Chemosphere No. 5, pp 231 - 236, 1977. Pergamon Press. Printed in Great Britain.

ANALYSIS OF POLYCHLORINATED DIBENZOFURANS IN YUSHO OIL USING HIGH RESOLUTION GAS CHROMATOGRAPHY - MASS SPECTROMETRY

Christoffer Rappe and Anders Garå
Department of Organic Chemistry, University of Umeå
S - 901 87 Umeå, Sweden

and

Hans Rudolf Buser and Hans-Paul Bosshardt
Swiss Federal Research Station
CH - 8820 Wädenswil, Switzerland

(Received in UK 7 April 1977; accepted for publication 15 April 1977)

Introduction

Polychlorinated biphenyls (PCBs) are industrial chemicals now known to be widely distributed in the environment. The commercial products are complex mixtures of at least 80 different substances. The toxic effect and the bioaccumulation of the discrete PCB-isomers vary remarkably.[1,2]

In 1970 Vos et al. identified polychlorinated dibenzofurans (PCDFs) as toxic impurities in European PCBs at the ppm level,[3] and the same has also been reported for American and Japanese PCBs.[4,5] Using packed-column GC/MS, Bowes et al. found that the most abundant PCDFs had the same retention time as 2,3,7,8-tetra-CDF and 2,3,4,7,8-penta-CDF.[5]

In 1968 more than 1200 persons in South-West Japan were intoxicated by consuming a commercial rice oil contaminated with 1000 ppm of a Japanese PCB (Kanechlor).[6] Nagayama et al. analyzed the rice oil (Yusho oil) and found 5 ppm of PCDFs. Consequently, the PCDF concentration in the Yusho oil was about 250 times higher than in ordinary Kanechlor

preparations. Nagayama et al. also found tetra- and penta-CDFs to be most abundant, but they also found small amounts of the tri- and hexachloro isomers.[6] Recently, Bowes et al. have reported that they found three isomers of both the tetra-CDF and penta-CDF, the dominating tetra-CDF had the same retention time on a packed column as 2,3,7,8-tetra-CDF.[7]

The toxic effects of the PCDFs are very similar to those reported for the polychlorinated dibenzodioxins (PCDDs), in both cases the 2,3,7,8-tetrachloro compound being the most toxic isomer.[1,2,8] Like PCDDs, both PCDFs and certain PCB isomers have been found to increase cytochrome P-450 activity and a number of drug metabolizing enzymes.[2,9]

In this paper, we report on the analysis of "Yusho oil C" using glass capillary column GC in combination with different mass spectrometric techniques.

Experimental

The clean-up of the Yusho oil (1.5g) was performed essentially as described before including alkaline saponification and chromatography on silica gel.[6] Final chromatography was carried out on an alumina-microcolumn using 10 ml portions of 2% and 50% methylene chloride in n-hexane.[10] The PCDF fraction was carefully evaporated and the residue redissolved in 100 µl of n-tetradecane. Similarily, a solution of synthetic 2,3,7,8-tetra-CDF was prepared in n-tetradecane at a concentration of about 1 ng/µl. Aliquots of 2 µl of sample were analyzed on OV-101 and OV-17 glass capillary columns (22 m x 0.36 mm ID) using an isothermal splitless injection technique as previously described.[11] The columns were coupled via a fused platinum capillary, leading directly into the ion-source of a Finnigan 1015 D GC-MS (election impact source at 70 eV). The columns were operated at 197°C (OV-101) and 207°C (OV-17) with a helium carrier gas pressure of 0.6 - 0.8 atm. A vaporizer temperature of 270°C was used, the interface was at 250°C.

Mass specific detection (mass fragmentography) of PCDFs was carried out by monitoring molecular ions at m/e 270 (tri-CDF), m/e 304 (tetra-CDF), m/e 338 (penta-CDF) and m/e 372 (hexa-CDF). At a further stage complete EI mass spectra were recorded using a Finnigan 4000 GC-MS equipped with a 6111 data system.

Figure 1 : Mass fragmentograms (OV-101 glass capillary columns at 197°C) of Yusho oil showing elution of PCDFs (m/e 270 = tri-, m/e 304 = tetra-, m/e 338 = penta- and m/e 372 = hexa-CDF).

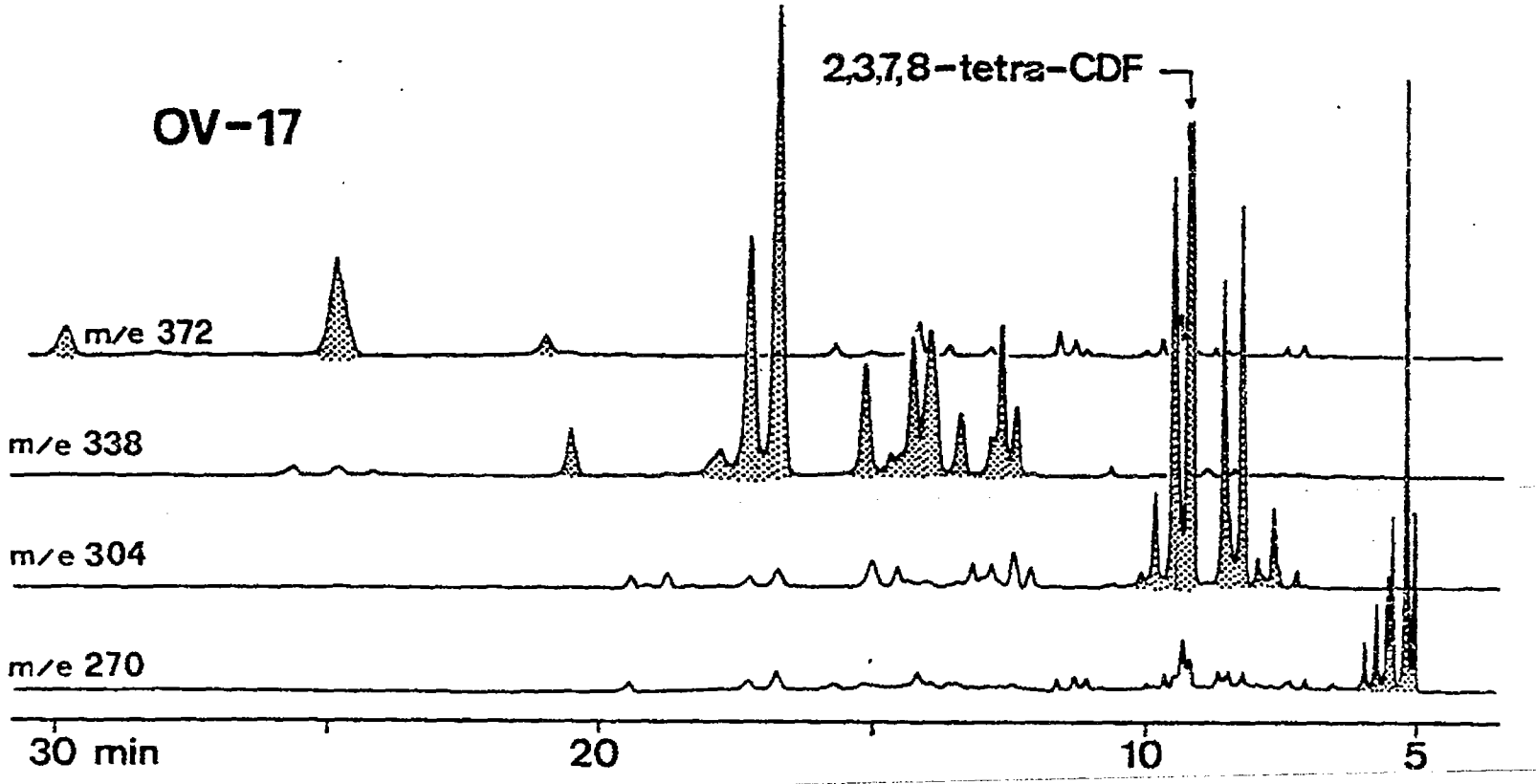

Figure 2 : Mass fragmentograms (OV-17 glass capillary column at 207°C) of Yusho oil showing elution of PCDFs (m/e 270 = tri-, m/e 304 = tetra-, m/e 338 = penta- and m/e 372 = hexa-CDF).

Results and Discussion

The mass fragmentograms using OV-101 and OV-17 columns are given in Fig. 1 and 2. The OV-101 is a non-polar column with a good grouping effect according to the number of chlorine atoms. The OV-17 is a semi-polar column, with more spreading of the positional isomers. Consequently, OV-17 appears to be better for an optimal separation of the isomeric PCDFs.

Fig. 1 and 2 also allow us to make an estimation of the number of tri-, tetra-, penta- and hexa-CDFs present in the Yusho oil (suspected isomers, Table 1). In the case of the most abundant isomers, the discrete PCDFs could be identified by running complete EI mass spectra. All the spectra were in agreement with published data, expected ion clustering and major fragmentation (M^+-COCl, M^+-COCl-Cl_2).

Table I

Number of PCDFs in Yusho Oil

	Cl_3	Cl_4	Cl_5	Cl_6
Suspected isomers	6	6	9	3
Identified isomers [a]	2	4	4	1

a) Identified by complete MS, no positional assignment.

Identical retention times were found for the major tetra-CDF peak and an authentic sample of the 2,3,7,8-tetra-CDF (501 sec on OV-101 and 557 sec on OV-17). By simple comparison of peak heights the estimate was made that 2,3,7,8-tetra-CDF amounts to at most 30% of the total tetra-CDFs.

Our investigation using high resolution GC strongly supports the assumption that 2,3,7,8-tetra-CDF is one of the main PCDFs in Yusho oil, an assumption so far only based on separations using packed columns. Optimal separation using high resolution gas chromatography is required when it is important to separate between a large number of positional isomers.

Acknowledgments

The authors are indebted to Dr. Yoshito Masuda, Fukuoka, Japan for the generous gift of the Yusho oil and to Dr. J.D. McKinney, Research Triangle Park, USA for the 2,3,7,8-tetra -CDF sample.

References

1. J.D. McKinney, K. Chae, B.N. Gupta, J.A. Moore and J.R. Goldstein, Toxicol. Appl. Pharmacol., 36, 65 (1976).
2. J.A. Goldstein, J.D. McKinney, G.W. Lucier, P. Hickman, H. Bergman and J.A. Moore, Toxicol. Appl. Pharmacol., 36, 81 (1976).
3. J.G. Vos, J.H. Koeman, H.L. van der Maas, M.C. ten Noever de Brauw and R.H. de Vos, Fd. Cosmet. Toxicol., 8, 625 (1970).
4. J.A.G. Roach and I.H. Pomerantz, Bull. Environ. Contam. Toxicol., 12, 338 (1974).
5. G.W. Bowes, M.J. Mulvihill, B.R.T. Simoneit, A.L. Burlingame and R.W. Risebrough, Nature, 256, 305 (1975).
6. J. Nagayama, M. Kuratsune, Y. Masuda, Bull. Environ. Contam. Toxicol., 15, 9 (1976).
7. G.W. Bowes, M.J. Mulvihill, B.R.T. Simoneit, A.L. Burlingame and R.W. Risebrough, Paper presented at Workshop on TCDD, Milan, Italy. Oct. 23-24 (1976).
8. E.E. McConnell, J.A. Moore, J.K. Haseman and M.W. Harris, Toxicol. Appl. Pharmacol., 37, 146 (1976).
9. A. Poland and E. Glover, Mol. Pharmacol., 9, 736 (1973).
10. H.R. Buser, J. Chromatogr., 107, 295 (1975).
11. H.R. Buser, Anal. Chem., 46, 1553 (1976).