

Rapid Determination Method of PCBs in Transformer Oil using Multiple Regression Analysis

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Abstract

The authors developed a rapid determination method for total PCB concentration using multiple regression analysis. This method is possible to determine accurate total PCB concentration using only 13 or 14 isomers (GC peaks).

Introduction

It is conceivable that 6 -10 million transformer and condenser oil sample are in Japan. Guideline of Japanese law is 0.5mg/kg for total PCB concentration. It is indispensable to develop "speedy" determination method for total PCB concentration. The authors already reported Fast GC technique to decrease time of measurement. In this paper we propose new quantitative method for total PCB concentration.

Methods

Method is noted below.

- (1) Set more than 2 origin for PCB (In this paper, there are 4 origin, KC-300, 400, 500 and 600. Another combination and/or other kinds of origin are also available.).
- (2) Measure/determine 13 or 14 GC peaks (Table 1). Detailed profiles of all 209 isomers were already known regarding each KC products.
- (3) Determine the ratio for 4 origins by a multiple regression analysis.
- (4) Calculate total concentration using the ratio of "Concentration of the sum total from 13 or 14 GC peaks" and "Total concentration of PCB".

Theoretical Confirmation

- (1) Total of 8 cases of KC mixture was made by mathematically (Table 2).
- (2) Disperse the abundance ratio of 209 PCB isomers for each KC at random ($\pm 25\%$, 50% and 100%). Number of computation frequency will be enough more than 500 times by graphical representation (Figure 1) Result shows this method is not so affect by scattering of chemical analysis.
- (3) Regarding the random dispersion for $\pm 25\%$, 14, case of calculation by 13 and 11 GC peak were carried out (refer to Table 1). The "13" and "11" GC peak calculations are mean "no need" for "di" and "tri" homologue analysis respectively. Especially regarding "di", it's important from the point of view of chemical separation technique (pretreatment procedure). Because di-CBs analysis are difficult caused by its physical chemical properties. Results shows there are no significant difference between the "14" and the "13".

Table 1. Number of peak and major isomer.

peak number	homologue	major isomer including (BZ#)
s1	di	8
s2	tri	17,18
s3		28,31
s4	tetra	49,52
s5		44
s6		70,74
s7	penta	101
s8		110
s9		118
s10	hexa	149,151
s11		132,153
s12	hepta	138
s13		183,187
s14		180

Apply to electrical oil sample

This method was applied to 10 samples. Results are shown in Table-5. Difference between "total concentration by sum of 209 isomers" and "total concentration calculated by this method" are considered within variability of GC/MS measurement.

Table 2. KC mixture for theoretical confirmation.

case	KC-300	KC-400	KC-500	KC-600
1	1.00	0.00	0.00	0.00
2	0.00	1.00	0.00	0.00
3	0.00	0.00	1.00	0.00
4	0.00	0.00	0.00	1.00
5	0.50	0.50	0.00	0.00
6	0.00	0.50	0.50	0.00
7	0.00	0.00	0.50	0.50
8	0.25	0.25	0.25	0.25

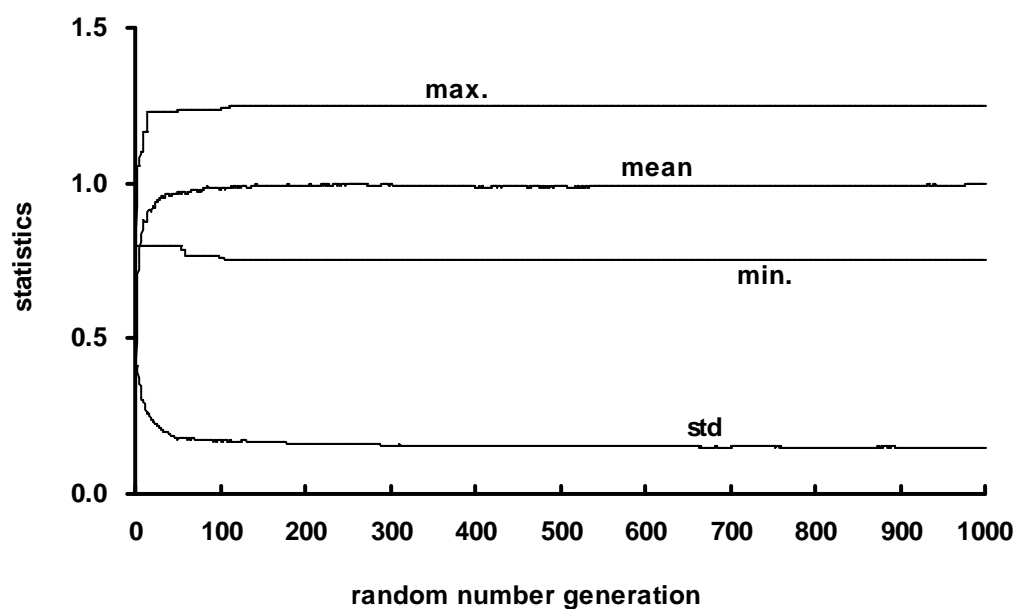


Figure 1. Relationship between the number of computation frequency at $\pm 25\%$ (CV 15%) and statistical results.

Table 3. Random dispersion ($\pm 25\%$, 50% and 100%) for each 209 isomers of KC 300, 400, 500 and 600.

25% variation (using 14 peak)

case	others		KC-300		KC-400		KC-500		KC-600		correlation (mean)	
	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	coeff.	s.d.
1	0.00	0.56	1.01	0.13	0.00	0.09	0.00	0.05	0.00	0.04	0.98	0.04
2	0.00	0.51	0.00	0.07	1.00	0.12	0.00	0.06	0.00	0.03	0.98	0.04
3	-0.03	0.52	0.00	0.03	0.00	0.05	1.00	0.07	0.00	0.07	0.96	0.04
4	0.03	0.77	0.00	0.05	0.00	0.02	0.00	0.11	1.00	0.09	0.98	0.04
5	0.01	0.49	0.51	0.10	0.49	0.10	0.00	0.05	0.00	0.03	0.98	0.04
6	0.02	0.43	0.00	0.04	0.50	0.09	0.50	0.06	0.00	0.04	0.95	0.04
7	0.05	0.56	0.00	0.04	0.00	0.04	0.49	0.08	0.50	0.07	0.96	0.04
8	0.00	0.40	0.25	0.05	0.25	0.06	0.25	0.05	0.25	0.04	0.91	0.04

50% variation (using 14 peak)

case	others		KC-300		KC-400		KC-500		KC-600		correlation (mean)	
	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	coeff.	s.d.
1	0.07	1.13	0.97	0.27	0.01	0.17	-0.01	0.09	0.00	0.07	0.93	0.04
2	-0.02	1.01	0.00	0.14	1.01	0.23	-0.01	0.11	0.00	0.06	0.92	0.04
3	0.01	0.98	0.00	0.06	0.00	0.11	0.99	0.15	0.00	0.14	0.87	0.04
4	-0.02	1.55	0.00	0.10	0.00	0.04	0.00	0.22	1.01	0.17	0.92	0.04
5	0.01	1.00	0.49	0.20	0.50	0.20	0.00	0.09	0.00	0.06	0.93	0.04
6	0.05	0.89	-0.01	0.09	0.50	0.17	0.50	0.11	0.00	0.09	0.84	0.04
7	-0.07	1.15	0.01	0.07	0.00	0.07	0.51	0.16	0.51	0.15	0.87	0.04
8	0.03	0.84	0.25	0.10	0.25	0.12	0.25	0.10	0.25	0.09	0.73	0.04

100% variation (using 14 peak)

case	others		KC-300		KC-400		KC-500		KC-600		correlation (mean)	
	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	coeff.	s.d.
1	-0.07	2.30	1.04	0.52	-0.02	0.35	0.01	0.18	0.00	0.15	0.78	0.04
2	0.06	2.08	-0.01	0.28	1.00	0.49	-0.01	0.23	0.00	0.13	0.75	0.04
3	0.07	1.96	-0.01	0.11	0.00	0.22	1.00	0.29	-0.01	0.28	0.64	0.04
4	0.10	2.98	-0.01	0.20	0.00	0.08	-0.01	0.43	1.00	0.36	0.74	0.04
5	0.05	2.00	0.51	0.38	0.47	0.38	0.00	0.19	0.00	0.12	0.77	0.04
6	-0.07	1.74	0.00	0.17	0.52	0.35	0.49	0.22	0.01	0.17	0.62	0.04
7	-0.04	2.25	0.00	0.14	0.00	0.14	0.50	0.32	0.50	0.30	0.63	0.04
8	0.05	1.68	0.24	0.22	0.25	0.24	0.25	0.20	0.24	0.17	0.51	0.03

Table 4. calculation by 14, 13 and 11 peak at variation 25%.

25% variation (using 14 peak)

case	others		KC-300		KC-400		KC-500		KC-600		correlation (mean)	
	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	coeff.	s.d.
1	0.00	0.56	1.01	0.13	0.00	0.09	0.00	0.05	0.00	0.04	0.98	0.04
2	0.00	0.51	0.00	0.07	1.00	0.12	0.00	0.06	0.00	0.03	0.98	0.04
3	-0.03	0.52	0.00	0.03	0.00	0.05	1.00	0.07	0.00	0.07	0.96	0.04
4	0.03	0.77	0.00	0.05	0.00	0.02	0.00	0.11	1.00	0.09	0.98	0.04
5	0.01	0.49	0.51	0.10	0.49	0.10	0.00	0.05	0.00	0.03	0.98	0.04
6	0.02	0.43	0.00	0.04	0.50	0.09	0.50	0.06	0.00	0.04	0.95	0.04
7	0.05	0.56	0.00	0.04	0.00	0.04	0.49	0.08	0.50	0.07	0.96	0.04
8	0.00	0.40	0.25	0.05	0.25	0.06	0.25	0.05	0.25	0.04	0.91	0.04

25% variation (using 13 peak)

case	others		KC-300		KC-400		KC-500		KC-600		correlation (mean)	
	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	coeff.	s.d.
1	-0.02	0.63	1.00	0.12	0.00	0.10	0.00	0.04	0.00	0.04	0.99	0.04
2	-0.04	0.82	0.00	0.07	1.01	0.14	0.00	0.07	0.00	0.05	0.98	0.04
3	0.01	0.79	0.00	0.03	0.00	0.07	0.99	0.08	0.00	0.08	0.96	0.04
4	0.08	1.13	0.00	0.06	0.00	0.04	-0.01	0.13	1.00	0.11	0.98	0.04
5	0.02	0.69	0.50	0.09	0.50	0.11	0.00	0.05	0.00	0.04	0.98	0.04
6	-0.06	0.67	0.00	0.04	0.50	0.09	0.50	0.07	0.00	0.05	0.95	0.04
7	0.03	0.86	0.00	0.04	0.00	0.05	0.50	0.09	0.50	0.09	0.96	0.04
8	0.00	0.63	0.25	0.06	0.25	0.07	0.25	0.06	0.25	0.06	0.89	0.04

25% variation (using 11 peak)

case	others		KC-300		KC-400		KC-500		KC-600		correlation (mean)	
	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	exist.	s.d.	coeff.	s.d.
1	0.02	0.50	0.99	0.37	0.00	0.21	0.00	0.05	0.00	0.04	0.99	0.04
2	0.03	0.86	0.05	0.82	0.97	0.47	0.00	0.10	0.00	0.07	0.99	0.04
3	0.03	0.77	0.01	0.38	0.00	0.20	0.99	0.08	0.00	0.08	0.95	0.04
4	0.09	1.20	0.00	0.23	0.00	0.13	-0.01	0.15	1.00	0.11	0.98	0.04
5	0.00	0.64	0.50	0.59	0.50	0.32	0.00	0.08	0.00	0.05	0.99	0.04
6	0.06	0.69	0.01	0.55	0.49	0.30	0.50	0.08	-0.01	0.06	0.96	0.04
7	0.03	0.92	0.01	0.26	-0.01	0.15	0.50	0.10	0.50	0.09	0.95	0.04
8	0.00	0.60	0.23	0.39	0.26	0.21	0.25	0.07	0.25	0.06	0.90	0.04

Table 5. Example of results using this method for actual oil sample.

No.	(A) Total PCB conc. (sum of 209 isomers) (mg/kg)	(B) Total PCB con. using this method (mg/kg)	Difference from assigned value $100 - ((B) \times 100 / (A))$ (%)	Major KC origin by this calculation
1	1.22	1.19	-2.46	300
2	0.356	0.343	-3.65	300
3	0.336	0.344	2.38	400
4	1.21	1.23	1.65	400
5	0.419	0.412	-1.67	500
6	0.311	0.306	-1.61	500
7	0.986	0.988	0.20	300, 400, 500
8	0.925	0.925	0.00	400, 500
9	0.895	0.874	-2.35	500, 600
KC mix	0.477	0.477	0.00	300, 400, 500, 600

KC mix: Not an oil sample. This sample was a mixture of KC 300, 400, 500 and 600 at same weight of each KC.