ANALYSIS OF POLYHALOGENATED DIBENZO-p-DIOXINS AND -FURANS: GENERATION OF A DATABASE CONTAINING NUMBER OF POSSIBLE ISOMERS AND ISOTOPIC ABUNDANCES

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ABSTRACT

A pascal program is presented that allows the determination of the number of possible isomers as well as the calculation of the isomer abundance patterns of halogenated compounds. The method is applied to the analysis of polychlorobromo dibenzo-p-dioxins (PXDD), polychlorobromo dibenzofurans (PXDF) and interfering halogenated organic compounds in GC-MS analysis.

INTRODUCTION

The number of possible isomers poses a major problem in the analysis of polychlorinated-p-dibenzodioxins (PCDD) and -furans (PCDF). There are 135 different PCDFs and 75 PCDDs. However, if brominated compounds are included, numbers rise to 1701 individual polychlorobromo-p-dibenzodioxins (PXDDs) and 3321 polychlorobromo-p-dibenzofurans (PXDF) (see tables 1 and 2). This corresponds to 570 (for dioxins and furans) different ion masses for the isotopic clusters around the parent ions. Consideration of the M-COCl$^+$ or M-COBr$^+$ ions leads to another 408 ion masses. The same number of different ion masses arises for the respective ^{13}C labelled compounds which are commonly used as internal standards. From these ion masses one has to choose appropriate masses for selected ion monitoring in GC-MS analysis - alternatively, they can be used for identification purposes. To master this immense amount of calculations, algorithms have been devised and implemented in a PASCAL program called IONBASE to give a listing of all possible masses and their expected relative abundance. Furthermore, the number of possible isomers to be expected for each congener is of interest, although not all isomers theoretically postulated necessarily occur in actual samples. The calculation can give an upper limit for the number of peaks detected in an ion trace.

With IONBASE a database of ion masses, isotopic abundances and number of isomers is generated. The database can be expanded to include compound classes which might interfere in the analysis of PXDD, PXDF. Ion masses common to a PXDD or PXDF and an interfering compound can easily be detected by sorting the database by masses and looking for identical or close masses.

DIOXINS									
Total no. of isomers: 1901									
Br / Cl	0	1	2	3	4	5	6	7	8
0	2	2	10	14	22	14	10	2	1
1	2	14	42	70	70	42	14	2	
2	10	42	114	140	114	42	10		
3	14	70	140	140	70	14			
4	22	70	114	70	22				
5	14	42	42	14					
6	10	14	10						
7	2	2							
8	1								
Sum	76	256	472	448	98	312	34	4	1

Table 1: Number of PXDD congeners and isomers for 0 to 8 chlorine resp. bromine atoms

FURANS									
Total no. of isomers: 3321									
Br / Cl	0	1	2	3	4	5	6	7	8
0	1	4	16	28	38	28	16	4	1
1	4	28	84	140	140	84	28	4	
2	16	84	216	280	216	84	16		
3	28	140	280	280	140	28			
4	38	140	216	140	38				
5	28	84	84	28					
6	16	28	16						
7	4	4							
8	1								
Sum	136	512	912	896	572	224	60	8	1

Table 2: Number of PXDF congeners and isomers for 0 to 8 chlorine resp. bromine atoms.

METHODS

The program IONBASE was written in TURBO PASCAL ([1]), a pascal version for personal computers. TURBO PASCAL itself uses 1 to 2 MByte of hard disk space, whereas for running the programs presented about 200 kByte are needed. The output may again use up to 500 kByte.

The number of possible isomers is determined by the following procedure:

1. Represent each individual isomer as a number in the tridecimal system (because of 3 possible substitutions: H, Cl, Br) with the number of digit's equal to the number of substitution positions, i.e. 8 for dioxins and furans. The tridecimal number is stored as an array indexed from 0 to 7 representing positions 1,2,3,4,6,7,8 and 9 of the dioxin/furan molecule.
2. Eliminate symmetric isomers by performing appropriate symmetry operations with all possible tridecimal numbers and discarding mirror images (figure 1).

By redefining the symmetry operations and adjusting the length of the tridecimal number IONBASE can easily be applied to a different compound class.

The abundance of ions in the isotopic cluster is calculated as follows: For an ion containing only one species of "A+2" elements, in the cases of interest i.e. either n bromines or n chlorines, there will be a cluster of ions with n+1 peaks (here labelled 0 through n). The relative abundance of all peaks i (with i running from 0 to n, i corresponding to i in the expression "M+(2*i) ion") in that cluster is given by an expression derived from the binomial expansion ([2]). For a compound containing n chlorines and m bromines the probabilities of encountering a particular number of "heavy" isotopes in an ion have to be combined.

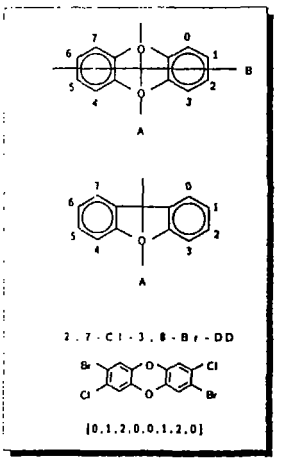

Figure 1. Axes of symmetry and numbering of substitution positions as used within the program IONBASE for dibenzo-p-dioxin (top) and dibenzo-p-furan (middle). At the bottom the structure of 2,7-dichloro-3,8-dibromo-dibenzo-p-dioxin is given to illustrate the encoding of the substitution pattern.

Name	Ion.	Miso	MW	acc	abu	rk	C	C*	H	O	Cl	Br
Cl3 Br2 Dioxin	M+ 0	140	441.757	r	31	4	12	0	3	2	1	2
Cl3 Br2 Dioxin	M+ 2	140	443.754	r	92	2	12	0	3	2	1	2
Cl3 Br2 Dioxin	M+ 4	140	445.751	r	100	1	12	0	3	2	1	2
Cl3 Br2 Dioxin	M+ 6	140	447.748	r	50	3	12	0	3	2	1	2
Cl1 Br2 Dioxin	M+ 8	140	449.745	r	12	5	12	0	3	2	1	2
Cl3 Br2 Dioxin	M+10	140	451.742	r	1	6	12	0	3	2	1	2
Cl4 Br2 Dioxin	M+ 0	114	475.718	r	24	4	12	0	2	2	4	2
Cl4 Br2 Dioxin	M+ 2	114	477.715	r	78	2	12	0	2	2	4	2
Cl4 Br2 Dioxin	M+ 4	114	479.712	r	100	1	12	0	2	2	4	2
Cl4 Br2 Dioxin	M+ 6	114	481.709	r	63	3	12	0	2	2	4	2
Cl4 Br2 Dioxin	M+ 8	114	483.706	r	31	5	12	0	2	2	4	2
Cl4 Br2 Dioxin	M+10	114	485.703	r	4	6	12	0	2	2	4	2
Cl4 Br2 Dioxin	M+12	114	487.700	r	0	7	12	0	2	2	4	2

Table 3: "Raw" output of the program IONBASE without any specific selection of ions. This is the output for Cl_3Br_2 dibenzo-p-dioxin and for Cl_4Br_2-dibenzo-p-dioxin. Abbreviations are explained in the text, *C stands for ^{13}C

RESULTS AND DISCUSSION

An example of "raw output" from IONBASE is given in table 3. It contains the compound- and ion-name, type of the ion ("M+..."), number of possible isomers, ion mass (for electron impact ionization), an accuracy parameter, the relative abundance of the ion within its cluster, its abundance rank within the cluster, and the atomic composition.

The database output which is an ASCII textfile can be retrieved into spreadsheet programs (e.g. Lotus-1-2-3,

Quattro). In the spreadsheet, one can sort by ion abundance rank, to get the most abundant ions only, sort by number of oxygens to separate dioxins and furans, etc. By sorting the ions according to mass one can easily detect interferences.

Other compound classes can be included in the database, e.g. polyhalogenated-biphenyls (PXBs), polyhalogenated biphenylenes (PXBEs), polyhalogenated-biphenylethers, polyhalogenated-naphtalenes (PXNs), polyhalogenated-biphenylenes (PXBenes) and polyhalogenated-diphenylketones (PXDPKs). With these included the potential for finding interferences because of overlapping ion masses is even greater. One can also get a list of all the isomers, or of a subset of interest, e.g. all penta-XDD substituted in positions 2,3,7 and 8.

CONCLUSIONS

The pascal program IONBASE is a powerful tool for assisting in the analysis of polyhalogenated compounds by GC-MS, especially by SIM. Besides eliminating the need for manual calculation of ion masses, comparison of different compounds is readily feasible, interfering ions of known compound classes can be found, and the number of isomers for a particular compound is indicated. Furthermore, all isomers of interest can be obtained in a listing.

REFERENCES

1. TURBO PASCAL, Version 5.5, Borland International, 1800 Green Hills Road, Scotts Valley, CA 95066-0001, USA

2. McLafferty F.W.: *Interpretation of Mass Spectra*. Mill Valley, CA: University Science Books. 3rd ed., 1980