

DETERMINATION OF PCBs IN TRANSFORMER OIL AND CHEMICALLY DEGRADED OIL BY ISOTOPE DILUTION METHOD WITH HRGC/MS : 3-LAB INTERCALIBRATION STUDY AND EVALUATION OF NEW CALIBRATION PCB MIXTURE

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Introduction

Polychlorinated biphenyls (PCBs) are among the neutral organic industrial chemicals most commonly of concern as environmental contaminants¹. PCBs are persistent, and have the potential for harmful biological effects. Although there are 209 possible PCB configurations (congeners), perhaps half that number accounts for nearly all of the environmental contamination attributable to PCBs. Still fewer congeners are both prevalent and either demonstrably or potentially toxic. The most consequential of these have the ability to induce aryl hydrocarbon metabolizing mixed-function oxidase (MFOs).

While PCBs are industrial chemicals, their applications and usage mainly centered for electrical appliances such as electrical transformers, capacitors, insulating properties and thermal oil. Therefore, PCBs are major source of environmental contamination from electrical transformers in many parts of the world². Mainly in some countries, transformer oils are one of the major routes of PCBs exposure to the environment rather than industrial source³⁻⁴. Chemical decomposition method was approved to treat PCB contaminated oils. Furthermore, chemical decomposition of PCB leads biphenyl and lower chlorinated PCBs.

In order to understand the contribution of PCBs by transformer oils, we determined PCBs in transformer oil and chemically degraded transformer oil by isotope dilution method using HRGC/MS. For the quality assurance, the study was undertaken from 3 laboratories.

Materials and Methods

Standards, Transformer Oil and Analysis

In general, commercial standards were not mixed and available individually and or mixture of few congeners. Very recently, commercially available native and isotope labeled individual PCB standard mixtures (from mono- through deca- chlorobiphenyls) was developed by Wellington Laboratories at Canada. Particularly, this mixture was developed specially with our consultation and idea that used for analysis (Table 1). These standard solution mixtures (namely; TK-BPA series) contain predominant PCB congener in each chlorine degree in commercial PCBs and co-planar PCBs. Four variety of transformer oil (viz., PCB free oil, PCB fortified oil, PCB polluted oil and chemically degraded oil) was used for intercalibration study. Each laboratory use same standard solutions, as for as native and isotope labeled is concern. Clean up and analysis has been followed in HRGC/MS according to the Japanese method.

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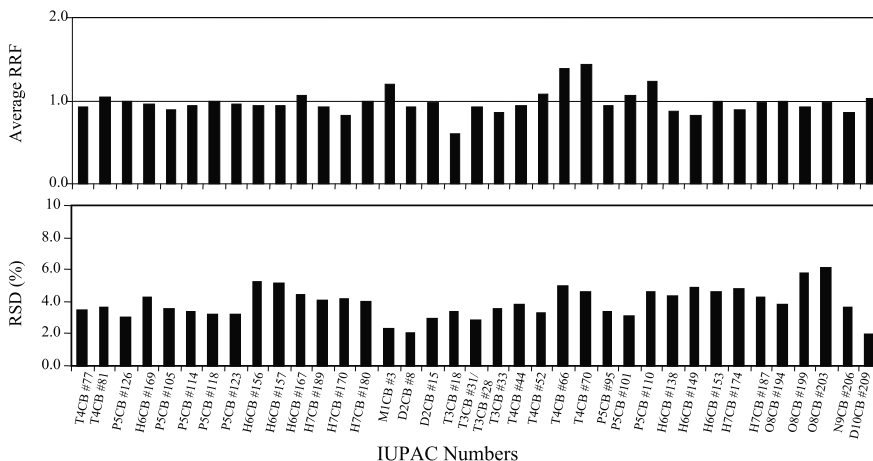


Figure 1. Average RRF and RSD (%) in two monitor ions by mono- through deca-PCBs.

Cleanup

The oil sample of each layer was initially dissolved in *n*-hexane containing 10 % toluene. From this, aliquot of the sample (approximately 0.1 g of the causal oil) was extracted with *n*-hexane saturated with dimethyl sulfoxide (DMSO) after the addition of 22 ¹³C₁₂-labeled PCB internal standards that includes co-planar PCBs (Wellington Laboratories). The DMSO phase was re-extracted with *n*-hexane after with the presence of *n*-hexane-washed water. Further, the concentrated hexane layer was subjected into a column chromatographic clean-up procedure described as follows; the column chromatographic consisted a multi-layer silica column (silica, 10 % AgNO₃/silica, silica, 22 % H₂SO₄/silica, 44 % H₂SO₄/silica, silica, 2 % KOH/silica, silica) with hexane as a mobile phase⁵⁻⁶.

HRGC/MS Analysis

For quantification and identification, HRGC (HP6890, Hewlett Packard)/HRMS (Autospec Ultima, Micromass) fitted DB-5MS column (60 m, 0.32 mm i.d., 0.25 um film thickness, J&W Scientific) was used. The temperature was programmed with the following order; 150 °C for 1-min. (20 °C/min.) to 185 °C, (2 °C/min.) to 245 °C, hold for 3-min., (6 °C/min.) to 290 °C. The interface temperature was programmed as 5-10 °C higher than the maximum value of each temperature program. The carrier gas was helium and the electron impact ionization energy was 35-40eV. The MS was operated in selected ion monitoring for each congener group. Two ions were monitored for each isomer and congener group. The Laboratories B and C use DB-5 (J&W Scientific) GC columns. Only slight variation of temperature in between laboratory has been applied.

Results and Discussion

We classified 5-point calibration mixture of 1, 4, 20, 80, 400 pg/ml (Table 1). The tri- through hepta- chlorobiphenyls concentrations was half of the concentrations of mono-, di-, octa-, non- and deca- chlorobiphenyls in native standard. Whereas, the internal standard concentrations was set as 200 pg/ml for of mono-, di-, octa-, non- and deca- chlorobiphenyls and 100 pg/ml for tri- through hepta- chlorobiphenyls. At final a total of 15 data set (5 point, n=3) can be obtained based on various concentration levels. The average RRF data of 37 isomers from 15 samples has been plotted in upper case of Figure 1. In addition, the RSD % calculated based on the RRF values for each isomer has been shown in lower case of Figure 1. On the whole, average RRF for 37 isomers was 0.979 when TrCB-18,

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Table 1. List of PCB calibration standard mixtures.

Native standard		Internal Standard [†]
IUPAC Number	Chlorine positions	IUPAC Number
#3	4-MeCB	#3
#8	24'-DiCB	#15
#15	44'-DiCB	#15
#18	225'-TriCB	#28
#31	245'-TriCB	#28
#28	244'-TriCB	#28
#33	234'-TriCB	#28
#52	2255'-TeCB	#52
#44	2235'-TeCB	#52
#70	2344'-TeCB	#52
#66	2344'-TeCB	#52
#81	3445'-TeCB*	#81
#77	3344'-TeCB*	#77
#95	22356'-PeCB	#101
#101	22455'-PeCB	#101
#110	23346'-PeCB	#101
#123	23445'-PeCB**	#123
#118	23445'-PeCB**	#118
#105	23344'-PeCB**	#105
#114	23445'-PeCB**	#114
#126	33445'-PeCB*	#126
#149	2234556'-HxCB	#153
#153	224455'-HxCB	#153
#138	223445'-HxCB	#153
#156	233445'-HxCB**	#156
#157	233445'-HxCB**	#157
#167	234455'-HxCB**	#167
#169	334455'-HxCB*	#169
#187	22345556'-HpCB	#180
#174	2233456'-HpCB	#180
#180	2234455'-HpCB***	#180
#170	2233445'-HpCB***	#180
#189	2334455'-HpCB**	#189
#199	22334566'-OxCB	#194
#203	22344556'-OxCB	#194
#194	22334455'-OxCB	#194
#206	2233445556'-NoCB	#206
#209	2233445566'-DeCB	#209

*, ** and *** denotes respectively, non-, mono- and di-*ortho* PCBs
 All other CB congeners without astrisk mark represent major PCBs
¹-¹³C₁₂-labeled; The IUPAC number of native standard was calculated
 against IUPAC of internal standard in the same row for calibration.

TeCB-66, 70, PeCB-110 taken into consideration. Most considerably, the average RSD% for 37 isomers was calculated as 3.86 % (ranges 1.97-6.30 %). Collectively, difference of RRF was observed when calculate lower and higher values. These results indicate different response when we calculate by different native and ¹³C₁₂-labeled PCBs for calculation (Table 1).

In general, congener pattern was different in between type of PCBs and in between laboratory (Table 2). The detection limit of 0.1 ng/g was found for the samples. Notably, PCB fortified oil contained greatest concentrations of mono- to tetra-CBs (930-1300 ng/g). While PCB free oil showed ND to 17 ng/g. Only PCB fortified oil and PCB polluted oil contained all homologues of PCBs such as mono-CBs to Deca-CBs depending upon the lab (Table 2). Chlorobiphenyl No.118 was predominant congener in all the samples followed by 105, 77, 180 and other congeners. While co-planar PCBs such as chlorobiphenyl Nos. 126, 169 and 189 were not detected in most of samples including PCB fortified oil, PCB polluted oil and chemically degraded oil. The contribution of non-*ortho* PCB congeners was 0-15 to the total PCBs and the dioxin-like PCBs were with the ranges of 0-19. Homologue pattern was dominated by trichlorobiphenyls followed by tetrachlorobiphenyls, dichlorobiphenyls, penta- to octachlorobiphenyls, mono- and nonachlorobiphenyls and decachlorobiphenyls. Chlorobiphenyl No. 28 was predominant isomer in most of the samples whereas, CB-194 was detected at very low levels.

Collectively, our study demonstrated for the first time about highly contaminated and less contaminated transformer oil PCBs homologue and congener pattern in 3-laboratory study and our results provided the chemical degradation of PCBs was apparent. However, based on our results in our study, it is very useful to know the exact source of mono- to decachlorobiphenyls including co-planar PCBs from Kanechlor mixture, incineration, industrial and environmental sources due to different chlorination degree in between these different sample matrix. Furthermore, different isomer/congener pattern also possible to know using these method.

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Table 2. Concentrations (ng/g) of PCB congeners in variety of transformer oils in 3-interlaboratory study.

PCB-type Lab ^a	PCB free Oil		PCB fortified Oil			PCB polluted Oil			Chemical degraded Oil		
	A	B	A	B	C	A	B	C	A	B	C
#3 ^b	ND	ND	25	38	39	3.2	7.2	2.3	52	100	63
#8	ND	ND	43	65	21	8.1	12	2.9	57	90	29
#18	ND	ND	51	40	49	10	5.1	12	18	9.5	15
#31 ^c	ND		35		2.4	7.1	9	0.72	9.3		0.31
#28 ^d	ND	1.8	50	60	35	9.8	16	8.5	2.9	16	8.2
#33	ND	ND	27	29	11	6	6.6	2.6	9.8	9.3	3.2
#52	ND	1.7	33	36	12	25	23	7.3	1.1	4.7	0.7
#44	ND	1.6	31	25	38	12	9.2	15	1.4	2.6	2.3
#70	ND	2.7	27	39	18	19	23	13	ND	2.9	ND
#66	ND	2.4	18	28	13	8.4	12	6.4	ND	3.4	ND
#95	ND	ND	23	16	5.6	35	22	7.9	ND	ND	ND
#101	ND	ND	22	32	7	45	52	12	ND	ND	ND
#110	ND	ND	25	23	22	49	37	40	ND	ND	ND
#118	ND	ND	15	19	5.3	37	43	13	ND	ND	ND
#105	ND	ND	9	10	6.5	18	19	13	ND	ND	ND
#149	ND	ND	44	25	36	36	25	27	ND	ND	ND
#153	ND	ND	36	35	21	35	40	22	ND	ND	ND
#138	ND	ND	39	33	21	53	46	34	ND	ND	ND
#187	ND	ND	25	20	11	8.8	7.7	5.3	ND	ND	ND
#174	ND	ND	20	14	21	9.5	6.4	11	ND	ND	ND
#180	ND	ND	38	38	35	18	19	21	ND	ND	ND
#170	ND	ND	18	12	14	11	10	9.9	ND	ND	ND
#199	ND	ND	16	21	7.7	3.7	5.3	1.4	ND	ND	ND
#203	ND	ND	14	24	6.2	4.4	6.9	1.8	ND	ND	ND
#194	ND	ND	10	1.2	9.9	3.7	5.5	3	ND	ND	ND
Co-planar PCBs											
#81	ND	ND	ND	ND	0.38	ND	ND	ND	ND	ND	ND
#77	ND	1.8	2.3	3	2.7	1.1	2.1	1.3	ND	ND	0.21
#105	ND	ND	9	10	6.5	18	19	13	ND	ND	0.16
#114	ND	ND	ND	ND	0.22	1.2	1.3	0.64	ND	ND	ND
#118	ND	ND	15	19	5.3	37	43	13	ND	ND	0.13
#123	ND	ND	1.3	1.2	0.17	2.2	2.4	N.D.	ND	ND	ND
#126	ND	ND	ND	ND	0.09	ND	ND	ND	ND	ND	ND
#156	ND	ND	2.7	2.8	1.6	5.8	6.1	3.4	ND	ND	ND
#157	ND	ND	ND	ND	0.6	1.4	1.1	0.9	ND	ND	ND
#167	ND	ND	ND	2.8	0.85	2.3	6.6	1.2	ND	ND	ND
#169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
#180	ND	ND	38	38	35	18	19	21	ND	ND	0.12
#170	ND	ND	18	12	14	11	10	9.9	ND	ND	ND
#189	ND	ND	ND	ND	0.31	ND	ND	0.2	ND	ND	ND
Homologues pattern											
M1CBs	N.D.	N.D.	76	110	100	6.2	11	4.3	220	190	240
D2CBs	N.D.	N.D.	110	130	84	18	15	9.4	180	200	160
T3CBs	N.D.	1.7	240	200	220	50	52	55	76	68	71
T4CBs	N.D.	15	170	310	160	82	120	66	6.3	35	10
P5CBs	N.D.	N.D.	120	150	65	260	240	120	N.D.	N.D.	1
H6CBs	N.D.	N.D.	140	130	130	170	160	150	N.D.	N.D.	0.56
H7CBs	N.D.	N.D.	140	130	130	71	62	73	N.D.	N.D.	0.12
O8CBs	N.D.	N.D.	57	87	39	16	24	11	N.D.	N.D.	N.D.
N9CBs	N.D.	N.D.	5.4	9.2	4.1	1.1	N.D.	N.D.	N.D.	N.D.	N.D.
D10CB	N.D.	N.D.	N.D.	N.D.	0.33	N.D.	N.D.	1.1	N.D.	N.D.	0.22
Total PCBs	ND	17	1100	1300	930	670	680	490	480	490	480

^adenotes lab A= Shimadzu Techno Research INC., lab B=Kaneka Techno Research Corporation and lab C= METOCEAN Environment INC.
^bthe numbers represents IUPAC number of particular PCB congener; ^cpossible interference; detection limit 0.1 ng/g; ND=not detected.

References

1. Mc Farland V.A. and Clarke U. (1989) Environ Health Perspect., 81, 225
2. Senthil Kumar K., Kannan K., Subramanian A.N. and Tanabe S. (2001) Environ Sci Pollut Res., 8, 35
3. Senthil Kumar K., Watanabe M., Kannan K., Subramanian A.N. and Tanabe S. (1999a) Toxicol Environ Chem., 71, 221
4. Senthil Kumar K., Kannan K., Sinha R.K., Tanabe S. and Giesy J.P. (1999b) Environ Toxicol Chem., 18, 1511
5. Takasuga T., Inoue T., Ishida T. and Ireland P. (1996) Organohalogen Compounds 27, 391
6. Takasuga T., Inoue T. and Ohi E. (1995) J Environ Chem., 5, 647
7. Yao Y., Takasuga T., Masunaga S. and Nakanishi J. (2002) Chemosphere, 46, 1