128.	2,2',3,3',4,4'
129.	2,2',3,3',4,5
130.	2,2',3,3',4,5'
131.	2,2',3,3',4,6
132.	2,2',3,3',4,6'
133.	2,2',3,3',5,5'
134.	2,2',3,3',5,6
135.	2,2',3,3',5,6'
136.	2,2',3,3',6,6'
137.	2,2',3,4,4',5
138.	2,2',3,4,4',5'
139.	2,2',3,4,4',6
140.	2,2',3,4,4',6'
141.	2,2',3,4,5,5'
142.	2,2',3,4,5,6
143.	2,2',3,4,5,6'
144.	2,2',3,4,5',6
145.	2,2',3,4,6,6'
146.	2,2',3,4',5,5'
147.	2,2',3,4',5,6
148.	2,2',3,4',5,6'
149.	2,2',3,4',5',6
150.	2,2',3,4',6,6'
151.	2,2',3,5,5',6
152.	2,2',3,5,6,6'
153.	2,2',4,4',5,5'
154.	2,2',4,4',5,6'
155.	2,2',4,4',6,6'
156.	2,3,3',4,4',5
157.	2,3,3',4,4',5'
158.	2,3,3',4,4',6
159.	2,3,3',4,5,5'
160.	2,3,3',4,5,6
Hexachlorobiphenyls	
161.	2,3,3',4,5',6
162.	2,3,3',4',5,5'
163.	2,3,3',4',5,6
164.	2,3,3',4',5',6
165.	2,3,3',5,5',6
166.	2,3,4,4',5,6
167.	2,3',4,4',5,5'
168.	2,3',4,4',5',6
169.	3,3',4,4',5,5'
Heptachlorobiphenyls	
170.	2,2',3,3',4,4',5
171.	2,2',3,3',4,4',6
172.	2,2',3,3',4,5,5'
173.	2,2',3,3',4,5,6
174.	2,2',3,3',4,5,6'
175.	2,2',3,3',4,5',6
176.	2,2',3,3',4,6,6'
177.	2,2',3,3',4',5,6
178.	2,2',3,3',5,5',6
179.	2,2',3,3',5,6,6'
180.	2,2',3,4,4',5,5'
181.	2,2',3,4,4',5,6
182.	2,2',3,4,4',5,6'
183.	2,2',3,4,4',5',6
184.	2,2',3,4,4',6,6'
185.	2,2',3,4,5,5',6
186.	2,2',3,4,5,6,6'
187.	2,2',3,4',5,5',6
188.	2,2',3,4',5,6,6'
189.	2,3,3',4,4',5,5'
190.	2,3,3',4,4',5,6
191.	2,3,3',4,4',5',6
192.	2,3,3',4,5,5',6
193.	2,3,3',4',5,5',6
Pctachlorobiphenyls	
194.	2,2',3,3',4,4',5,5'
195.	2,2',3,3',4,4',5,6
196.	2,2',3,3',4,4',5',6
197.	2,2',3,3',4,4',6,6'
198.	2,2',3,3',4,5,5',6
199.	2,2',3,3',4,5,6,6'
200.	2,2',3,3',4,5',6,6'
201.	2,2',3,3',4',5,5',6
202.	2,2',3,3',5,5',6,6'
203.	2,2',3,4,4',5,5',6
204.	2,2',3,4,4',5,6,6'
205.	2,3,3',4,4',5,5',6
Nonachlorobiphenyls	
206.	2,2',3,3',4,4',5,5',6
207.	2,2',3,3',4,4',5,6,6'
208.	2,2',3,3',4,5,5',6,6'
Decachlorobiphenyls	
209.	2,2',3,3',4,4',5,5',6,6'

3. Samples for analysis

Samples of waste oils in which the PCB´s contents were determined have been supplied to Central Laboratory of Petroleum by Veritas Petroleum Services, N-1322 Høvik, Oslo, Norway. All delivered samples were labeled by country, code and number as is shown in Table 3. A total of 34 samples of waste oils collected from different countries as specified in Table 2 were analyzed.

Table 2. Samples for analysis.

Region	Country	Samples
Africa	Kenya	3
	Senegal	4
Asia	Indonesia	3
	Pakistan	4
	Singapore	1
	South Korea	4
South America	Brazil	4
	Chile	3
	Ecuador	3
Nord America	Mexico	5

4. Experimental

4.1. Preparation of samples.

As the samples of waste oils had very complex composition and contained some "disturbing" substances they were purified before GLC analysis. The crude sample was separated using column chromatography in accordance with the PN-72/C-04025 standard.

Three fractions were obtained :

I. Paraffinic - naphtenic fraction,

II. Aromatic fraction,

III. Gum containing fraction.

Our previous studies have shown that 85 - 97% of standard Aroclors /Aroclors 1248, 1254, 1260/ deliberately introduced into oil were then present in aromatic fraction, so correction factors have been calculated. Then the solvent /n-hexane or iso-octane/ was evaporated and the sample was again diluted with the solvent /1 : 50 or 1 : 100/ and purified with concentrated sulphuric acid and/or with the use of Florsil Column. /Florsil activated at 130°C/. The samples prepared in accordance with above summarized procedure were analyzed by GLC method.

4.2. Gas - liquid chromatography analysis.

The determinations of PCB´s in waste oils delivered were based on EPA Standard /9/. The following materials and conditions were used :

1. GLC apparatus with ECD N-50 C detector.
2. Columns : 2500 mm x 4 mm packed with 100/200 mesh Gas-Chrom Q coated with 3% OV-1 stationary phase.

3. Standards : Aroclors 1242, 1248, 1254, 1260, 1262 were dissolwed in oils; solutions with concentrations of 0.1, 0.2, 0.5, 1.0, 2.0 ppm were used.

4. Temperatures : columns 170 - 200°C

Temperatures :	columns	170 - 200°C
	detector	250°C
	injector	250°C.

The chromatograph was connected with the IBM computer, and the calculations of results were performed in an automated procedure. The precision of determinations of PCB´s was better than 0.5 ppm.

5. Results

The results of PCB´s determinations of oils studied are listed in Table 3. As can be seen from the Table 3 seven samples contain more than 25 ppm of PCB´s. These are 4 samples from Senegal /83, 34, 29, 30 ppm/, 1 from Brazil /93 ppm/ and 2 samples from Mexico /26, 30 ppm/. The concentrations of PCB´s in all ether samples were below 10 ppm. In 20 samples from different countries the PCB´s contents were < 5 ppm. In this class are included all samples from Indonesia, Singapore, Chile and Pakistan. Only 3 samples /one from Singapore, one from Pakistan an one from Mexico/ contain no PCB´s. As the past history of the samples was not konwn, more comprehensive discussion of results can not be performed.

Table 3. The results of determinations of PCB´s in samples of waste oils.

Samples: Country	Code	Number	Content of PCB´s /ppm/
Indonesia	A	7910488	2
	E	7910492	<1
	F	7910493	1
Pakistan	A	7920183	0
	B	7920184	4
	C	7920285	2
	D	7920286	2
Singapore	A	7910231	0
South Korea	A	7910265	9
	B	7910266	7
	C	7910267	0
	D	7910268	3
Brazil	C	7920003	5
	D	7920004	7
	E	7920005	8
	F	7920006	93
Chile	A	7910766	2
	E	7910770	3
	F	7910771	2
Eucador	C	7910586	6
	D	7910587	2
	E	7910588	9
Kenya	A	7910671	8
	C	7910672	3
	D	7910673	<1
Senegal	A	7920025	83
	B	7920026	94
	C	7920027	29
	D	7920028	30
Mexico	A	7920411	26
	B	7920412	0
	C	7920413	32
	D	7920414	2
	E	7920415	0

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