# ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS USING SIMULTANEOUS DUAL GAS CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY

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## Introduction:

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) are two classes of environmental contaminants. Seventeen congeners exist that are substituted in the 2,3,7,8 position and are considered to be the most toxic[1,2]. Due to the large number (210) of compounds of the PCDD/F family, gas chromatographic (GC) separation of these from the cluster of less toxic isomers is a difficult task[3]. At present no commercially available column can separate all 2,3,7,8 substituted congeners from the remaining PCDD/F. The co elution of less toxic with toxic congeners can cause false TEQ related results, because mass spectrometry cannot differentiate between toxic and non toxic congeners within the same homologous group.

To overcome this, the analysis is performed using at least two capillary GC columns[4,] 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 should be used in addition for specific separation. Exchange of a GC column on a HRGC-HRMS system is usually a time consuming procedure.

Significant time saving can be achieved using a mass spectrometer coupled to two GCs[5,6], that allows switching between two different GC columns, without disturbing the measurement conditions of the mass spectrometer.

The aim of the present work was to develop a method that permits to work simultaneously with both GCs in order to further improve time savings.

**Materials and Methods:**

The instrumentation used for the study was a Finnigan MAT 95 XL (Thermo Electron Corp.) coupled to two 6890 series gas chromatographs (Agilent Corp.) with PTV injectors. In order to improve chromatographic resolution and analysis speed, hydrogen was used as carrier gas.
A Schmidlin NMH hydrogen generator was used to provide the carrier gas.
A software modification of the standard analysis procedure was done to permit to the two gas chromatographs to perform two injections simultaneously.
Temperature gradient on the apolar column in GC oven #1 was set to get in a short time a high temperature in order to achieve fast elution of all PCDD/F congeners, whereas the temperature program for GC oven #2 for the polar column was more moderate. This permits to have elution of the first eluting congeners (tetra) on the polar column after the elution of last eluting compounds (octa) on the apolar column. The multiple ion detection mode (MID) was used to perform tetra trough octa homologous acquisition on apolar column and subsequently tetra trough octa acquisition for the polar column.
Conditions GC 1:
Apolar column: Agilent DB-5ms, 60 m, 0.25 mm ID, 0.1 µm film
Oven temperature: 80°C (2 min.), 40°C/min to 220 °C, 4°C/min. to 260°C, 30°C to 320°C (2min.)
Injector: PTV in solvent vent mode, carrier: Hydrogen 2mL/min., transfer line: 260°C.
Conditions GC2:
Polar column: Restek RTX-2330, 60 m, 0.25 mm ID, 0.1 µm film
Oven temperature: 80°C (2 min.), 25°C/min to 190 °C, (5 min.), 2.5°C/min. to 240°C, 10°C to 260°C (8min.).
Injector: PTV in solvent vent mode, carrier: Hydrogen 2mL/min., transfer line: 260°C.
Mass spectrometer:
High resolution multiple ion detection (MID) operating in electron impact (EI) mode at 40 eV.
Ten MID groups are used to monitor PCDD/F (tetra-octa and tetra-octa).
Diluted calibration standards for US-EPA method 1613 were injected.

**Results:**

In Fig. 1 is reported a single chromatogram with elution of all PCDD/F congeners from apolar column in the first part and elution of all PCDD/F congeners from polar column in the second part of the chromatogram. In this way eventually non resolved chromatographic peaks on a apolar column in the first part of the chromatogram can be resolved in the second part of the chromatogram on a polar, more isomer separation specific column.
By using two columns of different polarity in two GC ovens its possible to optimize independently the temperature gradients, without limiting the less polar column to the lower maximum temperature usually applicable for polar column.

Fig. 1: Total ion current chromatogram using simultaneously a apolar and a polar CG column

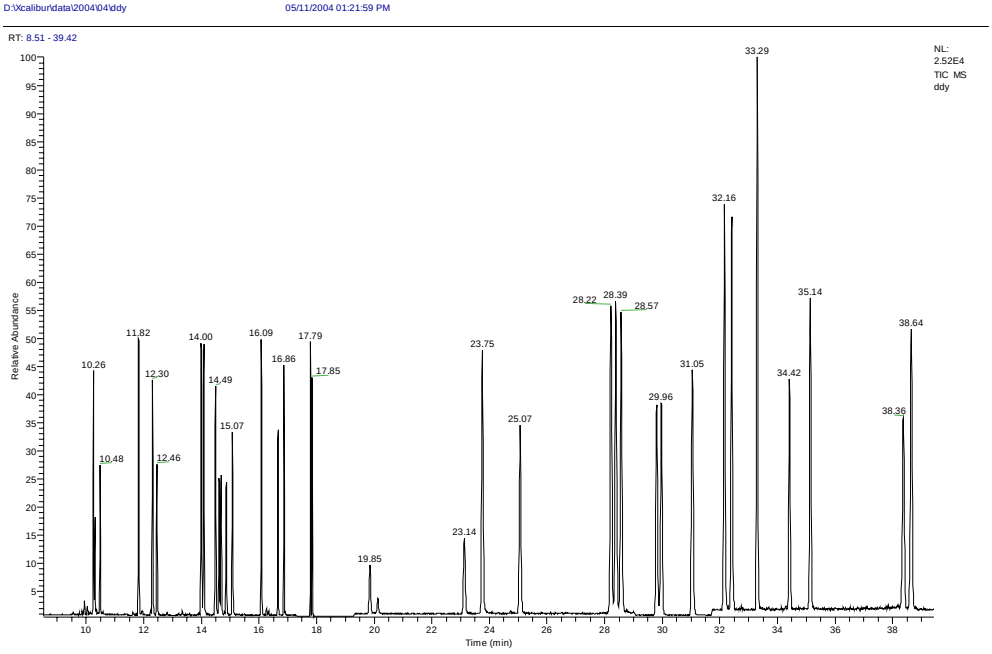


Table 1: Assignment of the chromatographic peaks

| Congener | Retention Time (min.) | |
|---|---|---|
| | DB 5ms | RTX 2330 |
| 1,2,3,4-TCDD ($^{13}C_{12}$) | 10.31 | 20.13 |
| 2,3,7,8-TCDD | 10.48 | 19:85 |
| 1,2,3,7,8-PeCDD | 12.46 | 25.07 |
| 1,2,3,4,7,8-HxCDD | 14.62 | 29.81 |
| 1,2,3,6,7,8-HxCDD | 14.69 | 29.96 |
| 1,2,3,7,8,9-HxCDD | 14.87 | 31.05 |
| 1,2,3,4,6,7,8-HpCDD | 16.66 | 34.42 |
| 1,2,3,4,6,7,8,9-OCDD | 17.79 | 38.64 |
| 2,3,7,8-TCDF | 10.26 | 23.14 |
| 1,2,3,7,8-PeCDF | 11.82 | 23.75 |
| 2,3,4,7,8-PeCDF | 12.30 | 28.57 |
| 1,2,3,4,7,8-HxCDF | 14.00 | 28.22 |
| 1,2,3,6,7,8-HxCDF | 14.09 | 28.39 |
| 1,2,3,7,8,9-HxCDF | 15.07 | 32.16 |
| 2,3,4,6,7,8-HxCDF | 14.49 | 33.29 |
| 1,2,3,4,6,7,8-HpCDF | 16.09 | 32.41 |
| 1,2,3,4,7,8,9-HpCDF | 16.86 | 35.14 |
| 1,2,3,4,6,7,8,9-OCDF | 17.85 | 38.36 |

Fig. 2: First part of the chromatogram related to separation on the apolar DB-5ms

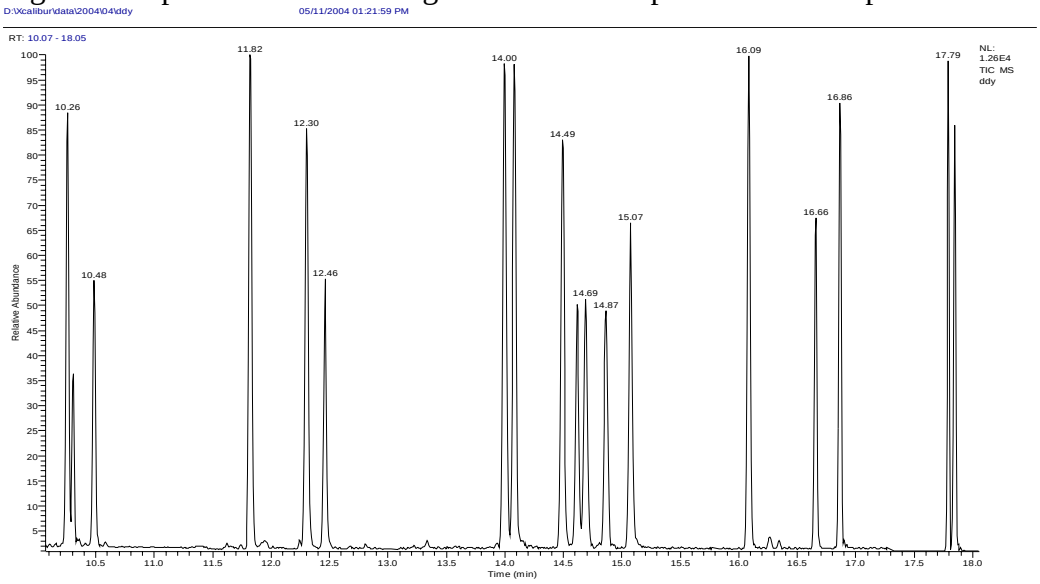
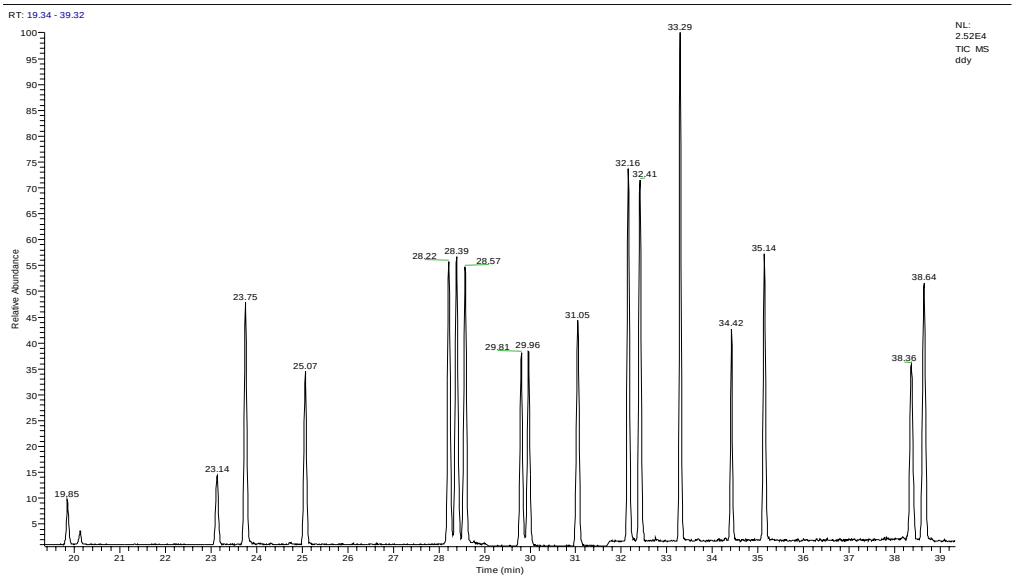



Fig. 3: Second part of the chromatogram related to separation on the polar RTX-2330



**Conclusions:**

With simultaneous injection of samples on two GCs equipped with columns of different polarity coupled to one high resolution mass spectrometer, a single chromatogram showing the separation of PCDD/F congeners on two different stationary phases can be obtained. With this simple and robust system it is possible to perform toxic isomer specific PCDD/F analysis together with homologous groups determination in less than 40 minutes.

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