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Relative electron-capture detector response of selected polychlorinated biphenyl congeners Influence of detector temperature and design☆

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Abstract

Molar and mass responses for polychlorinated biphenyls (PCBs) IUPAC Nos. 28, 52, 77, 101, 126, 138, 153, 169 and 180 were determined for electron-capture detectors of two different designs, Model 400 (Carlo Erba) and PU 4400/03 (Philips Scientific). The detector temperature influences the response level of different PCB congeners in different ways. The course of the dependences of the molar responses on temperature in the range 150–360°C varies for different congeners. It is also influenced by the design of the detector. The presence of oxygen in the gas passing through the detector influences the response of PCB congeners. The application of the relative responses determined at one detector temperature to another temperature can produce a relative error of several tens per cent. The same is valid for the application of the relative responses from one detector design to another design. The error with different oxygen contents in the carrier gas can also be 100%.

1. Introduction

Polychlorinated biphenyls (PCBs) are prominent environmental contaminants [1] and belong among eleven global chemical pollutants [2]. Owing to their high stability, their effect on the environment and their harmful effects on human health, PCBs are among the most frequently investigated analytes in environmental analytical chemistry. The electron-capture detector (ECD) is the most often used detection system for trace analysis of PCBs. The ECD temperature is known to be an important parameter influencing the detector response; a variation of 3% can result in a 10% error in the evaluation of the capture coefficient [3]. There are a number of tabulated responses both for selected [4–6] PCBs and for all PCB congeners [7,8]. They were measured under different experimental conditions and for different ECD types. Many data on experimental conditions under which the responses were determined are incomplete.

The basic idea of this work was to study the behaviour of selected PCB congeners in ECDs at different detector temperatures. The effects of the detector design and amount of oxygen in the gas on the course of the temperature dependences were also investigated. Six PCB congeners used to follow threshold limits for total PCBs in food [9] with IUPAC designation [10] Nos. 28, 52, 101, 138, 153 and 180 (the standard compounds) and three most toxic congeners with

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IUPAC Nos. 77, 126 and 169 (the toxic compounds) were selected. The standard congeners are used for congener-selective determination of PCBs. The toxic congeners are most important for congener-selective determination with respect to evaluation of the toxic effects of PCBs.

2. Experimental

2.1. Materials

PCBs Nos. 28, 52, 77, 101, 126, 138, 153, 169 and 180 were obtained from Promochem (Germany). The carrier and make-up gas (nitrogen) with a stated content of 6 ppm (v/v) of oxygen was purchased from Linde-Technoplyn (Czech Republic). For some PCB analyses nitrogen as carrier gas can be advantageous. For the preparation of nitrogen containing less than 1 ppm of oxygen, an oxygen scrubber from Hewlett-Packard USA) was used. An HP-5 capillary column (I.D. 0.53 mm) from Hewlett-Packard was employed. For injection of liquid samples, 75SN Grob and 7001N syringes from Hamilton (Bonaduz, Switzerland) were used.

2.2. Apparatus

Two gas chromatographs were used: a PU 4400 (Philips Scientific, Cambridge, UK) with a PU 4400/03 ECD detector and an HRGC 5300 Mega Series (Carlo Erba, Milan, Italy) with a Model 400 ECD. Both detectors are coaxial models.

The experimental conditions for the PU 4400 were as follows: the packed column, 3.1 m × 4.0 mm I.D., Chromosorb W AW (80–100 mesh) with 10% of SE-54; column temperature, 210°C; flow-rates of nitrogen containing 6 ppm of oxygen and nitrogen containing less than 1 ppm of oxygen, 45.0 ± 0.3 ml min^{-1}; injector temperature, 230°C; volume injected, 1 μl of a solution containing 0.5 ng of each PCB congener in hexane; detector temperature, increased from 150°C to 360°C at 30°C min^{-1}; no make-up gas; constant-current mode; detector current 12.

The experimental conditions for the HRGC 5300 were as follows: HP-5 capillary column, length 30 m × 0.53 mm I.D.; film thickness, 0.88 μm; temperature programme, initially 60°C (held for 2 min), increased at 20°C min^{-1} to 200°C, at 5°C min^{-1} to 230°C and at 3°C min^{-1} to 260°C (held for 10 min); flow-rate of nitrogen containing less than 1 ppm of oxygen, 7.8 ± 0.2 ml min^{-1}; on-column injector; volume injected, 1 μl of a solution containing 0.5 ng of each PCB congener in hexane; detector temperature, increased from 150°C to 390°C at 30°C min^{-1}; total flow-rate through the detector, 33.0 ± 0.3 ml min^{-1}; constant-current mode; pulse voltage, 50.0 V; pulse width, 1 μs; reference current, 1.0 nA; attenuation, 128.

The PCB congener responses at each temperature used fall within the linear response range of both detectors.

For processing the signals from the detectors an HP 3393A integrator (Hewlett-Packard) was used. The response values given are the arithmetic averages of three parallel measurements of the peak area.

The congeners used are presented in Table 1. Quantification of the data obtained was performed with the values of the molar (MR) and mass responses (WR): $MR_i = A_i M_i / m_i$ where M_i is the molecular mass of congener i, m_i the amount of congener i injected in grams and A_i the area in digits given by the integrator; $WR = A/m_i$.

Table 1
PCB congeners tested

PCB No.	Substitution pattern	Number of chlorine atoms
28	2,4,4′	3
52	2,2′,5,5′	4
77	3,3′,4,4′	
101	2,2′,4,5,5′	5
126	3,3′,4,4′,5	
138	2,2′,3,4,4′,5	6
153	2,2′,4,4′,5,5′	
169	3,3′,4,4′,5,5′	
180	2,2′,3,4,4′,5,5′	7

Table 2
Molar responses (*MR*) and relative molar responses (*RMR*)

PCB No.	Model 400		PU 4400		RMR_{PU}/RMR_{400}
	$MR \times 10^{-14}$	*RMR*	$MR \times 10^{-14}$	*RMR*	
28	6.7	0.96	11.6	0.58	0.60
52	1.8	0.26	5.1	0.25	0.96
77	5.8	0.83	34.0	1.69	2.04
101	7.0	1.00	20.1	1.00	1.00
126	12.3	1.76	53.3	2.65	1.51
138	16.8	2.40	58.9	2.93	1.22
153	11.5	1.64	79.7	3.98	2.43
169	17.7	2.53	65.1	3.24	1.28
180	26.8	3.83	93.3	4.64	1.21

Detector temperature = 400°C.

3. Results and discussion

3.1. Congener response

Table 2 presents the values of the molar and relative molar responses of PCB congeners at 300°C with the gas containing less than 1 ppm of oxygen. The molar responses on the Model 400 ECD increase in the order of PCBs 52, 77, 28, 101, 153, 126, 138, 169 and 180. The highest molar responses in the group with the same number of chlorine atoms are found for PCB congeners 77, 126 and 169 (toxic congeners). The molar responses on the PU 4400 detector increase in the order of PCBs 52, 28, 101, 77, 126, 138, 169, 153 and 180. As with the Model 400 ECD, congener No. 180 has the highest molar response. The toxic congeners again have the highest responses except for No. 169, which has a lower molar response than No. 153.

Table 3 gives the mass and relative mass responses of individual congeners. The order of the values is similar to that for the molar responses, except that the order of congeners 28 and 101 for the Model 400 ECD and of congeners 126 and 138 for the PU 4400 is changed. Toxic congeners also have the highest mass response. The magnitude of the response depends not only on the number of chlorine atoms in the biphenyl molecule but also on the structure of the congener (see also refs. 4 and 5).

3.2. Influence of ECD temperature on the response of PCBs

For comparison of the courses of the dependences of the response on the ECD temperature, PCB molar responses were related to the molar response of congener No. 28 at a detector temperature of 150°C. Fig. 1 shows the courses

Table 3
Mass responses (*WR*) and relative mass responses (*RWR*)

PCB No.	Model 400		PU 4400		RWR_{PU}/RWR_{400}
	WR	*RWR*	*WR*	*RWR*	
28	2.60	1.21	4.50	0.73	0.60
52	0.62	0.29	1.75	0.28	0.97
77	1.98	0.93	11.60	1.88	2.02
101	2.14	1.00	6.16	1.00	1.00
126	3.76	1.76	16.60	2.69	1.53
138	4.65	2.17	16.3	2.65	1.22
153	3.19	1.49	22.1	3.59	2.41
169	4.90	2.29	18.0	2.92	1.28
180	6.78	3.17	23.6	3.83	1.21

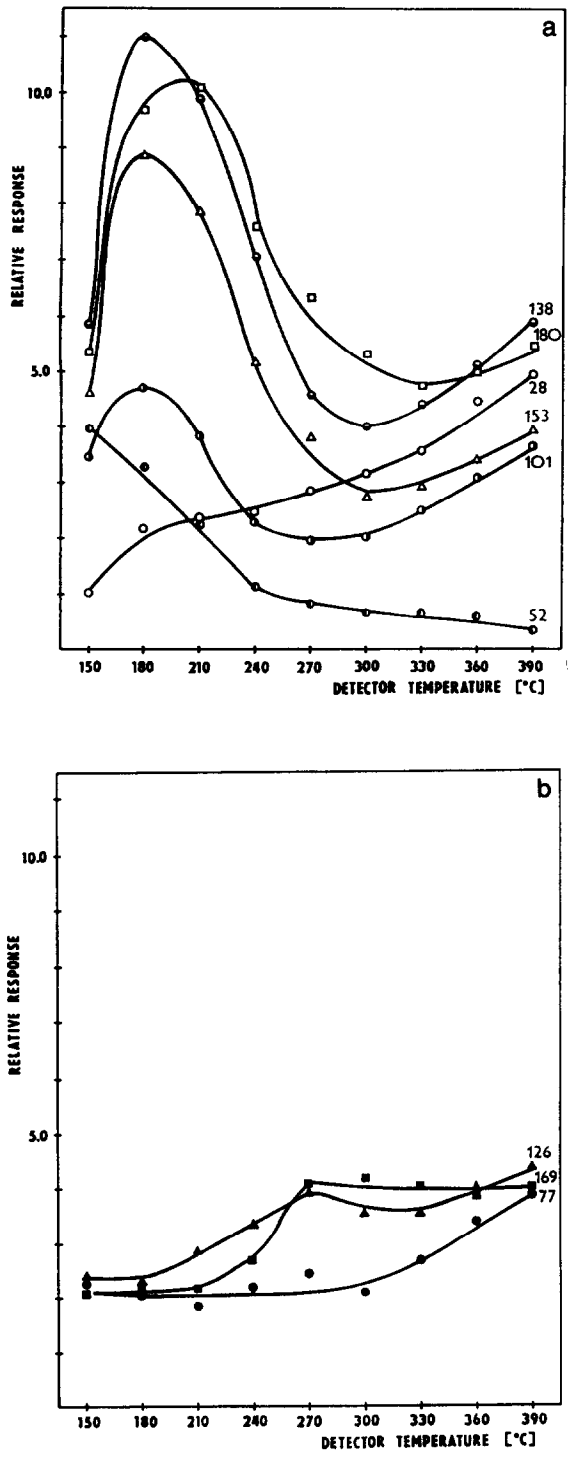


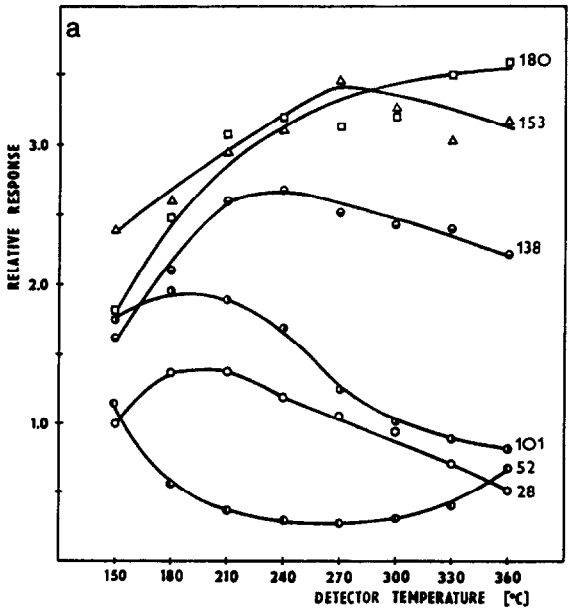
Fig. 1. Relative molar responses of selected PCBs with the Model 400 ECD.

of the congener dependences on the Model 400 ECD with nitrogen containing less than 1 ppm of oxygen and Fig. 2 shows the courses for the PU 4400 ECD with the same oxygen content in the gas. Fig. 3 shows the courses for the PU 4400 ECD with nitrogen containing 6 ppm of oxygen. The dependences are divided into two panels to permit a clear comparison of the dependences of standard and toxic congeners, respectively.

The PCB congener responses change with the ECD temperature in different ways. The order of the magnitudes of the congener relative responses also changes. The effect of the ECD temperature on the response of the PCBs is analysed in greater detail for the Model 400 ECD. At 150°C the magnitudes of the relative responses increase in the order of PCBs 28, 169, 77, 126, 101, 52, 153, 180 and 138 and at 330°C the order is PCBs 52, 101, 77, 153, 28, 126, 169, 138 and 180 (Fig. 1a and b). The change in the detector temperature by 180°C causes an important change in the order of the responses. In the range from 270 to 360°C, to which a detector is heated for the detection of analytes of low volatility, there are various changes in the relative molar responses of PCB congeners. This is important information which must be taken into account when quantifying the data obtained by an ECD. This is also demonstrated by the data in Table 4, giving the relative molar responses of the congeners at 180, 300 and 360°C on both detectors. The response changes are accidental at different temperatures on both detectors. This follows more clearly from the relative errors originating from application of the responses found at one detector temperature to another temperature (300°C). With changes in the detector temperature serious errors in the quantification of congeners may occur. Both positive and negative errors occur for different congeners and they reach up to 370%.

3.3. Influence of congener structure on the course of the response dependence

The influence of the congener structure on the course of the response dependence is analysed in a greater detail for the Model 400 detector. The



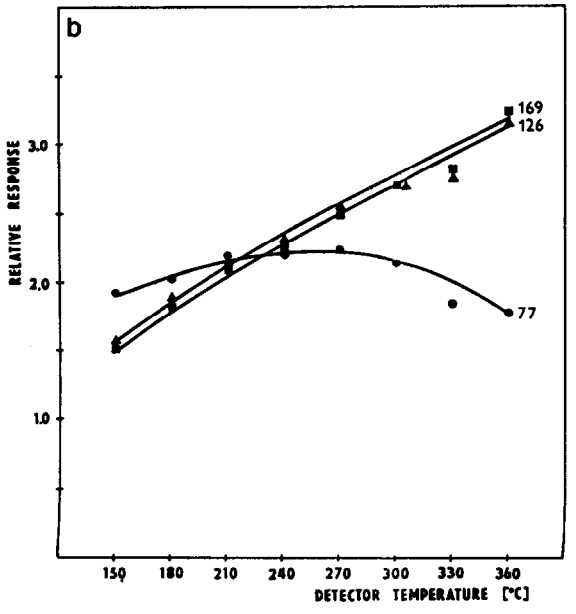
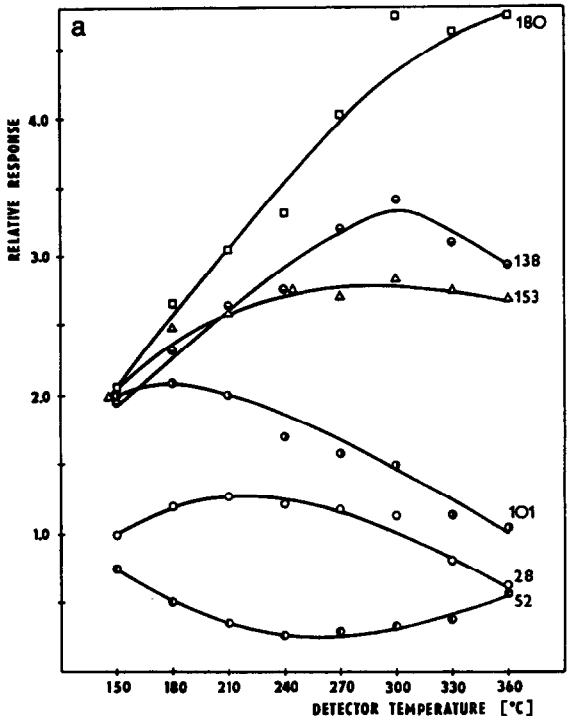


Fig. 2. Relative molar responses of selected PCBs with the PU 4400/03 ECD without oxygen in nitrogen.



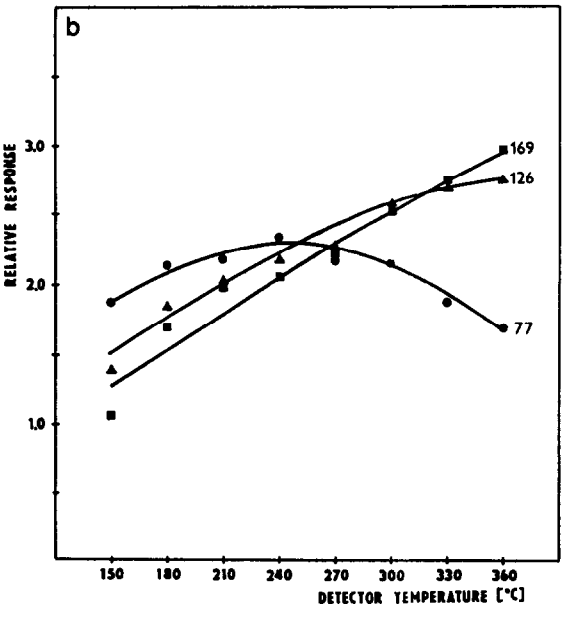


Fig. 3. Relative molar responses of selected PCBs with the PU 4400/03 ECD with 6 ppm of oxygen in nitrogen.

Table 4
Relative molar responses (*RMR*) for different detector temperatures and their relative errors (%) with respect to the *RMR* at 300°C

PCB No.	CE					PU				
	180°C		300°C: *RMR*	360°C		180°C		300°C: *RMR*	360°C	
	RMR	%		*RMR*	%	*RMR*	%		*RMR*	%
28	2.2	−31	3.2	4.5	+41	1.3	+44	0.9	0.5	−44
52	3.3	+371	0.7	0.6	−14	0.6	+100	0.3	0.7	+133
77	2.1	0	2.1	3.4	+62	2.0	−5	2.1	1.8	−14
101	4.7	+153	2.0	3.1	+55	2.0	+102	1.0	0.8	−20
126	2.3	−36	3.6	4.0	+11	1.9	−30	2.7	3.2	+19
138	11.0	+175	4.0	5.1	+28	2.1	−12	2.4	2.2	−8
153	8.9	+230	2.7	3.4	+26	2.6	−22	3.3	3.2	−3
169	2.2	−48	4.2	3.9	−7	1.9	−30	2.7	3.2	+19
180	9.7	+83	5.3	5.0	−6	2.5	−22	3.2	3.6	+13

dependences in Fig. 1a show that congeners Nos. 101, 153, 180 and 138 have maximum responses in the temperature range 180–200°C, No. 28 has the maximum response at 390°C and No. 52 at 150°C. In the given temperature range the response dependences of congeners Nos. 101, 153, 180 and 138 have one maximum and one minimum. The response for congener No. 28 increases monotonically with increase in temperature, whereas that of congener No. 52 decrease. For congeners Nos. 77, 126 and 169 the difference in the response dependences with variation in temperature is not so important (Fig. 1b).

From comparison of the response dependences of the congeners with the same number of chlorine atoms the following conclusions can be drawn.

Tetrachlorobiphenyls

The response of congener No. 52 decreases with increase in temperature and that of No. 77 remains constant in the range 150–300°C and then increases; in the range 150–210°C No. 52 has a higher response whereas above 210°C it is congener No. 77.

Pentachlorobiphenyls

The response of congener No. 126 increases with the increase in temperature with a local maximum at 270°C. No. 101 has the highest response at 180°C; in the range 150–220°C No. 101 has a higher response, whereas above 220°C it is No. 77.

Hexachlorobiphenyls

The responses of congeners Nos. 138 and 153 have the highest value at 180°C and the lowest at 300°C; for congener No. 169 the response increases up to 270°C and then remains constant; No. 169 has a higher response than No. 153 in the temperature range 260–390°C; congener No. 138 has a higher response over the whole range of temperatures.

The changes in the courses of the congener response dependences on ECD temperature are assumed to be due to different electron-capture mechanisms at different detector temperatures [11].

3.4. Dependence of the response on the detector design

The design and dimensions of the ECD cell plays an important role in its performance. The electron-capture coefficients in different ECDs can therefore differ.

The difference between Figs. 1a and 2a and between Figs. 1b and 2b gives an idea of the influence of different ECD designs (Model 400 and PU 4400) on the PCB congener relative responses and on the courses of the temperature dependences. With the Model 400 ECD a capillary column was used. The make-up gas flow-rate was such as to produce an overall gas flow-rate through the detector similar to that in the PU 4400 ECD with a packed column. These overall flow-rates through the ECD were optimized according to the detector design. The dependences of the relative responses have different shapes on the two detectors. The response maxima for PCBs Nos. 101, 138 and 153 are shifted to higher temperatures on the PU 4400. The response of No. 180 increases monotonically with increase in temperature. The response of No. 28 decreases monotonically from 210°C, in contrast to the course on the Model 400 ECD. No. 77 exhibits the maximum response on the PU 4400 at *ca.* 270°C. Congeners Nos. 126 and 169 have different courses of the response dependences, their response increasing almost linearly with increase in temperature.

In Table 5 we compare published data and our results for the mass responses of individual congeners relative to congener No. 101. The differences are large: the difference between the lowest and the highest relative response on different types of ECD (and with different experimental conditions) is almost sevenfold (Nos. 153 and 180). The differences are caused by the experimental conditions, *i.e.*, the detector temperature, flow-rate and purity of the gases, the detector regime (frequency and width of pulses) and the amount of solutes (in consequence of the limited ECD linearity). The PCB responses in the literature are mostly related to octachloronaphtalene (OCN), which should minimize the influences of the experimental conditions and apparatus on the response. However, it follows from Table 5 that in spite of this, considerable differences exist between the published data for the relative responses of PCBs.

Tables 2 and 3 give a comparison of the relative responses we measured on two different ECDs at the same detector temperature, the other experimental conditions being different. The relative response ratio (the ratio of the relative responses of the same congener on the two different types of ECD) does not remain constant for the two types of detector investigated even at the same detector temperature. If congener No. 101 is taken as a basis (relative response = 1), the molar ratio varies in the range from 0.60 (No. 28) to 2.43 (No. 153) and the mass ratio varies from 0.60 (No. 28) to 2.41 (No. 153). The error in the application of both relative molar and mass responses of the congener from one ECD type to another therefore reaches several hundred per cent.

Table 5
Comparison of published relative mass responses with those obtained in this work

Ref.	PCB No.								
	28	52	101	138	153	180	77	126	169
12			1.00	0.82	0.82	0.74			
13		0.72	1.00	1.32	1.74	1.66			
14	0.28	1.15	1.00	1.58	0.90	0.99			
5		0.89	1.00	1.18	1.19				
8[a]	0.78	0.76	1.00	0.62	0.90	0.60	1.10	1.35	0.77
8[a]	0.89	0.81	1.00	0.72	0.60	0.62	0.91	1.44	0.81
8[a]	0.91	0.82	1.00	0.70	0.60	0.62	0.84	1.46	0.82
8[a]	1.17	1.21	1.00	0.92	0.55	1.01	2.01	1.84	1.08
8[a]	1.45	1.17	1.00	0.94	0.52	0.97	2.13	1.89	1.10
This work (Model 400 ECD)	1.21	0.29	1.00	2.17	1.49	3.17	0.93	1.76	2.29
This work (PU 4400 ECD)	0.73	0.28	1.00	2.65	3.59	3.83	1.88	2.69	2.92

[a] Different columns and internal standards were used.

3.5. Influence of oxygen

The effect of different amounts of oxygen in the gas in the ECD on the responses of PCB congeners was studied by using carrier gases with different oxygen contents. The influence of the presence of 6 ppm of oxygen on the relative response and the course of the response dependences on temperature can be seen from Figs. 2a and 3a (without oxygen) and Figs. 2b and 3b (with oxygen). A 6 ppm concentration of oxygen in nitrogen increases the relative responses of Nos. 180 and 138 and decreases those of No. 153 over the whole range of temperature. The relative responses of the other congeners are not significantly affected. The courses of the dependences do not differ significantly. The relative error in the determination of the responses using a gas with different oxygen contents can be up to 100%.

4. Conclusions

With different temperatures of the ECD various changes in the relative molar and mass responses of the selected PCB congeners occur; for this reason relative errors of several tens per cent may occur on application of the values of relative responses from one detector temperature to another.

The temperature course of the responses depends on the type of ECD used and on the content of oxygen in the gas passing through it.

Separation is the main problem in PCB congener analysis. However, accuracy of the quantitative results is also important. The profound differences among the temperature dependences of the various PCB congener responses can have a significant effect on the analytical results. There is a tendency to apply the same relative response factors in all PCB analyses. However, it is not possible to use published relative congener responses for different ECD temperatures and designs. A difference of 60°C above 300°C (the minimum detector temperature that is generally used in PCB analysis) results in errors of several tens per cent.

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