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Citation for published version (APA):

Krupcik, J., Kocan, A., Petrik, J., Leclercq, P. A., & Ballschmiter, K. (1993). Reference standards for quantitative trace analysis of PCB's by GC. Technical PCB formulations for the calibration of ECD and MSD responses. *Chromatographia*, 35(7-8), 410-418. <https://doi.org/10.1007/BF02278595>

DOI:

[10.1007/BF02278595](https://doi.org/10.1007/BF02278595)

Document status and date:

Published: 01/01/1993

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Reference Standards for Quantitative Trace Analysis of PCB's by GC. Technical PCB Formulations for the Calibration of ECD and MSD Responses

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Key Words

Capillary gas chromatography
Polychlorinated biphenyls (PCBs)
Quantitative analysis
Detector response factors (FID, ECD, MS)

Summary

The composition of any technical PCB formulation can be determined directly by analyzing the PCB sample by gas chromatography with a flame ionization detector (GC-FID), provided the relative molecular masses of the components are known. The responses of electron capture and selected-ion monitoring, mass-spectra detectors can then be calibrated for individual PCB congeners by correlation of the chromatographic patterns with those of concentrated PCB samples obtained by GC-FID. This procedure, which uses a given technical PCB formulation as a secondary reference standard mixture, is to be preferred over existing calibration methods, when results with $\pm 10\%$ errors are acceptable because commercial PCB formulations cover the whole range of chlorination products.

Introduction

Capillary gas chromatography (GC) with an electron capture detector (ECD), or a mass spectrometric detector in the selected-ion monitoring mode (MS-SIM), provides the best specificity and selectivity for trace analysis of polychlorinated biphenyls (PCBs) in various environmental and biological samples [1].

It is known that the ECD response to PCBs is dependent both on the number of chlorine atoms

present as well as on the chlorine substitution pattern on the biphenyl skeleton [1, 3, 4]. Owing to very poor reproducibility, published responses and response factors cannot simply be applied for calibration under various instrumental and working conditions. Therefore, the ECD response to PCBs must be calibrated prior to GC-ECD trace analysis. As there are 209 PCB congeners, it is a time-consuming and expensive task to carry out such calibrations using the full set of congeners on a daily laboratory basis. For this reason, quantitation requires secondary standards or certified PCB standards available to the many analysts presently involved in PCB trace analysis.

An acceptable solution for calibrating responses for 203 of the 209 PCBs was published by Cooper et al. [2], who used a mixture containing 31 reference PCB congeners, each of which representing a group of congeners with similar response factors. A similar concept was proposed by the Canadian Marine Research Institute where 51 PCB congeners are used [5].

The specificity of GC-MS-SIM analysis of PCBs is excellent with regard to the number of halogen atoms and the relative molecular mass. However, there are problems of distinguishing isomers because of lack of specific masses, corresponding to the isomeric structure in the fragmentation pattern of the spectra. For PCBs the most important electron-ionization, mass-spectra feature is the molecular ion cluster (M^+). The ions selected for MS-SIM, PCB monitoring represent the most abundant peak in each of the M^+ ion clusters. The application of the GC-MS-SIM method for selective trace determinations of PCB congeners and total PCB content, requires calibration of MS-SIM responses. A mixture of nine reference PCB congeners was used for the calibration of MS-SIM mean responses of isomeric groups, using a computerized capillary GC-MS system [6]. Individual response factors within an isomer group, however, varied by a factor of 1.16–2.15 [1] or 1.3–4.6 [6], which is almost unacceptable for trace GC-MS-SIM analysis.

In a previous paper [7] we described a new procedure to derive, from any technical PCB formulation, a secondary reference standard mixture suitable for calibration. The aim of this paper is to report experience of those secondary reference standards for calibration of ECD, MS-TIC and MS-SIM responses.

Experimental

Gas Chromatography

A HP 5890A gas chromatograph, equipped with FID and ECD detectors was used (Hewlett Packard, Waldbronn, FRG). GC-FID and GC-ECD chromatograms were recorded and evaluated by a HP 3393 integrators. Separations were performed on a 50 m $\times$ 0.2 mm i.d. fused-silica capillary-column, coated with a cross-linked polydimethylsiloxane elastomer (PONA column, Hewlett Packard). The column temperature was programmed from 180 °C at a rate of 1 °C min⁻¹. The detectors were maintained above the final column temperature: FID at 300 °C, ECD at 320 °C, respectively. Helium, at a linear velocity of 40 cm s⁻¹ at 180 °C, was used as carrier gas, and nitrogen, at 100 ml min⁻¹, as make-up gas for the ECD.

GC-MS

A HP 5890A gas chromatograph combined with a HP 5970B MSD was used for total-ion-current (GC-MS-TIC) and selected-ion monitoring (GC-MS-SIM) (all instruments Hewlett Packard). The GC working conditions were the same as those given above for GC-FID and GC-ECD.

The GC-MS interface was kept at 250 °C; the electron energy was 70 eV, and the electron multiplier was operated at 2200 V. With GC-MS-SIM, the following ions (*m/z*) were monitored: 188.00, 222.00, 255.95, 291.90, 325.90, 359.85, 393.85 and 429.75 dalton, with a dwell time of 45 ms each. With GC-MS-TIC, mass spectra were scanned from *m/z* 50 to *m/z* 480 every second.

Samples and Sample Introduction

Samples of technical PCB formulations, both for GC as well as for GC-MS, were diluted in *n*-hexane (5 μ g ml⁻¹) and injected using an inlet splitter operated at 280 °C, with a 1 : 100 ratio. Aroclor 1242, Aroclor 1260, Delor 103 and Delor 106 were from Chemko Strážske (Slovakia).

Results and Discussion

In a previous paper [7] we showed that any technical PCB formulation analyzed by GC-FID can be used as a secondary reference mixture for calibrating EC and MS detection, used frequently in PCB trace analysis. One of the requirements for the exploitation of such procedures is to analyze technical PCB formulations by GC with all appropriate detection techniques under

Table I Mass responses (R), mass response factors (RF) and relative mass response factors (RRF) of major^a congeners found for ECD by GC of Aroclor 1242.

SN ^b	R 10 ⁶ cnts pg ⁻¹	RF ng 10 ⁻⁷ cnts ⁻¹	RRF	RRF ^c	RRF ^d
4	0.1799	55.57	2.73	14.01	4.44
6	0.9993	10.01	1.57	1.38	3.25
5				4.40	5.49
8	0.6531	15.31	2.41	2.54	1.98
19	0.9369	10.67	1.68	1.73	2.12
18	0.6485	15.42	2.42	1.67	1.05
15				4.90	2.88
17	0.7371	13.57	2.13	1.27	1.04
27	1.837	5.444	0.855	1.06	1.33
16				1.17	1.16
32	1.146	8.724	1.37	1.88	1.14
26	1.625	6.153	0.967	0.869	0.997
25	2.289	4.369	0.686	1.05	2.05
31	1.144	8.745	1.37	0.932	1.05
28	1.434	6.975	1.10	0.613	0.803
33				1.17	1.07
53	1.217	8.214	1.29	1.43	1.16
22				0.479	0.325
51	1.820	5.496	0.864	0.873	1.63
45	1.731	5.778	0.908	0.970	1.01
46	1.752	5.708	0.897	1.12	-
52				1.25	0.625
69	1.146	8.728	1.37	0.653	0.772
49	1.414	7.075	1.11	0.808	0.744
48	1.857	5.384	0.846	0.942	0.922
47	1.665	6.004	0.943	0.618	0.619
44*	1.571	6.364	1.00	1.00	1.00
37				0.903	1.68
42	1.004	9.955	1.56	0.662	0.709
41				0.958	0.850
64				0.863	0.603
71	2.095	4.773	0.750	1.12	1.13
72				0.950	0.500
40	2.328	4.295	0.675	0.726	0.725
74	1.831	5.462	0.858	0.781	0.603
70				0.796	0.597
76	1.657	6.036	0.948	0.904	1.02
66				0.811	0.766
95	1.793	5.576	0.876	1.18	1.03
55				0.632	0.603
60	2.351	4.253	0.668	0.516	0.634
101	2.123	4.711	0.740	0.784	0.800
99				0.855	1.00
113	2.454	4.074	0.640	0.868	0.531
77	1.248	8.015	1.26	1.38	0.691
110	3.056	3.727	0.514	0.806	-

* reference PCB,

^a contents > 0.2 % considered as major constituents,

^b systematic PCB numbering according to Ballschmiter et al. [8],

^c recalculated from data published by Mullin et al. [4],

^d recalculated from data published by Cooper et al. [2].

similar conditions. In the following we shall show the use of the major constituents of Aroclor 1242 and Aroclor 1260.

Calibration of ECD

Figures 1 and 2 show separations of Aroclor 1242 and Aroclor 1260, respectively, under conditions similar to those published for the separation of these formula-

Table II Mass responses (R), mass response factors (RF) and relative mass response factors (RRF) of major^a PCB congeners found for ECD by GC of Aroclor 1242.

SN ^b	R 10 ⁶ cnts pg ⁻¹	RF ng 10 ⁻⁷ cnts ⁻¹	RRF	RRF ^c	RRF ^d
52	1.452	6.885	1.77	3.10	1.32
66				2.00	1.61
95	1.492	6.705	1.72	2.92	2.17
84				3.86	1.6
89	1.526	6.554	1.69	2.31	0.757
92				2.41	1.82
90				2.12	2.10
101	1.487	6.723	1.73	1.94	1.68
87	2.944	3.396	0.874	1.27	1.06
148	1.676	5.968	1.54	2.34	2.07
110	2.146	4.661	1.20	1.99	-
151	2.227	4.490	1.16	1.65	0.921
135	2.047	4.885	1.26	1.84	1.43
144	3.020	3.311	0.852	1.48	1.33
118				1.49	1.32
149	1.472	6.795	1.74	2.26	1.42
134	2.599	3.848	0.990	1.77	1.28
146	1.177	8.497	2.19	1.78	2.30
132	2.007	4.983	1.28	1.77	1.51
153	1.513	6.608	1.70	1.88	0.967
141	3.094	3.232	0.832	0.958	0.528
179	2.295	4.357	1.12	1.57	1.37
130				1.36	1.49
176	2.995	3.339	0.859	1.22	-
138				1.57	1.19
163	2.083	4.802	1.24	1.30	1.34
164				1.31	1.25
158	3.040	3.289	0.846	1.14	0.947
159				1.30	1.32
182	2.216	4.513	1.16	1.15	1.10
187				1.15	0.724
128	2.728	3.666	0.943	1.09	1.63
183	3.010	3.323	0.855	1.33	1.20
167	3.201	3.124	0.839	1.22	1.09
174	2.467	4.053	1.04	1.61	1.34
177	2.549	3.923	1.01	1.28	0.641
156				0.932	1.04
171	3.187	3.138	0.807	1.11	1.09
172				1.10	1.57
192	3.172	3.152	0.811	0.810	0.704
180*	2.573	3.886	1.00	1.00	1.00
170	2.779	3.598	0.926	1.73	0.862
190	3.823	2.615	0.673	0.988	0.858
196				1.05	1.26
203	3.701	2.702	0.695	0.795	0.829

* reference PCB,

^a contents > 0.4 % considered as major constituents,

^b systematic PCB numbering according to Ballschmiter et al. [8],

^c recalculated from data published by Mullin et al. [4],

^d recalculated from data published by Cooper et al. [2].

tions by GC-FID [7]. To identify peaks in these chromatograms, systematic PCB numbering according to Ballschmiter et al. [8] was used, as described for GC-FID chromatograms [7]. The very good agreement for the corresponding chromatograms, obtained by from Aroclor 1242 and Aroclor 1260 with GC-FID [7] and GC-ECD (Figures 1 and 2), allowed straight forward correlation. Knowing the major constituent composition of Aroclor 1242 and 1260 as previously determined [7], mass responses (R), mass response factors (RF) and relative mass response factors (RRF) were calculated for the major PCB congeners found in Aroclor 1242 and 1260. The results are in Tables I and II, respectively. For comparison, RRF values were recalculated from the data published by Mullin et al. [4] and Cooper et al. [2] and included in Tables I and II for corresponding pure congeners.

Although GC-ECD is the method of choice for trace analysis, it is obvious from Figures 1 and 2 and Tables I and II that even capillary columns give peak overlap. In such cases the determination of individual congeners is very difficult, even if the response factors of all congeners are known. Determination of partially co-eluting PCB congeners is further complicated if PCB isomers overlap, because it is difficult to determine the response values.

Consequently, the responses determined for overlapping congeners, including isomers, by using technical PCB formulations are more realistic than mean response factors determined from single standard response factors. The composition of overlapping congeners, differing in the number of chlorine atoms, was determined by GC-MS-SIM (see below). This, however, was not considered in Tables I and II, where for all overlapping peaks only one RRF is given as determined from the detector responses and the corresponding contents in Aroclor 1242 or 1260 [7].

Comparison of corresponding measured and published RRF values in Tables I and II shows reasonable agreement in many cases. However, in both Tables I and II relatively large differences between corresponding RRF's occur when peaks overlap. In these instances it is not feasible to tabulate ECD, RRF data for individual PCBs.

Calibration of MS-TIC

Figures 3 and 4 show chromatograms for Aroclor 1242 and 1260, respectively, reconstructed by computer from experimental data. The chromatographic conditions were again similar to those published for the separation of these formulations [7]. Comparing the chromatograms obtained by separating Aroclor 1242 and 1260 with both GC-FID [7] and GC-MS-TIC (Figures 3 and 4), very good agreement of retention times and chromatographic patterns can be obtained. Since in all cases equal amounts of PCBs were analyzed, comparison of the signal-to-noise ratios shows that the sensitivity of both the FID and MS-TIC for corresponding PCBs is practically the same.

Figure 3

Computer reconstructed chromatogram of 100ng Aroclor 1242 by GC-MS-TIC. Details, see Experimental.

Figure 4

Computer reconstructed chromatogram of 100ng Aroclor 1260 by GC-MS-TIC. Details, see Experimental.

The mass responses (R), mass response factors (RF) and relative mass response factors (RRF) of the major congeners, found by MS-TIC detection by analysis of Aroclor 1242 and 1260, are in Tables III and IV, respectively. From the data in Tables I to IV it follows that, for corresponding PCBs, the MS-TIC technique gives higher responses than ECD. In spite of this, MS-TIC is much less sensitive in practice, because its noise level is about 10^3 times higher than that for ECD. From Tables III and IV it further follows that the responses do not differ substantially ($R = 1.186 \times 10^7$ counts, standard deviation $\sigma = 0.182 \times 10^7$ Table III, and

Table III Mass responses (R), mass response factors (RF) and relative mass response factors (RRF) of major^a PCB congeners found for MS-TIC by GC of Aroclor 1242.

SN ^b	R, 10 ⁷ cnts ng ⁻¹	RF, ng 10 ⁻³ cnts ⁻¹	RRF
4	1.011	9.895	1.22
6	1.178	8.486	1.05
5			
8	1.005	9.946	1.23
19	1.407	7.109	0.879
18	0.9993	10.00	1.24
15			
17	1.033	9.679	1.20
27	1.714	5.835	0.722
16			
32	1.062	9.414	1.16
26	1.146	8.730	1.08
25	1.253	7.983	0.988
31	1.092	9.161	1.13
28	1.102	9.074	1.12
33			
53	1.101	9.086	1.12
22			
51	1.123	8.904	1.10
45	1.445	6.921	0.856
46	1.826	5.476	0.677
52			
69	1.185	8.439	1.04
49	1.199	8.342	1.03
48	1.082	9.243	1.14
47	1.157	8.641	1.07
44*	1.237	8.084	1.00
37			
42	1.008	9.921	1.23
41			
64			
71	1.180	8.478	1.05
72			
40	1.144	8.743	1.08
74	1.181	8.466	1.05
70			
76	1.156	8.648	1.07
66			
95	1.138	8.791	1.09
50			
60	1.132	8.830	1.09
101	1.057	9.457	1.17
99			
113	1.292	7.742	0.958
77	1.199	8.337	1.03
110	1.105	9.047	1.12

$\bar{R} = 1.186, \sigma = 0.182$

$\overline{RRF} = 1.094$

* reference PCB,

^a contents > 0.2 % considered as major constituents,

^b systematic PCB numbering according to Ballschmiter et al. [8].

$R = 1.074 \times 10^7$, standard deviation $\sigma = 0.109 \times 10^7$ Table IV) which allows, without calibrating the responses, to analyze the PCB samples semiquantitatively in GC-MS-TIC mode in weight percent.

Figures 5 and 6 show the separation of Aroclor 1242 and 1260, respectively, reconstructed by computer from experimental data obtained by monitoring the most abundant M⁺ ions (see Figures 7–10). Comparison of Figures 3 and 4 with Figures 5 and 6 shows a very

Table IV Mass responses (R), mass response factors (RF) and relative mass response factors (RRF) of major^a PCB congeners found for MS-TIC by GC of Aroclor 1260.

SN ^b	R, 10 ⁶ cnts pg ⁻¹	RF, ng 10 ⁻⁷ cnts ⁻¹	RRF
52	1.224	8.172	0.828
66			
95	1.223	8.177	0.828
84			
89	1.038	9.629	0.975
92			
90			
101			
87	1.238	8.077	0.817
148	1.108	9.027	0.914
110	1.150	8.693	0.881
151	1.234	8.102	0.821
135	0.9806	10.20	1.03
144	0.8701	11.49	1.16
118			
149	1.085	9.219	0.934
134	0.9123	10.96	1.11
146	1.129	8.854	0.897
132	1.202	8.317	0.842
153	1.121	8.918	0.903
141	1.1846	8.442	0.855
179	0.9715	10.29	1.04
130			
176	0.9650	10.36	1.05
138			
163	1.127	8.873	0.899
164			
158	0.8875	11.27	1.14
159			
182	1.074	9.311	0.943
187			
128	0.9878	10.12	1.02
183	1.052	9.502	0.962
167	1.254	7.974	0.808
174	1.028	9.728	0.985
177	1.073	9.319	0.944
156			
171	1.164	8.591	0.870
172			
192	0.9689	10.321	1.04
180*	1.013	9.872	1.00
170	0.9801	10.20	1.03
190	0.9936	10.06	1.02
196			
203	0.9908	10.09	1.02
194	1.006	9.940	1.01

$R = 1.074, \sigma = 0.109$

$RRF = 0.955$

* reference PCB,

^a contents > 0.4 % considered as major constituents,

^b systematic PCB numbering according to Ballschmiter et al. [8].

similar chromatographic pattern but the signal-to-noise ratio is much higher in Figures 5 and 6 since the sensitivity of the MS-SIM technique is much higher than MS-TIC for PCBs.

Calibration of MS-SIM

From data obtained from Aroclor 1242 and 1260 by GC-MS-SIM, the computer constructed single-ion mass-chromatograms (fragmentograms) shown in Figures

Figure 5
Computer reconstructed chromatogram (summed MS-SIM responses versus time) of 50ng Aroclor 1242 by GC-MS-SIM. Details, see Experimental.

Figure 6
Computer reconstructed chromatogram (summed MS-SIM responses versus time) of 50ng Aroclor 1260 by GC/SIM. Details, see Experimental.

7-10. In the electron impact mass spectra, the most abundant ions correspond to even masses in the molecular ion clusters (M^+), followed by M^+-Cl_2 fragments at $(M-70)^+$. Far less abundant is the $(M-35)^+$ cluster at odd masses. It is obvious in Figures 4

and 5 that the co-eluting PCB isomers cannot be resolved. Co-eluting congeners, containing fewer chlorines than the monitored congener, do not interfere with the measured M^+ ions produced by latter. Fragment ions produced by co-eluting congeners containing

Figure 7
Partial fragmentograms (m/z 222, 256) of 50ng Aroclor 1242 by GC-MS-SIM. Details, see text.

Figure 9
Partial fragmentograms (m/z 292, 326) of 50ng Aroclor 1260 by GC-MS-SIM. Details, see text.

Figure 8
Partial fragmentograms (m/z 292, 326) of 50ng Aroclor 1242 by GC-MS-SIM. Details, see text.

more chlorines than the test congener, however, can interfere. Therefore, characterization of congeners by their response in an M^+ ion cluster was verified by the absence of pertinent ions of higher mass.

As already mentioned, PCBs undergo a characteristic loss of two chlorines to produce a $(M-70)^+$ cluster that partially overlaps the M^+ cluster produced by a congener containing two chlorines less. These clusters contain ions that have the same masses but differ in relative abundance, which can be detected in full mass spectra but not in fragmentograms. Therefore, to verify

Figure 10
Partial fragmentograms (m/z 360, 394, 430) of 50ng Aroclor 1260 by GC-MS-SIM. Details, see text.

a tentative assignment of the level of chlorination, the observed relative abundance of isotope clusters had to be sufficiently similar to expected relative abundances.

Table V Mass responses (R), mass response factors (RF) and relative mass response factors (RRF) of the major PCB congeners found for MS-SIM by GC of Aroclor 1242 and 1260.

SN ^b	R, 10 ⁶ cnts ng ⁻¹	RF, ng 10 ⁻⁷ cnts ⁻¹	RRF	SN ^b	R, 10 ⁶ cnts ng ⁻¹	RF, ng 10 ⁻⁷ cnts ⁻¹	RRF
Dichlorobiphenyl isomers (m/z 222)				Hexachlorobiphenyl isomers (m/z 360)			
4	1.706	5.860	1.62	148	3.470	2.882	0.770
7, 9	3.106	3.220	0.888	151	2.599	3.847	1.03
6	3.850	2.598	0.716	135	2.390	4.183	1.12
5, 8*	2.758	3.626	1.00	144	2.585	3.869	1.03
15	2.582	3.872	1.07	149	2.354	4.248	1.13
Trichlorobiphenyl isomers (m/z 256)				134	2.423	4.127	1.10
19	2.066	4.840	1.22	131	3.099	3.226	0.968
18	1.916	5.219	1.31	146	2.758	3.626	1.01
17	1.959	5.105	1.28	132	2.725	3.669	0.980
27	3.103	3.222	0.811	153*	2.671	3.744	1.00
16, 32	2.190	4.566	1.15	141	2.506	3.991	1.07
26	3.103	3.222	0.811	130	2.889	3.468	0.926
25	3.014	3.318	0.835	138, 163, 164	2.707	3.694	0.98
31	2.951	3.389	0.853	158	3.172	3.153	0.842
28*	2.518	3.971	1.00	129	2.689	3.719	0.993
33	2.706	3.695	0.930	128	3.758	2.661	0.711
22	2.795	3.578	0.901	167	3.909	2.558	0.683
Tetrachlorobiphenyl isomers (m/z 292)				156	3.452	2.897	0.774
53	2.732	3.666	0.811	Heptachlorobiphenyl isomers (m/z 394)			
51	2.781	3.595	0.797	179	2.038	4.908	0.887
45	2.239	4.466	0.989	176	1.732	5.775	1.04
46	2.062	4.851	1.07	178	2.106	4.748	0.858
52	2.400	4.167	0.923	175	1.631	6.131	1.11
49	2.578	3.880	0.860	182, 187	1.858	5.383	0.973
48	2.885	3.466	0.768	183	2.056	4.865	0.880
47	2.453	4.077	0.903	185	2.117	4.724	0.854
44*	2.215	4.514	1.00	174	1.793	5.570	1.01
42	3.427	2.918	0.646	177	1.699	5.885	1.06
41, 64, 71, 72	3.197	3.128	0.693	171	2.020	4.951	0.895
40	2.131	4.692	1.04	172, 192, 147	1.807	5.533	1.00
70, 76	3.509	2.850	0.631	180*	1.807	5.533	1.00
66	3.326	3.006	0.666	193	2.002	4.996	0.903
56, 60	4.034	2.479	0.549	191	2.207	4.531	0.819
77	3.657	2.734	0.606	170	1.753	5.704	1.03
Pentachlorobiphenyl isomers (m/z 326)				190	2.120	4.716	0.853
95*	2.855	3.503	1.00	Octachlorobiphenyl isomers (m/z 430)			
84, 92	3.748	2.668	0.762	199	2.020	4.951	0.772
90, 101	3.017	3.314	0.946	198	1.397	7.159	1.12
99, 113	3.974	2.516	0.718	201	1.559	6.415	1.00
97	3.775	2.663	0.760	196, 203	1.670	5.987	0.933
87	2.264	4.416	1.26	195	1.469	6.808	1.06
110	3.928	2.546	0.727	194	1.613	6.200	0.966
82	2.833	3.530	1.01	205	1.192	8.392	1.31
124	2.851	3.507	1.00				
118	2.560	3.907	1.11				

* reference PCB

In Figures 7–10, further interference is caused by a (M-Cl)⁺ fragment ion-cluster containing a single naturally occurring ¹³C isotope. That cluster contains ions with the same mass and relative abundance as the ¹²C isotope M⁺ cluster of isomers containing one chlorine less. This ¹³C contribution is not constant (varies between 5–15 % of corresponding M⁺ ions) and cannot be filtered. It is, inter alia, one of the main sources of error, arising from overlapping PCB congeners with different number of chlorines, which influences the precision of the RRF measurements.

Table V shows mass responses, mass response factors and relative mass response factors of the major PCB congeners found by the MS-SIM technique, by GC of

Aroclor 1242 and 1260. From the data in Table V it follows that the response of the MS-SIM technique differs to a much greater extent than those in Tables III and IV for MS-TIC techniques. Consequently, RRF values in each isomer group also differ substantially.

Table VI shows mean responses their standard deviations (σ_R) and maximum ratio of response ($R_{\max}/R_{\min}$), calculated for each PCB isomer group from the results in Table V. For comparison, $R_{\max}/R_{\min}$ data published by Gebhart et al. [6] are included. Relatively good agreement is seen from comparison of measured and published values, except for hexa and heptachlorobiphenyl isomers. From Tables V and VI it is obvious that the MS-SIM technique must be calibrated

Table VI Mean responses ($\bar{R}$), standard deviations ($\sigma_{\bar{R}}$) and maximum response ratios ($R_{\max}/R_{\min}$) calculated for each PCB isomer group from the results in Table V.

PCB isomers	$\bar{R}$ 10 ⁶ cnts ng ⁻¹	$\sigma_{\bar{R}}$ 10 ⁶ cnts ng ⁻¹	$R_{\max}/R_{\min}$ Exp	$R_{\max}/R_{\min}$ Publ ^a
Dichlorobiphenyls	2.800	0.781	2.26	1.8
Trichlorobiphenyls	2.484	0.657	1.62	2.1
Tetrachlorobiphenyls	2.852	0.607	1.95	1.8
Pentachlorobiphenyls	3.178	0.617	1.75	2.1
Hexachlorobiphenyls	2.898	0.474	1.65	3.1
Heptachlorobiphenyls	1.922	0.180	1.36	2.9
Octachlorobiphenyls	1.560	0.257	1.70	1.6

^a results published by Gebhard et al. [6], relative to chrysene-d₁₂.

Table VII Comparison of minimum counts, amounts and contents corresponding to signal-to-noise ratio of 3 : 1 as found by GC of 2,2', 3,5'-tetrachlorobiphenyl (peak No. 44).

Detector	Counts	Amount, pg	Content, ppb
FID	1 · 10 ¹²	100	100
MS-TIC	4 · 10 ⁶	400	400
MS-SIM	3 · 10 ⁴	5	5
ECD	6 · 10 ³	0.5	0.5

prior to its use for PCB trace analysis. The use of mean response factors for each PCB isomers group, as proposed by Gebhart et al. [6], is therefore not applicable as the error can easily exceed fifty percent.

Comparison of FID, ECD, MS-TIC and MS-SIM

Table VII compares minimum counts, amounts and contents corresponding to a signal-to-noise ratio of 3 : 1 as found by analysis of 2,2', 3,5'-tetrachlorobiphenyl (peak No. 44) using on-column injection. From Table VII it follows that ECD is the most sensitive detector for PCBs. MS-SIM detection is also applicable although its sensitivity is about ten times smaller than that of the ECD. Negative-ion (methylene chloride and/or oxygen) chemical-ionization, mass spectrometry might be used to advantage for trace PCB analysis

because its sensitivity approaches that of ECD [9]. Calibration of this technique is the subject of further investigation. Table VII also shows that FID and MS-TIC are not sufficiently sensitive for trace analysis. The validity of the last is, however, relative as the data given in Table VII were calculated from non-smoothed signals. It is likely that the use of suitable smoothing can improve the signal-to-noise ratio to such an extent that even FID and MS-TIC can be exploited. This subject is currently being studied at the Analytical Chemistry Department, CHF STU in Bratislava and will be published separately.

Acknowledgement

This work was supported by a grant No. 1/990927/92 of the Slovak Ministry of Education.

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Received: Nov 6, 1992

Revised manuscript

received: Dec 23, 1992

Accepted: Jan 6, 1993