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Multivariate data analysis to characterize gas chromatography columns for dioxin analysis

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ABSTRACT

Principal component analysis (PCA) was applied for evaluating the selectivity of 22 GC columns for which complete retention data were available for the 136 tetra- to octa-chlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). Because the hepta- and octa-homologues are easy to separate the PCA was focused on the 128 tetra- to hexa-CDD/Fs. The analysis showed that 21 of the 22 GC columns could be subdivided into four groups with different selectivity. Group I consists of columns with non-polar thermally stable phases (Restek 5Sil MS and Dioxin 2, SGE BPX-DXN, Supelco Equity-5, and Agilent DB-1, DB-5, DB-5ms, VF-5ms, VF-Xms and DB-XLB). Group II includes ionic liquid columns (Supelco SLB-IL61, SLB-IL111 and SLB-IL76) with very high polarity. Group III includes columns with high-percentage phenyl and cyanopropyl phases (Agilent DB-17 and DB-225, Quadrex CPS-1, Supelco SP-2331, and Agilent CP-Sil 88), and Group IV columns with shape selectivity (Dionex SB-Smectic and Restek LC-50, Supelco βDEXcst, Agilent VF-Xms and DB-XLB). Thus, two columns appeared in both Group I and IV (Agilent VF-Xms and DB-XLB). The selectivity of the other column, Agilent DB-210, differs from those of these four groups. Partial least squares (PLS) regression was used to correlate the retention times of the tetra- to hexa-CDD/Fs on the 22 stationary phases with a set of physicochemical and structural descriptors to identify parameters that significantly influence the solute-stationary phase interactions. The most influential physicochemical parameters for the interaction were associated with molecular size (as reflects in the total energy, electron energy, core–core repulsion and standard entropy), solubility (aqueous solubility and *n*-octanol/water partition coefficient), charge distribution (molecular polarizability and dipolar moment), and reactivity (relative Gibbs free energy); and the most influential structural descriptors were related to these parameters, in particular, size and dipolar moment. Finally, the PCA and PLS analyses were complemented with linear regression analysis to identify the most orthogonal column combinations, which could be used in comprehensive two-dimensional gas chromatography (GC × GC) to enhance PCDD/F separation and congener profiling.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) comprise 210 congeners, of which 136 contain 4–8 chlorine atoms. Among the 136 congeners, seventeen 2,3,7,8-substituted PCDD/Fs have been shown to be the most toxic in animal tests [1,2]. Due to the large number of isomers, their chromatographic separation is challenging. There have been a number of attempts to produce a GC column capable of resolving at least all the 2,3,7,8-substituted PCDD/Fs in a single run. Restek Rtx-Dioxin2 [3–5], SGE BPX-DXN [6], Agilent VF-Xms [7], and Restek Rxi-5Silms [8] have been developed to reduce the number of coelutions that occur when using traditional 5% phenyl-methyl (DB5-type) phases. However, no column has been developed that can separate all the 17 2,3,7,8-PCDD/Fs. Therefore, two injections on columns with different selectivity are required: one usually on a non-polar column, and the other on a polar column, often containing a phase with cyanopropyl groups (DB-225, SP-2330, SP-2331) [9–12].

However, in many cases it is necessary to characterize as many PCDD/Fs as possible, e.g. to identify a contamination source, source tracking, or explore PCDD/F formation or degradation mechanisms. In pioneering work, Ryan et al. [13] synthesized all 136 tetra- to octa-chlorinated DD/Fs and injected them on nine different GC columns, including non-polar, moderately polar, polar and liquid

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Table 1
22 GC columns used in the study and their temperature programs.

Column	Source	Phase	Column size (m × mm × μm)	Program	Ref
DB-XLB	Agilent	Non-polar, proprietary	60 × 0.18 × 0.18	160 °C (1 min), 35 °C/min to 230 °C (15 min), 10 °C/min to 260 °C (25 min), 10 °C/min to 310 °C (14 min)	[14]
LC-50	Restek	Dimethyl [50% liquid crystal]	20 × 0.25 × 0.10	120 °C (2 min), 30 °C/min to 190 °C, 3 °C/min to 260 °C (12 min)	[14]
βDEX_{cst}	Restek	Chiral, propriatory CD[a]	30 × 0.25 × 0.25	120 °C (2 min), 30 °C/min to 223 °C, 1 °C/min to 240 °C (58 min)	[14]
SLB-IL61	Supelco	Polar, ionic liquid	30 × 0.25 × 0.20	120 °C (2 min), 30 °C/min to 150 °C (10 min), 5 °C/min to 190 °C (15 min), 5 °C/min to 280 °C (5 min)	[14]
SLB-IL76	Supelco	Polar, ionic liquid	30 × 0.25 × 0.20	120 °C (2 min), 30 °C/min to 150 °C (10 min), 5 °C/min to 190 °C (15 min), 5 °C/min to 260 °C (5 min)	[14]
SLB-IL111	Supelco	Polar, ionic liquid	100 × 0.25 × 0.20	120 °C (2 min), 30 °C/min to 190 °C (30 min), 5 °C/min to 240 °C (15 min), 5 °C/min to 260 °C (20 min)	[14]
DB-1	Agilent	Non-polar, 100% dimethyl	60 × 0.32 × 0.25	120 °C (1 min), 50 °C/min to 180 °C, 3 °C/min to 280 °C	[13]
VF-Xms	Agilent	Non-polar, proprietary	60 × 0.25 × 0.25	160 °C (1 min), 35 °C/min to 230 °C (15 min), 10 °C/min to 250 °C (25 min), 10 °C/min to 310 °C (6 min)	[7]
VF-5ms	Agilent	Non-polar, 5% phenyl	60 × 0.25 × 0.25	160 °C (1 min), 27.5 °C/min to 215 °C (18 min), 5 °C/min to 225 °C (8 min), 5 °C/min to 310 °C (6 min)	[7]
DB-5ms	Agilent	Non-polar, 5% phenyl	60 × 0.25 × 0.25	160 °C (1.5 min), 30 °C/min to 220 °C (25 min), 5 °C/min to 240 °C (7 min), 5 °C/min to 310 °C (9 min)	[7]
DB-5	Agilent	Non-polar, 5% phenyl	30 × 0.32 × 0.25	120 °C (1 min), 50 °C/min to 180 °C, 3 °C/min to 280 °C	[13]
Rxi-5Silms	Restek	Non-polar, 5% phenyl	60 × 0.18 × 0.10	120 °C (1 min), 10 °C/min to 160 °C, 2.5 °C/min to 300 °C	[8]
Dioxin2	Restek	Non-polar, proprietary	40 × 0.18 × 0.18	120 °C (1 min), 10 °C/min to 160 °C, 4 °C/min to 320 °C (4 min)	[4]
BPX-DXN	SGE	Non-polar, proprietary	60 × 0.25	30 °C (1 min), 15 °C/min to 210 °C, 3 °C/min to 310 °C, 5 °C/min to 320 °C (hold)	[6]
Equity-5	Supelco	Non-polar, 5% phenyl	60 × 0.25 × 0.25	200 °C (2 min), 5 °C/min to 220 °C (16 min), 5 °C/min to 235 °C (7 min), 5 °C/min to 310 °C (10 min)	[7,18,19]
DB-17	Agilent	Semi-polar, 50% phenyl	30 × 0.32 × 0.25	120 °C (1 min), 20 °C/min to 160 °C, 3 °C/min to 280 °C	[13]
DB-210	Agilent	Polar, 50% trifluoropropyl	30 × 0.32 × 0.25	120 °C (0 min), 20 °C/min to 160 °C, 2 °C/min to 240 °C	[13]
DB-225	Agilent	Polar, 50% cyanopropyl, 50% phenyl	30 × 0.32 × 0.25	120 °C (0 min), 20 °C/min to 160 °C, 2 °C/min to 240 °C	[13]
CPS-1	Discont.[b]	Polar, 75% cyanopropyl, 25% phenyl	50 × 0.25 × 0.25	120 °C (1 min), 30 °C/min to 180 °C, 2 °C/min to 230 °C	[13]
SP-2331	Supelco	Polar, 90% cyanopropyl, 10% phenyl	60 × 0.25 × 0.20	120 °C (1 min), 50 °C/min to 200 °C, 2 °C/min to 260 °C	[13]
CP-Sil 88	Agilent	Polar, 100% cyanopropyl	50 × 0.22 × 0.20	150 °C (0 min), 30 °C/min to 180 °C, 2 °C/min to 230 °C	[13]
Smectic	Discont.	Ester [80% liquid crystal]	25 × 0.32 × 0.15	100 °C (1 min), 30 °C/min to 180 °C, 3 °C/min to 230 °C	[13]

[a] Cyclodextrin added to 14% cyanopropylphenyl/86% dimethyl polysiloxane.
[b] Production discontinued.

crystal columns. In addition, we recently investigated the selectivity of three ionic liquid stationary phases, two shape-selective phases and a non-polar, low-bleed phase, aiming to identify a column or column combination capable of separating all 136 tetra- to octa-CDD/Fs [14]. We found that two of the ionic liquid columns (Supelco SLB-IL61 and SLB-IL111) resolved or partially separated 106 and 100 congeners, respectively, of the 136 PCDD/Fs; considerably more than any of previously evaluated commercially available columns. However, more than 30 congeners were still unresolved. We concluded that (near) complete profiling of all 136 PCDD/Fs can only be achieved using two to three columns and combining the acquired data. However, this would be a tedious task.

It is therefore important to minimize the number of injections and columns used while still separating most of the 136 dioxins by performing comprehensive two-dimensional gas chromatography (GC × GC). In GC × GC two columns with different separation mechanisms are connected to enhance the peak capacity. A few studies have explored the capabilities of GC × GC for analyzing dioxins in food/feed samples, and all 2,3,7,8-PCDD/Fs have been successfully separated using a DB-XLB × LC-50 column set [15–17]. However, the cited studies provided no information on the separation of the other tetra- to octa-CDD/Fs.

The aim of this study was therefore to investigate the selectivity of all GC columns (22, listed in Table 1) for which there have been reported complete chromatographic data for the 136 tetra- to octa-CDD/Fs and to establish structure-retention relationships that can be used to properly select the stationary phases for the first and second dimension columns in GC × GC to ensure a high degree of chromatographic orthogonality, and a detailed PCDD/F profiling. Principal component analysis (PCA) was used to evaluate the selectivity and solute-stationary phase interactions of the 22 GC phases. Partial Least Squares (PLS) regression was then applied to explore correlations between the solute-stationary phase interactions and selected physicochemical and structural descriptors of the dioxins, and linear regression analysis was used to describe the orthogonality of GC × GC column combinations. Finally, the results of the multivariate and linear regression analyses were used as a basis for recommending suitable column combinations for separating the 136 PCDD/F congeners.

2. Experimental

2.1. Retention time data

Absolute retention times of 136 PCDD/F congeners on 22 stationary phases were compiled from the scientific literature [4,6–8,13,14,18,19]. Jack Cochran (Restek Company, USA) provided additional retention time data on the Rxi-5Sil MS column. The retention times were converted to minutes if not originally reported in absolute time units. The 22 columns are further described in Table 1.

2.2. Physicochemical property data

Twenty-one physicochemical variables and 37 structural descriptors (Table 2) were collected from published data [20–27] or created for this study. The data is available from the authors upon request. The physicochemical variables include: 8 energy descriptors, 4 charge descriptors, 3 thermodynamic descriptors, *n*-octanol/water partition coefficient (log P), aqueous solubility (−log S), dipole moment (Dm), mean molecular polarizability (*Mp*), molecular volume (Mv), and the affinity to the Ah-(dioxin) receptor. The variables were selected to represent energies, charge distributions and possibilities for intermolecular interaction. The structural descriptors were included as a complement to provide an independent description of the chlorine substitution patterns, which