

Confirmation of the DB-5MS column and the use in routine dioxin analysis

Ludwig Gruber, Helmut Santl*, Janet Seidl

Fraunhofer-Institute for Food Technology and Packaging, Schragenhofstr. 35, 80992 Munich, Germany

*present address: GfU - Gesellschaft für Umweltchemie, Schwanthalerstraße 32, 80336 Munich, Germany

Abstract

The newly offered DB-5MS column shows a different elution profile and better separation for some 2,3,7,8-substituted congeners than a conventional DB-5 phase. It also allows the determination of all PCDD/Fs within one analysis run. For the routine analysis of pulp, paper and sewage sludge samples the DB-5MS column has been successfully used for the last 1½ year. The only major problem for the analysis of fly ash and deposition samples are coelutions with the 2,3,4,7,8-PeCDF.

1. Introduction

In Germany generally polychlorinated Dibenzo-para-dioxins (PCDD) and polychlorinated Dibenzofurans (PCDF) are determined on two capillary columns of different polarity. For the 2,3,7,8-substituted PCDD/F's very polar columns are used (e.g. Supelco SP-2331). On these columns all 2,3,7,8-substituted dioxins and furans will be completely baseline separated except 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF. Only a partial separation is given on the 2,3,7,8-TCDF^{3,4}). The disadvantages of the SP-2331 column are very high column bleeding and poor temperature stability. Usually a short unpolar column is used for the OCDD/F identification and the group screening. For this use the DB-5 is a common column, which is easy to handle and has the advantages of higher temperature stability, less column bleeding, time separation of the homologue groups and higher sensitivity especially for higher chlorinated dioxins and furans.

Since two years the DB5-MS is offered as an improved form of the DB-5 phase. According to the manufacturer there should be no difference between these two columns. However the DB-5MS shows a different elution profile and better separation for some 2,3,7,8-substituted congeners.

ANA/BIOA

2. Experimental

A GC-column J&W DB-5MS with 60 m x 0.25 mm and 0.25 µm film thickness was used for the experiments. Standard solutions (table 1), fly ash and sewage sludge samples were analyzed to evaluate further non-2,3,7,8 substituted dioxins and furans not identified in the literature ²⁾. The results were compared with analyses on conventional DB-5 and SP-2331 columns.

GC/MS-conditions (for DB-5MS)

GC: Shimadzu GC-17A with split/splitless injector
injection volume: 2 µl splitless, splitless time: 1 min
Oven temp.: 160°C, 2 min, 20°C/min to 200°C
2°C/min to 280°C, 5°C/min to 300°C, 20 min
Carrier gas: helium with a head pressure of 180 kPa
Injector temp.: 280°C
Interface temp.: 290°C
MS: Shimadzu QP-5000, electron impact ionisation (EI) with 70 eV
Mode: Single Ion Monitoring (SIM)

Table 1: List of commercially available standards used for this investigation

PCDFs		PCDDs	
1,3,4,9-TCDF	1,3,4,6,8-PeCDF	1,2,3,9-TCDD	1,2,3,8,9-PeCDD
2,3,4,6,-TCDF	1,2,3,8,9-PeCDF	1,2,7,8-TCDD	1,2,3,4,7-PeCDD
1,2,6,7-TCDF	1,2,3,7,8-PeCDF	1,2,3,7/8-TCDD pair	1,2,3,4,7,8-HxCDD
1,2,7,9-TCDF	2,3,4,7,8-PeCDF	2,3,7,8-TCDD	1,2,3,6,7,8-HxCDD
2,3,4,7-TCDF	1,2,3,4,6,8-HxCDF	1,3,6,8-TCDD	1,2,3,7,8,9-HxCDD
1,3,6,8-TCDF	1,2,3,4,8,9-HxCDF	1,2,8,9-TCDD	1,2,4,6,7,9-HxCDD
1,2,8,9-TCDF	1,2,3,4,7,8-HxCDF	1,2,3,7,8-PeCDD	1,2,4,6,8,9-HxCDD
2,3,7,8-TCDF	1,2,3,6,7,8-HxCDF	1,2,4,6,8-PeCDD	1,2,3,4,6,7-HxCDD
1,2,3,4,8-PeCDF	1,2,3,7,8,9-HxCDF	1,2,4,7,9-PeCDD	

3. Results

On a DB-5 there are coeluting peaks at the retention time of the 2,3,7,8-TCDF. The 2,3,7,8-TCDF is coeluting with the 2,3,4,6-, 2,3,4,7-, 2,3,4,8-, 1,2,4,9- and 1,2,7,9-TCDF. ⁴⁾ Using the DB-5MS the 2,3,4,6-, 2,3,4,7- and 1,2,7,9-TCDF are baseline separated. The 2,3,4,8-TCDF is only separated with a 30% valley (see fig. 1). The 1,3,4,9- and 1,2,6,7-TCDF are eluting earlier and well-resolved from the 2378-TCDF on all three column types. The 1,2,4,9-TCDF was not commercially available for testing. In general almost all TCDF's are totally separated from the 2,3,7,8-TCDF on the DB-5MS phase. The separation efficiency for the TCDFs is similar to high polar column phases e.g. the SP-2331. On this phase the 2,3,4,8-TCDF is only partially separated from the 2,3,7,8-TCDF and it shows a rapid decrease of the resolution efficiency during use ⁴⁾.

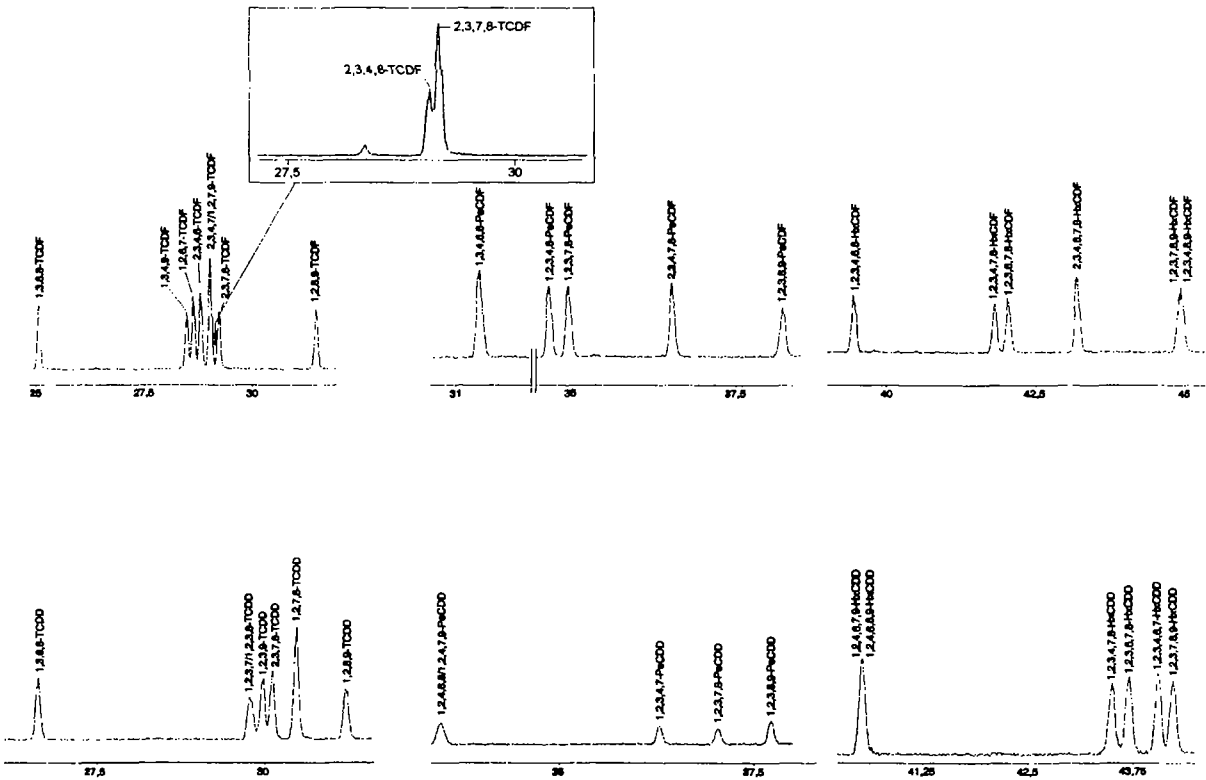


Fig. 1: Mass traces of tetra- to hexachlorinated PCDD/F standard mixture

ANA/BIOA

The DB-5MS provide a baseline separation of the 1,2,3,7,8-PeCDF, whereas the DB-5 phase showed a resolution of 80% from the 1,2,3,4,8-PeCDF. The SP-2331 has the disadvantage of a complete coelution of the 1,2,3,7,8- with the 1,2,3,4,8-PeCDF. The great disadvantage for the unpolar DB-5 phase is the coelution of the 2,3,4,7,8- with the 1,2,3,6,9-PeCDF and the interference of 1,2,6,7,9- and 1,2,4,8,9-PeCDF which are only minimally separated. This leads to incorrect high results for the 2,3,4,7,8- PeCDF especially for fly ash samples on a DB-5 column. Comparison runs of fly ash samples showed a better separation efficiency on the DB5-MS. At least one of these three non-2,3,7,8 isomers is totally resolved from 2,3,4,7,8-PeCDF. It could not be verified if there is a second isomer separated, because none of these substances were commercially available at this moment. Due to the TEF of 0.5 coelutions with the 2,3,4,7,8-PeCDF are the mayor disadvantage of the DB-5MS phase. In this matter it is noticeable that in opposite to the DB-5 column the 2,3,4,6,7-PeCDF eluates before the 2,3,4,7,8-PeCDF. I-TEq calculations of a certified fly ash sample showed differences between runs on a DB-5MS and a SP-2331 of about 10%. This was caused mainly by the 2,3,4,7,8-PeCDF values (see table 2). A complete separation is only possible on the polar SP-2331 phase. Own experiments and round robins showed that these interferences of the pentafuranes are only of minor importance in case of pulp & paper samples and sewage sludge samples.

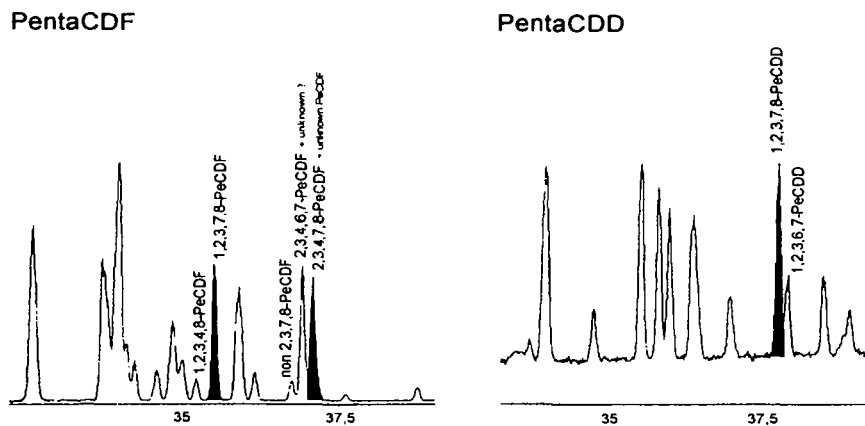


Fig. 2: PeCDF and PeCDD mass traces of a fly ash sample 1)

Table 2: Results (in ng/g) of a certified fly ash sample analyzed on a DB-5MS column and a SP-2331 column ¹⁾.

	DB5-MS column	SP-2331 column
2378-TCDF	1,61	1,58
2378-TCDD	0,21	0,18
12378-PeCDF	2,63	3,20
23478-PeCDF	2,84	2,29
12378-PeCDD	0,56	0,64
123478-HxCDF	1,79	2,14
123678-HxCDF	2,07	2,13
234678-HxCDF	1,45	0,96
123789-HxCDF	0,36	0,16
123478-HxCDD	0,22	0,26
123678-HxCDD	0,37	0,41
123789-HxCDD	0,34	0,47
I-Teq	2,93	2,68
BGA-Teq	2,48	2,44

On the DB-5 phase the 1,2,3,4,7,8-HxCDF coelutes with the 1,2,3,4,6,7-HxCDF. On the SP-2331 phase the 1,2,3,4,7,8-HxCDF could not be resolved from the 1,2,3,4,7,9-HxCDF, whereas on the DB-5MS there is a complete separation (fig. 1). For the 1,2,3,6,7,8-HxCDF on all three columns no interferences with other isomers occur. The 1,2,3,7,8,9-HxCDF is only partially separated (50%) from the 1,2,3,4,8,9-HxCDF on the DB-5 phase. On the DB-5MS phase these two isomers are completely interfered, this fact has been reported by Fraisse et al ²⁾, too.

The 2,3,7,8-TCDD is not completely separated from 1,2,3,7/8-TCDD pair on the DB-5 phase. These isomers are in use for the DB-5 as the Column Performance Mixture. On a 60m DB-5 column the height of a valley between 2,3,7,8- and 1,2,3,4-TCDD must not exceed 25% ⁵⁾. On the DB-5MS phase there is a complete separation for the 2,3,7,8-TCDD from 1,2,3,4- and 1,2,3,7/8-TCDD (fig. 1). An important change in the elution order could be observed on the DB-5MS. The 1,2,3,9-TCDD elutes between the 2,3,7,8- and the 1,2,3,7/8-TCDD pair with a 25% valley. Therefore this isomer would be the better choice for a Column Performance Mixture for the DB-5MS phase. On a new SP-2331 column the 2,3,7,8-TCDD is baseline separated, but during use the column performance decrease rapidly and after 20 to 50 runs one isomer of the 1,2,3,7/8-TCDD pair superposes. Ryan et al. ⁴⁾ identified this isomer as the 1,2,3,7-TCDD.

The 1,2,3,7,8-PeCDD is well resolved from other congeners on both column types, the DB-5 and the SP-2331. On the DB-5MS phase the 1,2,3,6,7-PeCDD eluates close to the 1,2,3,7,8-PeCDD with a 50%-valley (see fig. 2). All three 2,3,7,8-substituted HxCDDs are baseline separated on the DB-5MS and the SP-2331 phase, respectively. Remarkable is the change of the elution

ANA/BIOA

order, the 1,2,3,4,6,7-HxCDD elutes before the 1,2,3,7,8,9-HxCDD (see fig. 1) on the DB-5MS phase. Whereas on the usual DB-5 phase both isomers coelute.

4. Conclusions

For the routine analysis of paper, paper board and sewage sludge samples the DB-5MS has been successfully used for the last 1½ years. According to our experience, it can be concluded that the DB-5MS and the SP-2331 show comparable results. Both columns show coelutions, but none of them are of major importance for these kind of samples. The DB-5MS has the advantage of low bleed and a higher temperature stability. Moreover there is a time separation of the homologue groups, except for 1,2,8,9-TCDF which elutes after the 1,2,4,6,8/1,3,4,6,8-PeCDF pair (also reported by Fraisse et al. ²⁾). This allows the determination of all PCDD/Fs within one analysis run. The only major problem of the DB-5MS for the analysis of fly ash and deposition samples are coelutions with the 2,3,4,7,8-PeCDF.

Nevertheless for a complete separation of all seventeen 2,3,7,8-substituted PCDD/Fs from the non 2,3,7,8-substituted congeners it is necessary to run two separate analyses on a SP-2331 column and a DB-5MS column.

5. References

- 1) Quost, A., Möglichkeiten und Grenzen des Einsatzes eines niederauflösenden Quadrupolmassenspektrometers in der Dioxinanalytik im Vergleich mit einem hochauflösenden Massenspektrometer, Diploma thesis at Fachhochschule München, Fachbereich Physikalische Technik, April 1995
- 2) Fraisse, D., et al., Improvements in GC/MS strategies and methodologies for PCDD and PCDF analysis, Fresenius Journal of Analytical Chemistry, 1994, p. 155 - 158
- 3) Ballschmitter, K., et al., The Determination of Chlorinated Biphenyls, Chlorinated Dibenzodioxins, and Chlorinated Dibenzofurans by GC-MS, Journal of High Resolution Chromatography, Vol. 15, April 1992, p. 260 -270
- 4) Ryan, J. et al., Gas chromatographic separations of all 136 tetra- to octa-polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans on nine different stationary phases, Journal of Chromatography, 541 (1991), p. 131 -183
- 5) US-EPA, Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution, Revision A, April 1990