GC-MS Analysis of PCDD /F on two capillary columns of different polarity in the same GC-MS system.

Werner Tirler, Massimo Donegà

Eco-Center, via Lungo Isarco, 57 - 39100 Bolzano – Italy

Introduction:
Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) are two classes of environmental contaminants. Seventeen congeners are substituted in the 2,3,7,8 position and are considered to be the most toxic.
Due to the large number (210) of compounds of the PCDD/F family, gas chromatographic separation from the cluster of less toxic isomers [1] is a difficult task. At present no commercial available single column can separate all 2,3,7,8 substituted congeners from the rest of the PCDD/F.
Generally analysis is performed using at least two capillary gas chromatographic columns [2,3] of different polarity.
Non polar columns can separate chlorine homologous groups and all toxic congeners from each other but not from all non-toxic congeners. Thus, a polar column has to be used in addition [4,5] for specific separation.

Materials and Methods:
Analyte solution: Emission sample from municipal waste incineration spiked with ^{13}C labeled 2,3,7,8 substituted standards.
Gas chromatography: Hewlett Packard 6890 equipped with a PTV and On Column injector; fused silica capillary column Hewlett Packard HP 5ms and DB Dioxin from J&W Scientific, both 60 m length, 0,25 mm id., 0,25 µm film.
Mass spectrometry: MSD 5973 from Hewlett Packard.

Dual column applications are commonly used in pesticide analysis for resolution and verification improvements (Figures 1.)

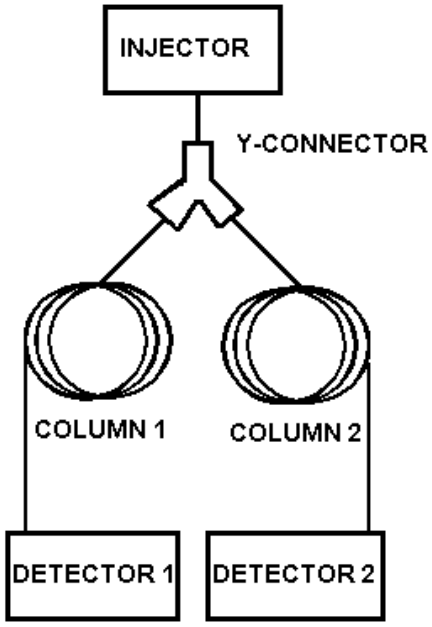

Figure 1. Column assembly used in pesticide analysis.

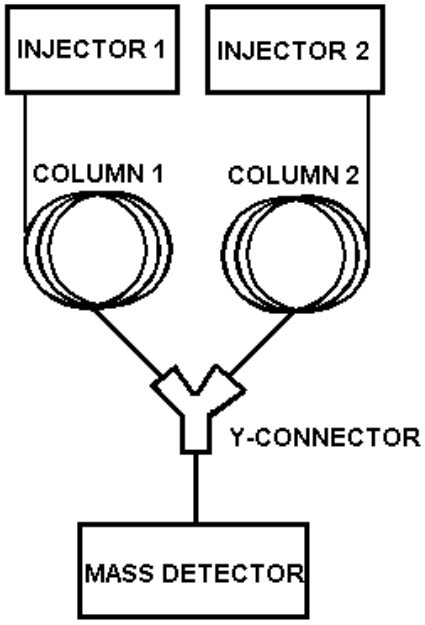

Figure 2. The configuration was adapted for GC-MS analysis as shown

For the present dioxin analysis application two injectors, each one connected to a GC-column of different polarity, were integrated into one GC-system. The outlets of the GC-columns were connected by a Y-connector and a short piece of deactivated fused silica was used as transfer line to connect the Y to the mass spectrometer (Figure 2).
Column union made by Y-connectors are like all Press Fit unions very simple, but need to be treated in a skillful way. The union must be properly tight. Due to the vacuum which is necessary for mass spectrometry, leaks must be avoided because they necessary introduce air in the system. This would reduce instrument sensitivity and also damage the instrumentation.
To perform a GC-run with the non-polar column one has to reduce the flow through the polar column to a minimum; e.g. 0,1 ml/min. The flow through the non-polar column has to set to normal values; e.g. 1 ml/min and the sample will be introduced by the injector connected to the non-polar column.
To perform the analysis with the polar column one has to proceed just the other way around. By using the instrument software these steps are simply programmable and changing between the two configurations is easily done.
For the non-polar column a HP-5ms was used and DB-Dioxin for the polar one.

Results and discussion:

Table 1:

CONGENER	I-TEF	ng TEQ	ng TEQ	ng TEQ
		Hp-5ms	DB-Dioxin	Mix HP-5ms –DB-Dioxin
2378 TCDD	1	0.043	<0.05	0.043
12378 PCDD	0.5	0.063	0.057	0.060
123478 HxCDD	0.1	0.018	**0.028**	0.018
123678 HxCDD	0.1	0.035	0.033	0.034
123789 HxCDD	0.1	0.025	0.022	0.024
1234678 HpCDD	0.01	0.020	0.019	0.019
OCDD	0.001	0.003	0.003	0.003
2378 TCDF	0.1	**0.088**	0.018	0.018
12378 PCDF	0.05	0.013	0.015	0.014
23478 PCDF	0.5	0.275	0.234	0.254
123478 HxCDF	0.1	**0.144**	0.057	0.057
123678 HxCDF	0.1	0.065	0.079	0.072
234678 HxCDF	0.1	0.087	0.086	0.086
123789 HxCDF	0.1	0.008	0.009	0.008
1234678 HpCDF	0.01	0.021	0.023	0.022
1234789 HpCDF	0.01	0.005	0.006	0.005
OCDF	0.001	0.002	0.002	0.002
SUMM		0.914	0.691	0.741

In Table 1 the results obtained by the use of a polar column (DB-Dioxin) and a non polar one (HP-5ms) are reported. Neither the polar nor the non-polar column are able to separate all 2,3,7,8 congeners from interfering coeluting isomers. By comparing the results one can see that the congeners are insufficiently resolved by using one column only. For example 2,3,7,8 TCDF is not resolved on the HP 5ms column and by using only this column you will find some overestimated value for this compound. But also the DB-Dioxin column alone has separation problems, we find that 1,2,3,4,7,8 HxCDD has some coeluting isomer. By working with at least two columns of different polarity and eliminating the interference data, the results will not be overestimated.
Using two GC-columns in one GC-MS system by connecting them by Y-connectors is a simple way to analyze samples on stationary phases of different polarity. Time consuming procedures like ventilation, change of the columns, conditioning the columns, evacuation and recalibration of the system can be avoided.

References:

1. Ryan JJ., Conacher HBS., Panopio LG., Lau PYB., Hardy JA., Masuda Y; *J. Chromatography*, **1991**, 541, 131.
3. Thanner G. and Moche W., *Monographien Umweltbundesamt*, **1994**, Bd. 50, Vienna (Austria).
2. European Committee for Standardization, EN 1948, **1996**, Brussels (Belgium).
4. Fraisse D., Paisse O., Nguyen L. and Gonnord MF; *Fresenius. J. Anal. Chem*. **1994**, 348, 154.
5. de Jong APJM., Liem AKD. and Hoogerbrugge R*; J. of Chromatography*, **1993**, 643, 91.