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A Novel CGC-CGC-MS Configuration for the Analysis of Polychlorodibenzodioxins and Polychlorodibenzofurans

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Summary

The analysis of polychlorodibenzodioxins and polychlorodibenzofurans on a novel multidimensional (CGC-CGC-MS) configuration is presented. The system is based on flow controlled column switching, allowing the simultaneous isomeric separation of tetrachloro-, pentachloro- and hexachloro-substituted dibenzodioxins and dibenzofurans on a polar column and the analysis of heptachloro- and octachloro-substituted dibenzodioxins and dibenzofurans on an apolar column. PTV injection in the solvent vent mode allows analysis of large sample sizes approaching in this way the sensitivity of CGC – high resolution MS.

Introduction

The analysis of polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) is a typical example of environmental trace analysis whereby both the selectivity of the separation and the sensitivity of detection have to be fully optimized in order to meet the specifications of official methods and directives.

PCDDs and PCDFs normally occur in complex matrices together with other chlorinated material. Although complex clean-up procedures are used, involving column chromatography or HPLC fractionation, interferences cannot be completely avoided and the specificity of mass spectrometric detection is required. In order to obtain the lowest detection limits, multiple ion detection mode is used (MID, SIM). Typically 3 to 4

ions per congener group (degree of chlorination) are selected. This is a compromise between sufficient selectivity (in combination with retention time data) and sufficient sensitivity. In this way, compounds can be detected at low pg level (typically 5–20 pg) using benchtop MS systems such as MSD or ITD.

Higher sensitivity can be obtained with CGC – high resolution MS. This combination, however, is very expensive, needs highly skilled operators and source cleaning often has to be carried out to maintain high sensitivity. For routine and contract laboratories this approach therefore is unremunerative. In this investigation, temperature programmed vaporization injection in the solvent vent mode, allowing large volume injections, was applied as an alternative to the high sensitivity of high resolution MS.

Due to the different toxicity of different PCDD and PCDF congeners, it is, however, also necessary to separate the different congeners. Especially the selective separation of the seven “2, 3, 7, 8” PCDDs and the ten “2, 3, 7, 8” PCDFs is here important. Correct column selection is therefore required. On an apolar column type (OV-1, SE-54, ...), a good separation according to the degree of chlorination is achieved together with sufficient separation for the heptachloro- and octachlorodibenzodioxins and dibenzofurans. The congeners of the complex groups of tetrachloro-, pentachloro- and hexachloro-dibenzodioxins and dibenzofurans, are insufficiently resolved and the “2, 3, 7, 8” congeners are coeluting with other congeners. This is illustrated in Figure 1, showing the total ion chromatogram of fly ash extract (upper chromatogram) and the ion chromatogram for tetrachlorodibenzofurans (m/e 306) and pentachlorodibenzofurans (m/e 340) (lower chromatogram).

A congener specific separation within these groups can be achieved on a polar cyanopropyl silicone column (type SP 2330, SP 2331) or on a smectic column (SB smectic). The separation of the fly ash extract on a cyanopropyl silicone column is shown in Figure 2. Congeners with difference in Cl-substitution degree are now overlapping. The upper trace shows the total ion chromatogram and the lower trace the ion chromatogram.

Dedicated to Professor Leslie S. Ettre on the occasion of his 70th birthday.

Figure 1
CGC-MS of fly ash extract on an apolar capillary column.
A. Total ion chromatogram.
B. Ion chromatograms for 4-Cl- and 5-Cl-furans.

Figure 2
CGC-MS of fly ash extract on a polar capillary column.
A. Total ion chromatogram.
B. Ion chromatograms for 4-Cl- and 5-Cl-furans.

Figure 3

PTV-CGC-CGC-MS configuration for the analysis of dioxins and furans.

1 = CIS injector, 2 = GC 1-apolar column, 3 = Switching device, 4 = Cold trap, 5 = GC 2-apolar and polar column, 6 = Dual column MS inlet, 7 = MSD, 8 = PC controlling switching device, 9 = PC controlling MSD. TL1: transfer line 1; TL2: transfer line 2. (M: monitor detector, S: Split).

Following analytical conditions are used:

Column A: 25 m x 250 μ m i.d. x 0.25 μ m SE-54

Column B: 60 m x 250 μ m i.d. x 0.2 μ m SP-2331

Column C: 10 m x 100 μ m i.d. x 0.2 μ m SE-54

Oven 1: 50 $^{\circ}$ C, 1 min iso, 20 $^{\circ}$ C/min, 320 $^{\circ}$ C hold

Oven 2: 50 $^{\circ}$ C, 18 min hold, 25 $^{\circ}$ C/min, 200 $^{\circ}$ C, 2 $^{\circ}$ C/min, 270 $^{\circ}$ C hold

Injection: PTV in solvent vent mode; 10 μ l injection
60 $^{\circ}$ C, 60 s hold (during injection), 12 $^{\circ}$ C/s,
320 $^{\circ}$ C, 180 s.

Cold trap: -50 $^{\circ}$ C, 17 min hold, 12 $^{\circ}$ C/s, 300 $^{\circ}$ C hold

Heart-cut: 0-14.5 min to column B,
14.50-16.0 min to column C.

MSD: SIM

Inlet pressure: 2.4 bar Helium

Mid pressure: 124 kPa Helium

grams for tetrachlorodibenzofurans (m/e 306) and pentachlorodibenzofurans (m/e 340). From the ion chromatogram the excellent separation of the different congeners is clear. On these columns, however, the retention times for the heptachloro- and octachloro-congeners are very high which also results in decreased detectability and moreover losses due to adsorption are noted for the heptachloro- and octachloro-congeners [1].

A chromatographic system is described, whereby, the tetrachloro-, pentachloro- and hexachloro-congeners are separated on a polar isomer specific column and the heptachloro- and octachloro-congeners are separated on an apolar column. This can be achieved in a single run using multidimensional CGC, whereby the tetrachloro-, pentachloro- and hexachloro-compounds are switched to the polar column and the heptachloro- and octachloro-compounds to the apolar column.

The described configuration is different from conventional multidimensional CGC whereby a pre-separation is achieved on a first column and a narrow fraction (heart-cut), containing the compound(s) of interest, is transferred to a second column for complete separation of co-eluting compounds [2]. In this multidimensional set-up, the eluent-stream from the pre-column is monitored by a detector to elucidate the heart-cut window.

Multidimensional separations of PCDDs and PCDFs were first described by Schomburg et al. [3]. Pre-separation was achieved on a polar column using an FID or ECD as monitor detector. Important fractions are heart-cut to an apolar column connected to a second ECD.

Figure 4

Illustration of detectability reached with CIS injection in the solvent venting mode.

This paper describes a novel multidimensional configuration using three capillary columns and one MSD for the simultaneous congener specific separations of PCDDs and PCDFs. The system is equipped with PTV injection to increase on sensitivity by large volume injection in the solvent vent mode.

Experimental

The PTV-CGC-CGC-MS configuration is illustrated in Figure 3. The system consists of two HP 5890 Series II gas chromatographs and one HP 5971 MSD. Injection is

made on a programmable cold injection system with a septumless head (CIS, Gerstel).

On the first column (25 m x 250 μ m i.d., 0.25 μ m df SE-54), a fast group separation is made. This separation is necessary to separate the tetrachloro-, pentachloro- and hexachloro-congeners from the heptachloro- and octachloro-congeners. Using a flow controlled column switching device (MCS, Gerstel), the first group (tetrachloro-, pentachloro- and hexachloro-) is transferred to a second column (60 m x 250 μ m i.d., 0.2 μ m df SP-2331) via transfer line 1. The transferred compounds are trapped in transfer line 1 using a cold trap. The second group (heptachloro- and octachloro-) are transferred to

Figure 5
Simultaneous recorded ion chromatograms for the dioxins.

Figure 6
Snapshot of 6-Cl dioxins with separation of the 2, 3, 7, 8-congeners.

a third column (10 m x 100 μ m i.d., 0.2 μ m df SE-54) via transfer line 2. This fraction is reconcentrated before the column in transfer line 2 using the same cold trap. After selective transfer of the two fractions, the cold trap is heated and both fractions are injected on their specific column. Both columns are connected to the same MSD.

The switching time between the two groups (group 1: tetrachloro-, pentachloro- and hexachloro-; group 2: heptachloro- and octachloro-), is determined by the characteristics of the first column (column A). The column is off-line tested before installation using a PCDD/PCDF test mixture. The profile shown in Figure 1A illustrates that the difference in retention times between hexachloro- and heptachloro-congeners is ± 2 minutes, making correct time-controlled switching easy. In principle, if only fine tuning of tetrachloro-, pentachloro- and hexachloro-congeners is of interest, the effluent from the pre-column can be monitored by installing a split line in transfer line 1 which is connected to a monitor detector (see option S to M in Figure 3). This configuration was not evaluated in this study as there was no need for.

Results and Discussion

The described multidimensional system offers a number of interesting possibilities for the analysis of PCDDs and PCDFs. First of all, using PTV injection with solvent venting, large volumes of sample can be injected. This is illustrated in Figure 4. In routine operation the MSD sensitivity is approximately 5 pg for tetrachlorodibenzofuran. Concentrations down to 400 fg/ μ l can be

detected if 25 μ l are injected. This example illustrates the sensitivity of the configuration.

In practical analysis, samples are normally concentrated under a nitrogen flow and redissolved in 50 to 100 μ l solvent. Lower solvent amounts leads to errors by incomplete wettability of the walls of the glass vessels. A 1 μ l injection out of a 50 μ l sample only represents a 2 % use of the sample whereas with PTV injection in the solvent vent mode 50 % of the sample is analyzed.

The most important advantage is however the simultaneous mass spectroscopic detection of all congeners whereby tetrachloro-, pentachloro- and hexachloro-congeners are separated on a polar column and heptachloro- and octachloro-congeners are separated on an apolar column. This is illustrated in Figure 5. The left trace shows the ion chromatograms for the tetrachloro- (m/e 322), pentachloro- (m/e 356) and hexachloro- (m/e 390) dioxins obtained from the polar column.

The right trace shows the ion chromatograms for the heptachloro- (m/e 424) and octachloro- (m/e 460) dioxins obtained on the apolar column.

Figure 6 shows a detailed picture of the hexachloro-dioxins congeners separated on the polar column. The toxic "2, 3, 7, 8-"congeners are marked with an asteriks, and are identified according to Ballschmiter [4].

In the same way, other dibenzodioxins and dibenzofurans can be detailed. By cryofocusing between the two CGC systems no resolution loss has been observed.

Since all tetrachloro-, pentachloro- and hexachloro-congeners are analyzed on two columns of different polarity, there is also less change of interference with other compounds (increase of selectivity).

Conclusion

A multidimensional system using flow switching between an apolar precolumn and two analytical columns (apolar and polar) allows the optimized analysis of all PCDDs and PCDFs in a single run. Using PTV injection and solvent venting high sensitivity is obtained.

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