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QUANTITATION OF HALOGENATED AROMATIC COMPOUNDS BY GAS CHROMATOGRAPHY—MASS SPECTROMETRY

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SUMMARY

Quantitation by gas chromatography—mass spectrometry and by gas chromatography—hydrogen flame ionization detection (GC—HFID) were compared for five classes of halogenated aromatic compounds. For the five classes of compounds studied (polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, polychlorinated diphenyl ethers, polychlorinated naphthalenes and polychlorinated biphenyls), relative peak areas based on both selected ion monitoring of ions in the molecular ion cluster, and total ion current peak areas gave good approximations to relative concentrations based on GC—HFID peak areas. Within each class of compounds, the molecular ion cluster peak areas are a fairly constant fraction of the total ion current peak areas, regardless of the number of chlorines in the molecule or the substitution pattern.

INTRODUCTION

Halogenated aromatic compounds occurring as environmental pollutants are often found as complex mixtures of classes, homologues, and isomers [1]. The quantitative analysis of such samples is complicated by coelution of related classes in typical fractionation schemes used during sample preparation. Further, some of these classes of compounds, for example the polychlorinated biphenyls (PCBs), are presently impossible to separate into individual, non-overlapping components even by capillary gas chromatography (GC) [2—6]. When several classes are present in the same sample, for example PCBs, poly-

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chlorinated diphenyl ethers (PCDPEs) and polychlorinated naphthalenes (PCNs), chromatographic separation into individual components becomes altogether out of the question. Under such circumstances quantitation by GC using electron-capture detection (ECD), hydrogen flame ionization detection (HFID) or mass spectrometry—total ion current (MS—TIC) gives invalid results due to superposition of components of differing detector responses.

There are 209 possible PCBs, 209 possible PCDPEs, and 75 possible PCNs; for the PCBs at least, over 130 of the 209 possible isomers have been observed in commercial preparations [5—7]. Standards are not available for all of the isomers that may occur in environmental samples, and it would be quite impractical to generate 493 individual calibration curves (209 for PCBs, 209 for PCDPEs and 75 for PCNs) even if all possible standards were available. Moreover, classes of compounds in addition to the three mentioned may also be present (for example the 135 possible polychlorinated dibenzofurans, PCDBFs, and the 75 possible polychlorinated dibenzo-p-dioxins, PCDBDs).

An approach to this problem based on a preliminary class fractionation (see Fig. 1) followed by GC—MS with selected ion monitoring (SIM) has been described previously [1]. Although this approach can deal with the co-chromatography problem, quantitation using this approach is only feasible if one can avoid the need for individual calibration curves for every compound present in the mixture. The present paper is concerned with a comparison of relative detector responses (HFID, TIC, SIM) to compounds of the classes found in Fractions 2 and 3 of the fractionation scheme shown in Fig. 1. The errors associated with the assumption that the relative detector response may be averaged for a given isomeric group are also considered.
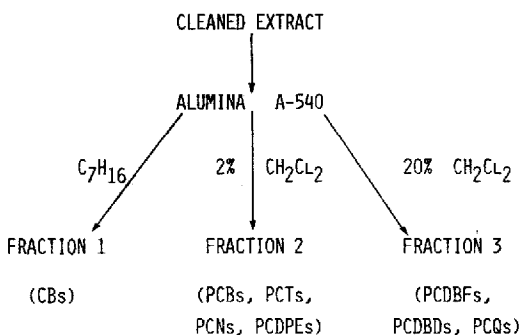

Fig. 1. Fractionation scheme.

EXPERIMENTAL

GC peak areas for fraction 2 mixtures were determined using a Varian 1200 gas chromatograph equipped with a hydrogen flame ionization detector, and fitted with a 2-m 3% OV-225 packed column. Fraction 3 GC—HFID analyses were done using capillary columns containing OV-1. Peak areas were measured with an Autolab System IV computing integrator. The chromatographic conditions have been detailed previously [1].

The analyses of fraction 2 and fraction 3 mixtures were performed on a VG Micromass 70/70F mass spectrometer, interfaced to a VG 2250 data system. The mass spectrometer was scanned from 670 to 20 a.m.u., at 1 sec per decade. The electron energy was 70 eV; source temperature was held at approximately 180°C. The mass spectrometer was equipped with a Hewlett-Packard HP 5710 gas chromatograph and a jet separator for packed column operation. A 2-m packed column containing 3% OV-225, programmed from 180 to 250°C, at 6°C/min, was used for the molecular ion cluster (MIC) and TIC analyses of fraction 2 mixtures. A capillary column containing Dexsil 410 (25 m) was used for the mixture analyses and the MIC and TIC determinations for the PCDBFs. An SE 30 (7 m) capillary column at 220°C, or programmed from 100 to 240°C at 10°C/min, or an OV-101 (11 m) capillary column programmed from 150 to 240°C at 10°C/min was used for the PCDBD analyses.

Molecular ion peak areas were determined by measuring the areas of the $[M+2]^+$ ion chromatograms, i.e., the ion containing one ^{37}Cl isotope, using the VG data system peak area program. The $[M+2]^+$ peak areas were then multiplied by weighting factors to give the areas in the entire MIC. The weighting factors were obtained from a table of relative probabilities of occurrence of the various isotope peaks [8]. TIC peak areas were determined from the peak areas of the total ion chromatogram and include all ion intensities in the entire mass range scanned.

Individual PCBs, PCDPEs, PCDBDs and PCDBFs were obtained from Analabs (North Haven, DE, U.S.A.) or RFR (Hope, RI, U.S.A.). The mixture of PCNs used was Halowax 1013 from Analabs. Solvents used were from Burdick and Jackson Labs. (Muskegon, MI, U.S.A.).

RESULTS AND DISCUSSION

Analysis of fraction 3 mixtures
PCDBDs. The results of the analyses of four dioxin mixtures are shown in Table I. If the HFID results are taken as the best approximation of the true relative concentrations, there is good correlation between the actual relative concentrations and those based on TIC peak areas and MIC peak areas. These relationships are shown in the following equations:

TIC%   = 1.02 (HFID%) − 0.49, $r = 0.9801$, $p < 0.001$

M⁺%   = 0.89 (HFID%) + 2.49, $r = 0.9494$, $p < 0.001$

$[M+2]^+$% = 1.00 (HFID%) + 0.06, $r = 0.9783$, $p < 0.001$

where p is the probability that the correlation coefficients are not significantly different from zero. The regression equation is given below:

% TIC carried by the MIC = 0.87 (No. of chlorines) + 44.02, $r = 0.3612$,
$$0.1 < p < 0.2$$

The low correlation coefficient indicates a poor correlation, so the % TIC carried by the MIC is not simply determined by the number of chlorines in the molecule.

TABLE I

RELATIVE PEAK AREAS BY HFID, M⁺, [M+2]⁺, AND TIC FOR FOUR DIOXIN MIXTURES

Component	HFID areas ($\pm$S.D.)	TIC areas ($\pm$S.D.)	MIC areas based on M^+ areas ($\pm$S.D.)	MIC areas based on $[M+2]^+$ areas ($\pm$S.D.)
Dioxin mixture A				
1-Cl₁	21.2±1.9	14.7±0.61	13.8±0.48	13.7±1.11
2,3-Cl₂	21.0±1.2	19.1±1.7	19.5±0.74	21.6±3.12
2,6,8-Cl₃	17.1±0.56	18.5±2.0	17.3±0.94	17.8±2.74
1,2,3,4-Cl₄	23.1±0.28	25.6±1.7	26.5±0.54	25.7±1.0
1,2,3,7,8-Cl₅	17.4±0.18	22.3±1.5	22.9±0.74	21.3±0.94
Dioxin mixture B				
2-Cl₁	9.27±0.30	6.7±1.2	7.1±0.25	7.0±0.97
2,7-Cl₂	16.40±0.37	17.4±3.4	14.4±1.0	15.5±1.36
2,3,7-Cl₃	14.70±0.10	13.8±2.6	15.5±0.65	13.7±1.8
2,3,7,8-Cl₄	8.09±0.11	7.1±1.1	8.0±0.47	8.1±0.53
1,2,3,7,8-Cl₅	51.6±0.87	55.1±3.6	54.9±1.6	55.8±3.8
Dioxin mixture C				
2,8-Cl₂	63.0±0.78	59.0±3.3	50.3±2.34	57.7±1.07
1,2,4-Cl₃	15.6±0.10	15.6±0.52	19.1±1.6	17.0±1.15
1,2,3,7,8-Cl₅	21.4±0.73	25.4±2.8	30.6±0.96	25.3±0.71
Dioxin mixture D				
1,2,4,7,8-Cl₅	27.5±1.6	24.5±1.4	26.4±0.46	24.1±0.67
1,2,3,6,7,8-Cl₆ 1,2,3,7,8,9-Cl₆	19.0±0.11 28.1±0.30 }	52.0±2.1	48.3±1.9	50.7±0.78
1,2,3,4,6,7,8-Cl₇	11.9±0.33	12.0±0.75	13.2±0.70	12.2±1.3
Octachloro-Cl₈	13.4±1.2	11.5±0.32	12.1±2.4	13.0±0.76

For there to be good correlations for MS—TIC peak areas with true relative concentrations, even for isomers containing different numbers of chlorines, the ionization cross sections for isomers containing different numbers of chlorines must be fairly constant. For molecular ion peak areas to also give good approximations to relative concentrations, independent of the number of chlorines in the molecule, then the portion of the TIC carried by the MIC must also be fairly constant. Alternatively, discrepancies may fortuitously cancel out.

The hydrogen flame ionization detector response to substituted aromatic compounds (peak area per μmole) generally tends to decrease as C—H bonds are replaced by C—Cl bonds. Although ways of correcting for this have been empirically developed for some compound classes [9], this has not been accomplished for PCDBDs due to lack of availability of a large number of highly pure individual standards in weighable quantities. Table I suggests that the relatively high response to monochloro PCDBDs and the relatively low response to highly chlorinated PCDBDs of the hydrogen flame ionization detector fortuitously cancel out when a least-squares regression line comparing HFID to TIC areas is calculated.

TABLE II

PERCENT OF THE TOTAL ION CURRENT CARRIED BY THE MOLECULAR ION CLUSTER FOR DIOXINS

Compound	Percent TIC carried by MIC ($\pm$ S.D.)
1-Cl$_1$	47.6$\pm$2.46
2-Cl$_1$	46.9$\pm$6.53
2,3-Cl$_2$	55.0$\pm$7.02
2,7-Cl$_2$	38.8$\pm$8.8
2,8-Cl$_2$	36.0$\pm$1.04
1,2,4-Cl$_3$	45.3$\pm$0.12
2,3,7-Cl$_3$	47.5$\pm$9.3
2,6,8-Cl$_3$	48.4$\pm$5.86
1,2,3,4-Cl$_4$	51.8$\pm$3.46
2,3,7,8-Cl$_4$	49.9$\pm$6.9
1,2,3,7,8-Cl$_5$	48.4$\pm$4.26
1,2,4,7,8-Cl$_5$	49.9$\pm$1.9
1,2,3,6,7,8-Cl$_6$ 1,2,3,7,8,9-Cl$_6$ }	46.1$\pm$3.6
1,2,3,4,6,7,8-Cl$_7$	51.4$\pm$2.4
1,2,3,4,6,7,8,9-Cl$_8$	53.1$\pm$6.5
Mean	47.4$\pm$4.9

TABLE III

RELATIVE PEAK AREAS BY HFID, M$^+$, [M+2]$^+$ AND TIC FOR TWO MIXTURES OF FURANS

Component	HFID areas ($\pm$ S.D.)	TIC areas ($\pm$ S.D.)	MIC areas based on M$^+$ areas ($\pm$ S.D.)	MIC areas based on [M+2]$^+$ areas ($\pm$ S.D.)
Furan mixture A				
2,3-Cl$_2$	9.99$\pm$0.18	9.5$\pm$3.2	8.3$\pm$2.0	8.3$\pm$1.6
2,4,6-Cl$_2$	17.70$\pm$0.25	16.1$\pm$2.9	16.4$\pm$1.4	15.7$\pm$1.4
2,3,8-Cl$_3$	8.58$\pm$0.16	8.5$\pm$2.3	9.4$\pm$2.4	9.1$\pm$1.9
2,3,6,8-Cl$_4$	10.40$\pm$0.31	9.5$\pm$2.0	10.2$\pm$1.6	9.8$\pm$2.1
2,4,6,8-Cl$_4$	15.10$\pm$0.84	14.6$\pm$1.8	14.9$\pm$0.50	13.8$\pm$1.8
1,3,4,7,8-Cl$_5$	23.7 $\pm$0.40	25.7$\pm$3.2	24.5$\pm$1.8	26.3$\pm$0.56
2,3,4,6,7,8-Cl$_6$	14.5 $\pm$1.18	16.1$\pm$3.2	16.2$\pm$2.4	17.0$\pm$1.5
Furan mixture B				
2,3,4,6,7,8-Cl$_6$	54.2$\pm$0.62	58.7$\pm$2.7	56.2$\pm$3.6	58.7$\pm$2.7
Octachloro-Cl$_8$	45.8$\pm$0.62	41.3$\pm$2.7	43.8$\pm$3.6	41.3$\pm$2.7

The portion of the TIC carried by the MIC for various isomers was studied, and the results are given in Table II. For these PCDBD's, the % TIC carried by the MIC was 47.4 $\pm$ 4.9%.

PCDBFs. A similar study was done on two mixtures of PCBDFs. The results of the mixture analyses are shown in Table III. Here again there was good cor-

relation between the HFID peak areas (taken as the best values), and the TIC and MIC peak areas, as shown in the following regression equations:

TIC% $= 1.03$ (HFID%) $- 0.58$, $r = 0.9894$

M^+% $= 1.01$ (HFID%) $- 0.25$, $r = 0.9963$

$[M+2]^+ = 1.03$ (HFID%) $- 0.62$, $r = 0.9870$

The % TIC carried by the MIC was calculated, and was fairly constant over all of the furan isomers studied (Table IV). The very poor correlation between the % TIC carried by the MIC and the number of chlorines in the molecule ($r = 0.0369$) indicates that these two parameters are independent.

TABLE IV

PERCENT OF THE TOTAL ION CURRENT CARRIED BY THE MOLECULAR ION CLUSTER FOR FURANS

Compound	Percent TIC carried by MIC ($\pm$ S.D.)
2,8-Cl_2	46.1$\pm$ 4.82
2,4,6-Cl_3	52.5$\pm$ 4.75
2,3,8-Cl_3	56.8$\pm$ 3.03
2,4,6,8-Cl_4	51.5$\pm$ 4.76
2,3,6,8-Cl_4	54.8$\pm$ 3.09
1,3,4,7,8-Cl_5	51.7$\pm$ 3.96
2,3,4,6,7,8-Cl_6	49.4$\pm$ 7.15
1,2,3,4,6,7,8,9-Cl_8	52.0$\pm$10.4
Mean	52.0$\pm$ 5.33

Analysis of fraction 2 mixtures

PCDPEs. Similar studies were done on a synthetic mixture of seven PCDPEs. Since no pure, individual standards were available, identification of the substitution pattern and relative molar response (RMR) calculations could not be done. The results of the mixture analysis are shown in Table V. Regression equations and correlation coefficients are given below:

TIC vs. FID : TIC $= 1.05$ (FID) $- 0.49$; $n = 7$, $r = 0.9995$, $p < 0.001$

TIC vs. $[M+2]$: TIC $= 0.84$ $[M+2] - 2.15$; $n = 7$, $r = 0.9899$, $p < 0.001$

FID vs. $[M+2]$: $[M+2] = 0.58$ (FID) $+ 0.45$; $n = 7$, $r = 0.9888$, $p < 0.001$

PCNs. The chloronaphthalenes studied were also only available as a mixture (Halowax 1013) that was not completely resolved by GC (see Fig. 2). In addition, the same degree of resolution was not obtained by all of the methods of detection compared. To obtain comparable quantitation results, some poorly resolved peaks were combined and others, where the degree of chlorination was uncertain, were omitted (see Table IV). Regression equations and correlation coefficients are given below:

TIC $= 1.03$ (HFID) $+ 0.29$; $n = 9$, $r = 0.991$, $p < 0.001$

$[M+2] = 0.97$ (HFID) $+ 0.48$; $n = 7$, $r = 0.953$, $p < 0.001$

TABLE V

RELATIVE PEAK AREAS BY HFID, [M+2] AND TIC, AND PERCENT TIC CARRIED
BY THE MOLECULAR ION FOR PCDPEs

Peak No.	PCDPE mix	HFID areas (± S.D.)	MIC areas based on [M+2] areas (± S.D.)	TIC areas (± S.D.)	Percent TIC carried by MIC
3	hexa	3.0±0.2	2.1±0.5	2.2±0.5	32.5
5	hepta	2.1±0.1	1.6±0.4	1.8±0.3	38.3
6	hepta	31.3±0.5	35.0±0.8	32.4±2.4	27.5
8	octa	34.2±0.5	41.7±1.6	35.6±1.4	37.6
9	octa	5.0±0.6	3.9±0.6	5.7±1.1	34.6
10	octa	6.2±0.2	4.2±0.6	5.7±1.1	23.6
12	nona	15.7±0.5	11.4±0.6	15.7±1.1	33.7
Mean					30.8±7.1

Calculations of % TIC carried by the MIC were also done on Halowax 1013. Since no pure standards were available, the substitution patterns of components in this mixture could not be determined. Moreover, since this mixture was much more complex than that of the PCDPEs, and some of the peaks were not completely resolved (see Fig. 2), even the number of chlorines in a particular peak could not always be determined. The results of calculating the % TIC carried by the MIC, assuming that the peak was due to a single component of the highest number of chlorines detected in the peak, are shown in Table VI.
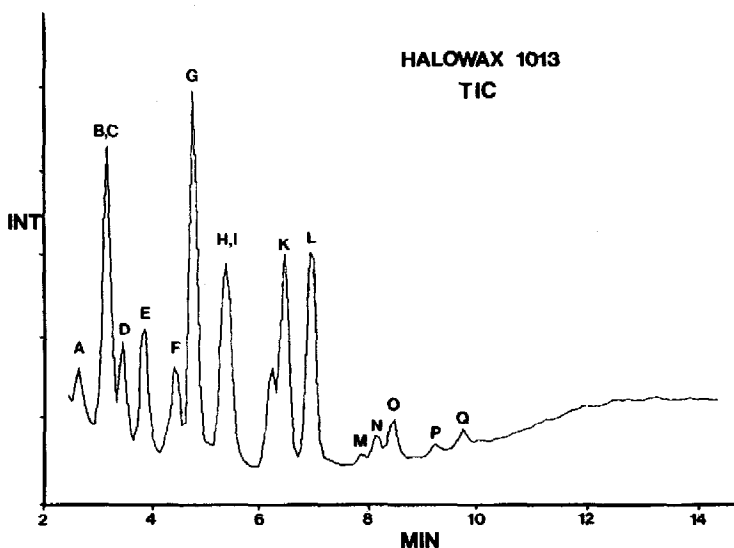

Fig. 2. GC—MS TIC chromatogram of Halowax 1013, a mixture of PCNs (OV-225, programmed from 180 to 250°C, at 6°C/min).

TABLE VI

RELATIVE PEAK AREAS BY HFID, [M+2] AND TIC, AND PERCENT OF THE TOTAL
ION CURRENT CARRIED BY THE MOLECULAR ION CLUSTER FOR PCNs

No. of Cl	Peak	HFID areas	MIC areas based on [M+2] area	MIC areas based on TIC area	Percent TIC carried by MIC
4	A	4.7	3.7	2.5	49.1
3	B			15.4	8.3
4	C				41.7
4	D				33.6
4	E	12.5	12.6	7.4	56.5
4	F				50.5
5	G				8.8
5	H, I	23.0	15.9	16.5	30.0
5	J, K	31.0	32.7	38.6	47.7
5	L	21.6	25.3	27.7	49.2
6	M, N, O	5.9	7.2	6.2	51.8
6	P	1.2	2.5	1.1	41.2
7	Q				52.2
Mean					48.0 ± 6.8
					(without peaks B and G)

TABLE VII

RELATIVE PEAK AREAS BY HFID, [M+2] AND TIC FOR PCBs

	HFID areas (± S.D.)	HFID areas (RMR-corrected) (± S.D.)	MIC areas based on [M+2] areas	TIC areas
PCB mix 1				
2,5,2′,5′	18.05 ± 0.23	16.64 ± 0.21	12.2	14.7
2,4,6,2′,4′,6′	18.75 ± 0.21	22.22 ± 0.25	20.5	21.8
2,3,4,5	16.95 ± 0.15	16.10 ± 0.14	16.4	16.6
2,4,5,2′,5′	19.12 ± 0.43	18.40 ± 0.41	17.6	19.1
2,3,6,2′,3′,6′	12.88 ± 0.14	12.84 ± 0.14	16.2	15.6
3,4,3′,4′	14.28 ± 0.074	13.80 ± 0.072	15.8	13.6
PCB mix 2				
2,3,4,5	27.5 ± 0.5	27.1 ± 0.5	23.0	23.3
2,3,4,5,6	34.4 ± 0.5	37.4 ± 0.5	29.9	31.3
2,3,5,6,2′,3′,5′,6′	17.2 ± 0.1	18.7 ± 0.2	25.0	22.7
2,3,4,5,2′,3′,4′,5′	19.9 ± 0.2	16.7 ± 0.2	22.4	22.7
PCB mix 3				
3,4,3′,4′	30.4 ± 0.5	29.9 ± 0.5	34.3	30.3
2,3,4,2′,5′	26.8 ± 0.5	23.9 ± 0.4	21.7	23.6
2,3,4,2′,3′,4′	22.9 ± 0.4	23.2 ± 0.4	22.6	22.8
2,3,5,2′,3′,5′	20.4 ± 0.3	22.9 ± 0.4	21.3	23.2

As can be seen from Table VI, most of the values for the % TIC carried by the MIC fall in the range 40—57%. If one assumes that this value should be a constant for PCNs, as was found to be the case for PCDBDs, PCDBFs, and PCDPEs, and that values in this range represent true values for this constant, then peaks which give lower values may be interpreted as resulting from coeluting components with fewer chlorines. The effect of lower molecular weight coeluting components would be to increase the TIC peak area, but would leave the MIC area unchanged, thus leading to a lower ratio. One example of where this may have occurred is peak G, where the observed % TIC carried by the MIC is 8.8%.

In this way, if the % TIC carried by the MIC has been shown to be a constant for a certain class of compounds, the ratio can be used as a check on peak purity in a mixture, at least as to whether or not the peak is likely to contain only components with the same number of chlorines.

PCBs. Three mixtures of PCBs were analyzed, and the results of quantitation based on HFID peak areas, HFID ppeak areas corrected for RMR according to the empirical rules described previously [9], MIC peak areas based on $[M+2]^+$ peak areas, and TIC peak areas were compared (Table VII). The RMD-corrected HFID values were taken as the best approximation to the actual relative concentrations [9]. The regression equations and correlation coefficients obtained are given below:

TIC vs. RMR-corrected HFID values: TIC = 0.71 (RMR-corrected HFID) +
$$+ 6.38, n = 14, r = 0.9052, p < 0.001$$

$[M+2]$ vs. RMR-corrected HFID values: $[M+2]$ = 0.75 (RMR-corrected HFID)
$$+ 5.54, n = 14, r = 0.8047, p < 0.001$$

HFID vs. RMR-corrected HFID values: HFID = 0.69 (RMR-corrected HFID) +
$$+ 6.51, n = 14, r = 0.7874, p < 0.001$$

where p is the probability that the correlation coefficient is not significantly different from zero.

The RMR-corrected HFID values, RMR-corrected $[M+2]^+$ values, and the % TIC carried by the MIC's are given in Table VIII for the sixteen PCB isomers studied. There was no correlation observed between the number of chlorines in the molecule and the % TIC in the MIC, and the average value for the % TIC in the MIC was 37.9 ± 5.5.

CONCLUSIONS

For the five classes of compounds studied (PCDBDs, PCDBFs, PCDPEs, PCNs, and PCBs), relative peak areas based on both SIM of ions in the MIC, and TIC peak areas gave good approximations to relative concentrations based on GC—HFID peak areas. Within each class of compounds, the MIC peak areas are a fairly constant fraction of the TIC peak areas, regardless of the number of chlorines in the molecule or the substitution pattern.

What this must mean is that not only are the ionization cross sections fairly constant for a given compound class, but that the energy distributions must also be such that the fraction of molecular ions which are formed but which

TABLE VIII

RELATIVE PCB MOLAR RESPONSES FOR HFID AND [M+2] PEAK AREAS, AND THE PERCENT TIC CARRIED BY THE MOLECULAR ION CLUSTER

RMR = 0.132 (No. of chlorines) + 0.202, r = 0.9956

PCBs		RMR corrected HFID values	RMR-corrected [M+2] values	Percent TIC carried by MIC
Tri	2,3,5		1.17	42.7
	2,4,4' + 2,5,4'			49.7
	Mean			46.2 ± 5.0
Tetra	2,3,4,5	0.958	0.694	38.1
	2,4,2',4' + 2,5,2',5'			36.4
	2,5,2',5'	1.036	0.596	30.9
	3,4,3',4'	1.006	0.902	42.5
	Mean	1.021 ± 0.02	0.749 ± 0.22	36.9 ± 4.8
Penta	2,3,4,5,6	0.867	0.802	38.2
	2,3,4,2',5'	0.994	0.757	30.6
	2,4,5,2',5'	1.000 (Reference)	1.000 (Reference)	34.4
	Mean	0.953 ± 0.08	0.853 ± 0.13	34.4 ± 3.8
Hexa	2,3,4,2',3',4'	1.036	0.731	33.0
	2,3,5,2',3',5'	0.928	0.731	30.6
	2,4,6,2',4',6'	0.819	1.125	39.6
	2,3,6,2',3',6'	0.976	1.418	38.5
	Mean	0.940 ± 0.09	1.001 ± 0.33	35.4 ± 4.3
Hepta from Aroclor 1254				
Octa	2,3,4,5,2',3',4',5'	1.120	1.398	39.7
	2,3,5,6,2',3',5',6'	0.867	1.122	44.0
	Mean	0.994 ± 0.18	1.260 ± 0.20	41.8 ± 3.0
Average of all PCBs studied		0.967 ± 0.08	0.957 ± 0.27	37.9 ± 5.5

have insufficient energy for fragmentation must also be fairly constant for a given class [10,11]. This fraction was fairly constant within each class, but varied from class to class (the % TIC carried by the MIC was 37.9 ± 5.5% for PCBs, 30.8 ± 7.1% for PCDPEs, 48.0 ± 6.8% for PCNs, 47.4 ± 4.9% for PCDBDs, and 52.0 ± 5.3% for PCDBFs). These results indicate that it should be possible to quantitate one member of a given compound class based on the calibration curve from SIM of a different isomer in the same class, even an isomer containing a different number of chlorines, and that the relative error introduced by doing this would be approximately 10–23%.

It should be noted that these % TIC carried by the MIC determinations were done on a magnetic sector instrument. The mass discrimination of a quadrupole mass spectrometer might lead to decreasing MIC values with increasing mass, or in this case, with increasing number of chlorines.

If the % TIC carried by the MIC were subject to a mass discrimination effect, this would in turn affect the use of MIC areas to approximate TIC peak areas.

Correction factors would probably be needed in order to use either TIC or MIC areas to determine relative concentrations, since these areas would be dependent on the mass distribution of the fragments. On a quadrupole mass spectrometer, even isomers with the same number of chlorines might not give constant MIC/TIC values if the mass distribution of the fragments differed significantly.

In the cases of the PCNs and PCDPEs, for which individual standards were unavailable, the possibility exists that the individual relative detector responses vary significantly for the hydrogen flame ionization detector but, fortuitously, in a similar manner to the TIC and SIM detectors. If this were the case there could be high correlation coefficients in spite of wide variations in responsivity. This possibility cannot be tested until a number of individual, isomeric PCDPEs and PCNs of appropriate chlorine numbers are available.

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