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Comparison of Series 5 gas chromatography column performances from a variety of manufacturers for separation of chlorinated dibenzo-*p*-dioxins and dibenzofurans using high-resolution mass spectrometry

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Abstract

An extended study of seven fused silica capillary gas chromatographic (GC) columns has been conducted with regard to separation of international toxic equivalent factor (I-TEF) isomers (tetra- through octa-chlorinated at 2,3,7,8 positions) of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) from closely co-eluted other isomers using high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS). The data are explicated in mass chromatograms of Series 5 GC columns from a variety of manufacturers (Varian CP-Sil 8 CB LowBleed/MS, Phenomenex ZB-5UMS, Agilent HP-5MS, Restek Rtx-5MS, Supelco Equity-5, J&W Scientific DB-5 and DB-5MS), according to relative retention times, and 2,3,7,8-substituted isomer concentrations for each of the columns tested. Results showed differences between 5% phenyl methyl silicone and 5% silphenylene (Si-arylene) silicone polymer type GC stationary phases in separation of 2,3,7,8-substituted PCDDs/PCDFs from closely co-eluted isomers. The separation differences for Si-arylene type columns resulted in lower toxic equivalence (TEQ) values compared to the siloxane-based columns. Because of differences in product nomenclature and manufacturing practices by various manufacturers, incorrect assumptions and comparisons may be made regarding the interchangeability of these columns for PCCD/PCDF separations. The data presented are the most comprehensive to date and provide a valuable addition to operational criteria for the standard US Environmental Protection Agency methods 1613b and 8290.

Keywords: Gas chromatography; High-resolution mass spectrometry; Dioxins; Furans; Toxic equivalent concentration

1. Introduction

The term “dioxins” commonly refers to two classes of organic compounds: polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). PCDDs and PCDFs are classified as persistent organic pollutants making them of particular concern to the international community [1]. There are some natural phenomena that produce PCDDs and PCDFs, such as forest fires [2], however these events are considered to be minor contributors in industrialized countries. Dioxins may be formed as an unintentional by-product of some industrial processes and other human activities, such as waste combustion, medical incinerators, tire and wood combustion, power generating facilities, combustion by gasoline and diesel powered vehicles, etc. [3].

Up to eight chlorine atoms can be placed on the basic structure, giving rise to 75 dioxin and 135 furan congeners. Out of these 210 compounds, only 49 PCDDs and 87 PCDFs contain four to eight chlorines and their generic chemical structures and acronyms are shown in detail in Table 1. In this smaller group of 136 compounds, there are 17 congeners with chlorines in the 2,3,7,8-positions that are considered to be of toxicological significance and their relative potencies are estimated by the toxic equivalent factor (TEF) [4]. The most toxic compound is considered to be 2,3,7,8-TCDD. Although the body of toxicity data available for 2,3,7,8-TCDD is greater than for other congeners, there are data available to

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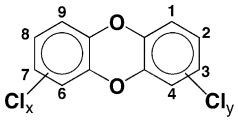
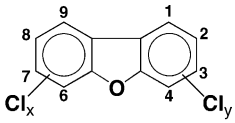
Table 1
Number of isomers of the PCDDs and PCDFs



PCDD



PCDF

Chlorines ($x+y$)	Acronyms	PCDD No. of isomers	PCDF No. of isomers
4	TCDD/TCDF	22	38
5	PnCDD/PnCDF	14	28
6	HxCDD/HxCDF	10	16
7	HpCDD/HpCDF	2	4
8	OCDD/OCDF	1	1
4–8	Total	49	87

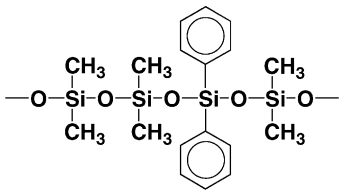
be able to estimate the relative toxicities based upon a number of criteria [4]. Table 2 lists the relative toxicities of the 17 dioxin and furans in terms of one of the accepted system of toxic equivalences (TEQs) that was proposed by the North Atlantic Treaty Organization (NATO) Committee on Challenges to Modern Society, also known as the international toxic equivalent factor (I-TEF) system [4]. The toxic equivalence of each compound (TEQ_i) is calculated by multiplying the concentration of the congener (C_i) by its I-TEF_i. The sum of the 17 individual TEQs gives a Total TEQ value (Eq. (1)) which is equivalent to the toxicity of all 17 toxic dioxins and furans in the sample, if all were present as 2,3,7,8-TCDD.

$$\text{TEQ} = \sum_i C_i \times \text{I-TEF}_i \quad (1)$$

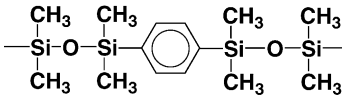
In order to establish the "true" TEQ value, accurate determination of isomer-specific concentrations of all 17 2,3,7,8-substituted dioxins and furans is required. The current US Environmental Protection Agency (EPA) methods for PCDDs and PCDFs have been developed mainly based on J&W DB-5 GC column performance [5–7]. However, this column cannot separate all 17 2,3,7,8-substituted dioxins and furans from their other closely co-eluting isomers [5–7]. To separate unresolved I-TEF isomers, particularly 2,3,7,8-TCDF,

Table 2
I-TEFs for 2,3,7,8-substituted dioxins and furans

Congener	I-TEF	Congener	I-TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PnCDD	0.5	1,2,3,7,8-PnCDF	0.05
		2,3,4,7,8-PnCDF	0.5
1,2,3,4,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	2,3,4,6,7,8-HxCDF	0.1
		1,2,3,7,8,9-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
OCDD	0.001	OCDF	0.001



DB-5



DB-5MS

Fig. 1. Polymer structures of 5% phenyl methyl silicone (DB-5) and 5% phenyl silphenylene silicone-based (DB-5MS) GC columns. Both columns consider being Series 5 GC columns with the same polarity.

the EPA methods suggest using one of a variety of different GC phases such as J&W DB-225, Supelco SP-2330, and SP-2331 as a complimentary tool. The EPA methods, however, give little guidance for the higher chlorinated 2,3,7,8-substituted dioxins and furans, especially the penta- and hexa-isomers where interferences are also present [8–11]. Depending on the sample matrix, the majority of the Total TEQ value may come from the higher chlorinated PCDDs and PCDFs. There have been published papers demonstrating the performance of other GC column stationary phases on PCDDs and PCDFs separation [8–15], however, there is little information showing the difference in separation of various Series 5 (5% phenyl-methyl silicone and 5% silphenylene silicone polymer based) GC columns which are currently on the market.

"Series 5" nomenclature of the GC columns normally classified stationary phases based on their polarity rather than selectivity. At least two polymer phase structures are commonly known for Series 5 GC columns as shown in Fig. 1 [16]. "Conventional" type GC columns such as J&W Scientific DB-5 have the siloxane backbone with phenyl group attached to the side chains. Supelco Equity-5, Restek Rtx-5MS, and Agilent HP-5MS are also typical "conventional" columns, *vide infra*. Rtx-5 and Rtx-5MS are virtually identical columns at the beginning of the production process. Columns which will give a lower bleed during the quality assurance test at the manufacturing site are labeled as "MS" [17]. As a "non-conventional" type of GC column; J&W Scientific DB-5MS has a phenyl ring in the polymer backbone intending to stiffen the polymer chain to reduce the amount of "back biting" and hence improve stability and lifetime [16]. Sometimes these "non-conventional" types of GC columns are referred to as silphenylene silicone or Si-arylene polymer based. Phenomenex ZB-5UMS is an R&D project at this time and recently NEW ZB-5MS (not tested in this study) has been introduced on the market. While both products employ engineered self cross-linking bonding they are not considered to be the same due to the difference in polymer phase structures [18]. We have no information about polymer phase of Varian CP-Sil 8 CB LowBleed/MS GC column, however,

we believe that both Varian and Phenomenex have either Si-arylene base or could use some different type of non-phenyl polymer chain stabilizer because there are more similarities in PCDDs/PCDFs isomer specific separation of DB-5MS, CP-Sil 8 CB LowBleed/MS, and ZB-5UMS columns compared to "conventional" type, see below. For purposes of this paper, we will define these three columns as a "non-conventional" or Si-arylene type.

In this study, the seven previously mentioned GC columns have been evaluated for separation of the 17 I-TEF isomers from closely co-eluting isomers. Furthermore, the Total TEQ values have been calculated for a variety samples from different matrices that have been analyzed on each of the columns.

2. Experimental

2.1. Standard preparation and sample description

The window standard was prepared by mixing Cambridge Isotope Labs. (CIL) (Andover, MA, USA) ED-1732-B and EF-1731-B window defining mixtures that contain the first and last eluting isomers for each of the tetra- through hepta-congener groups on DB-5 type GC column. In addition, native OCDD and OCDF were added to the above mixture in similar concentrations. An I-TEF calibration standard containing 15 different isomers and their ^{13}C-labeled isotopes (2,3,7,8-TCDD; 1,2,3,7,8-PnCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,6,7,8-HpCDD; OCDD; 2,3,7,8-TCDF; 1,2,3,7,8-PnCDF; 2,3,4,7,8-PnCDF; 1,2,3,4,7,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; and OCDF) was prepared "in house". The ^{13}C-labeled isotopes of two of the isomers, 1,2,3,6,7,8-HxCDD and 1,2,3,6,7,8-HxCDF, were not added in order to confirm their elution order with respect to 1,2,3,4,7,8-HxCDD and 1,2,3,4,7,8-HxCDF. All "real world" samples, except Sample No. 5, were collected and analyzed at The Dow Chemical Company. The samples represent a variety of matrices including: stack gas emissions, water, and soil. Stack samples were taken using a Dow proprietary method shown to be similar to EPA Method 23A [19]. Sample No. 5 was used as a column performance standard containing a combination of the CIL EDF-4147 PCDD/PCDF window defining and isomer specificity mix (DB-5), and all 17 I-TEFs calibration compounds. All sample weights were normalized to 1 g sample size.

2.2. Extraction and automated cleanup processes

Water samples were passed through Whatman GF/C (1.2 μm pore size) filter paper using a Buchner funnel and an Erlenmeyer flask. The filtered solids were spiked with 20 μL of 15 different 2,3,7,8-substituted ^{13}C-labeled PCDD/PCDF isomers containing 2 ng of TCDD/TCDF, 0.8 ng of PnCDD/PnCDF, 0.8 ng of HxCDD/HxCDF, 0.8 ng of HpCDD/HpCDF, 2 ng of OCDD/OCDF (2, 0.8, 0.8, 0.8, 2 ng) spiking standard and processed using a Sohxlet-Dean-Starks (SDS) [5] extraction with 250 mL of benzene for 18 h. The filtrate was liquid–liquid extracted by stirring for 18 h with 40 mL of 20% (v/v) benzene in hexane. The SDS extract and liquid–liquid extract were combined prior to solvent exchange. For soil samples, aliquots after SDS extraction were spiked with 20 μL of the ^{13}C-labeled PCDD/PCDF (2, 0.8, 0.8, 0.8, 2 ng) spiking standard. The XAD resin for stack samples was spiked with 10 μL of ^{13}C-labeled 1,2,3,7,8-PnCDF (1 ng) before sample collection and with 20 μL of the ^{13}C-labeled PCDD/PCDF (2, 0.8, 0.8, 0.8, 2ng, excludes 1,2,3,7,8-PnCDF) after SDS extraction but prior to solvent exchange, see below.

All cleanups were performed using the Power-Prep™ (Fluid Management Systems, Waltham, MA, USA) which is computer-controlled system of valves, pumps, and solenoids arranged in modules that automatically direct sample and solvent flow through a series of three disposable prepacked PTFE liquid chromatographic (LC) columns (multilayer silica, basic alumina, and carbon adsorbents) in a way similar to the manual process described in EPA method 1613b and 8290 [5,6]. This system has been successfully used in our laboratory for several years as well as by many other laboratories world-wide for PCDD/PCDF cleanup process in different matrices including: biological samples [20,21], incinerator fly ash [22], wood combustion ash [23], stack gas emissions, ambient air, and sludge [24,25].

The sample extracts, which are in benzene, cannot be directly introduced into the Power-Prep™ system without first performing a solvent exchange. Introducing the sample extracts in benzene would cause problems with the elution pattern of the PCDDs/PCDFs from the multilayer silica and basic alumina columns. Therefore, a benzene/iso-octane solvent exchange was performed on all sample extracts. The final extract volume after solvent exchange to iso-octane was 12 mL. The 12 mL of extract is pumped into the system and then flushed through a multilayer acid and caustic silica column with 90 mL of hexane into an alumina column. Interfering compounds were eluted from the alumina column with 60 mL of 2% (v/v) dichloromethane in hexane. The analytes were eluted from the alumina column and transferred into a carbon column with 120 mL 50% (v/v) dichloromethane in hexane. Additional interfering compounds were removed from the carbon column with 4 mL of 50% (v/v) ethyl acetate in benzene and 10 mL of hexane in the forward direction. These solvents for removing interferences from the carbon column are different than reported in literature [22] and the changes are based on manufacturer's recommendation. The final analyte collection is accomplished by reversing the direction of solvent flow through the carbon column with 50 mL of toluene. The first 5 mL of toluene is sent to waste and the rest is collected. The 45 mL of toluene used to wash the column is less than amount reported in some literature [21,22] and suggested by the manufacturer. By sending the first 5 mL of toluene to waste and using only 45 mL afterwards to wash the carbon column, more interferents are removed without

losing any significant amount of PCDDs/PCDFs. We think that this step in the automated cleanup procedure is very important because it puts less stress on the HRGC–HRMS equipment (GC column and ion source components, in particular), makes data interpretation easier, and improves overall data quality. After the effluent is collected, the samples are placed on the Turbo-Vap® LV Evaporator Concentration Workstation (Zymark, Hopkinton, MA, USA) and blown to approximately 0.2 mL at 50 °C under a purified nitrogen stream. Then, a solvent exchange was performed with 20 μL of nonane containing ^{13}C-labeled 1,2,3,4,7-PnCDD as an injection standard to account for autosampler injection variability.

2.3. HRGC–HRMS measurements

All PCDD/PCDF measurements were performed by HRGC–HRMS using a 5890 Series II gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) and a Finnigan MAT-95 double focusing magnetic sector mass spectrometer (Thermo Electron Co., Bremen, Germany) equipped with an electron ionization (EI) ion source operating in the positive ionization mode. Typical ionization conditions were electron energy of 48 eV, ion source temperature of 240 °C, and acceleration voltage of 4700 V. Mass spectrometer data were obtained in the selected ion monitoring (SIM) mode at resolution of 7100 (10% valley). All samples were introduced into the GC inlet system by a LEAP Technologies CTC A200S autosampler (Carrboro, NC, USA). For the HRGC analyses seven Series 5 fused-silica capillary columns of 60 m × 0.25 mm i.d. 0.25 μm film thickness were used: HP-5MS (Agilent Technologies), ZB-5UMS (Phenomenex, Torrance, CA, USA), Rtx-5MS (Restek, Bellefonte, PA, USA), Equity-5 (Supelco, Bellefonte, PA, USA), CP-Sil 8 CB LowBleed/MS (Varian, Walnut Creek, CA, USA), DB-5, and DB-5MS (J&W Scientific, Folsom, CA, USA). The GC oven temperature used for the columns was programmed from 200 °C (2 min hold) to 220 °C at 5 °C/min and held for 16 min, to 235 °C at 5.0 °C/min and held for 7 min, to 310 °C at 5 °C/min and held for 10 min at 310 °C. All GC conditions were kept consistent and as close as possible to EPA method 1613b [5] operating conditions for all columns tested. Furthermore, no specific effort was made to optimize GC conditions (temperature program in particular) to maximize resolution of I-TEF congeners for any specific column. The injection port and transfer line temperatures were at 270 and 250 °C, respectively, and the helium carrier gas was at ∼30 cm/s linear velocity in a splitless injection mode.

2.4. Quantitation and limit of detection

Quantitation of PCDDs/PCDFs was performed using the isotope dilution method [5]. I-TEF calibration standard was used for instrument calibration and computation of the average relative response factors. Native PCDDs/PCDFs and ^{13}C-labeled internal standards recoveries were quantified via an internal standard calculation procedure using ^{13}C-labeled 1,2,3,4,7-PnCDD as an injection standard. Peak areas were used in all calculations. All 2,3,7,8-substituted native isomers were identified based on co-elution with the ^{13}C-labeled isotope.

The limit of detection (LoD) has been calculated as 2.5 times noise value for all 2,3,7,8-substituted native isomers. The noise value was obtained using baseline peak-to-valley heights from the standard instrument software and stored into the ASCII file. The Dow Dioxin Data Reduction Package (DDDRP) as a software application for the Finnigan ICIS V8.2.1 data system [26,27] converts peak-to-valley measurements into the peak areas using the area-to-height ratio of the individual analytes in the calibration standard.

3. Results and discussion

The results indicate that Series 5 GC columns exhibited differences in isomer resolution; e.g. isomers co-eluting on the column from one manufacturer were found to have some degree of separation on a column from another manufacturer. Sometimes, elution order of isomers of interest might be different. HP-5MS, Rtx-5MS, and Equity-5 columns exhibit isomer elution orders identical to a DB-5 column. DB-5MS, CP-Sil 8 CB LowBleed/MS, and ZB-5UMS not only show differences in isomer resolution when compared to DB-5 type columns but also with respect to each other.

Table 3 represents the retention time data for all seven Series 5 GC columns tested using Sample No. 5 containing 15 ^{13}C-stable isotopes, described above, all 17 native 2,3,7,8-substituted isomers, and some of their closely eluting isomers. It was true for all columns that ^{13}C-labelled reference standards are eluted usually earlier than the corresponding unlabeled compounds (see Table 3). A similar observation was made by Korhonen and Mantykoski for 25 m × 0.20 mm i.d. 0.11 μm film thickness HP-5 column [28].

In general, we found that the Si-arylene base or "non-conventional" Series 5 GC columns have better chromatographic separation with respect 2,3,7,8-substituted PCDD/PCDF isomers. A portion of the data for the aqueous matrix is presented in Table 4. The "conventional" GC column results are combined together due to their identical chromatographic column performances. Our mass chromatographic data are very similar to others [8–11,14] with respect to isomer elution orders, however, some differences were noticed. GC parameters, particularly oven temperature, caused some differences in retention times and separation qualities.

We found at least one report in the literature in which Chang-Chien et al. [15] could not chromatographically resolve OCDD from OCDF with 30 m HP-5MS and Rtx-5MS columns. Our laboratory did not have any problem resolving those two congeners with any 30 or 60 m GC columns from any of the suppliers mentioned in this paper.

Table 3
Relative retention times on 60 m columns with respect to DB-5

CDDs/CDFs	EPA specificity	DB-5	Rtx-5MS	Equity-5	HP-5MS	DB-5MS	CP-Sil 8 CB/MS	ZB-5UMS
1,3,6,8-TCDD	Window	24:39	1.02	1.06	0.94	0.97	1.06	1.08
1,2,3,7/1,2,3,8-TCDD	Column performance	28:38	1.02	1.07	0.94	0.98	1.06	1.08
2,3,7,8-TCDD	I-TEF	28:52	1.02	1.07	0.94	0.98	1.07	1.08
2,3,7,8-TCDD (^{13}C)	I-TEF	28:50	1.02	1.07	0.94	0.99	1.07	1.10
1,2,3,9-TCDD	Column performance	29:10	1.02	1.07	0.94	0.97	1.05	1.09
1,2,8,9-TCDD	Window	30:57	1.02	1.07	0.94	0.97	1.06	1.07
1,2,4,6,8/1,2,4,7,9-PnCDD	Window	34:31	1.01	1.05	0.95	0.97	1.03	1.06
1,2,3,4,7-PnCDD (^{13}C)	Injection standard	37:31	1.01	1.04	0.96	0.98	1.03	1.05
1,2,3,7,8-PnCDD	I-TEF	38:08	1.01	1.04	0.96	0.99	1.03	1.06
1,2,3,7,8-PnCDD (^{13}C)	I-TEF	38:06	1.01	1.04	0.96	0.99	1.04	1.06
1,2,3,8,9-PnCDD	Window	39:00	1.01	1.04	0.96	0.98	1.03	1.04
1,2,4,6,7,9/1,2,4,6,8,9-HxCDD	Window	41:47	1.01	1.03	0.97	0.98	1.02	1.04
1,2,3,4,7,8-HxCDD	I-TEF	43:47	1.01	1.03	0.97	0.99	1.02	1.04
1,2,3,4,7,8-HxCDD (^{13}C)	I-TEF	43:47	1.01	1.03	0.97	0.99	1.02	1.04
1,2,3,6,7,8-HxCDD	I-TEF	43:56	1.01	1.03	0.97	0.99	1.02	1.04
1,2,3,7,8,9-HxCDD	I-TEF	44:22	1.01	1.03	0.98	0.98	1.02	1.03
1,2,3,7,8,9-HxCDD (^{13}C)	I-TEF	44:22	1.01	1.03	0.97	0.98	1.02	1.04
1,2,3,4,6,7-HxCDD	Window	44:22	1.01	1.03	0.97	0.98	1.02	1.04
1,2,3,4,6,7,9-HpCDD	Window	47:29	1.01	1.03	0.98	0.98	1.01	1.03
1,2,3,4,6,7,8-HpCDD	Window/I-TEF	48:29	1.01	1.03	0.98	0.98	1.01	1.03
1,2,3,4,6,7,8-HpCDD (^{13}C)	Window/I-TEF	48:28	1.01	1.03	0.98	0.98	1.01	1.03
OCDD	I-TEF	53:01	1.01	1.03	0.97	0.98	1.01	1.04
OCDD (^{13}C)	I-TEF	53:00	1.01	1.03	0.97	0.98	1.01	1.04
1,3,6,8-TCDF	Window	22:38	1.02	1.07	0.92	0.96	1.06	1.09
2,3,4,7-TCDF	Column performance	27:30	1.02	1.07	0.94	0.98	1.07	1.09
2,3,7,8-TCDF	I-TEF	27:30	1.02	1.07	0.94	0.99	1.08	1.10
2,3,7,8-TCDF (^{13}C)	I-TEF	27:27	1.02	1.07	0.94	0.99	1.08	1.10
1,2,3,9-TCDF	Column performance	29:08	1.02	1.07	0.94	0.98	1.07	1.07
1,2,8,9-TCDF	Window	30:56	1.03	1.07	0.94	0.98	1.07	1.07
1,3,4,6,8-PnCDF	Window	31:33	1.02	1.06	0.94	0.96	1.04	1.08
1,2,3,7,8-PnCDF	I-TEF	35:59	1.01	1.05	0.95	0.98	1.04	1.06
1,2,3,7,8-PnCDF (^{13}C)	I-TEF	35:57	1.02	1.05	0.95	0.98	1.04	1.06
2,3,4,7,8-PnCDF	I-TEF	37:26	1.01	1.04	0.96	0.99	1.04	1.06
2,3,4,7,8-PnCDF (^{13}C)	I-TEF	37:25	1.01	1.04	0.96	0.99	1.04	1.06
1,2,3,8,9-PnCDF	Window	39:12	1.01	1.04	0.96	0.99	1.04	1.05
1,2,3,4,6,8-HxCDF	Window	40:50	1.01	1.03	0.97	0.98	1.02	1.04
1,2,3,4,7,8-HxCDF	I-TEF	42:32	1.01	1.03	0.97	0.98	1.02	1.04
1,2,3,4,7,8-HxCDF (^{13}C)	I-TEF	42:31	1.01	1.03	0.97	0.98	1.02	1.04
1,2,3,6,7,8-HxCDF	I-TEF	42:43	1.01	1.03	0.97	0.98	1.02	1.04
2,3,4,6,7,8-HxCDF	I-TEF	43:34	1.01	1.03	0.97	0.98	1.02	1.04
2,3,4,6,7,8-HxCDF (^{13}C)	I-TEF	43:33	1.01	1.03	0.97	0.98	1.02	1.04
1,2,3,7,8,9-HxCDF	I-TEF	44:42	1.01	1.03	0.98	0.99	1.02	1.04
1,2,3,7,8,9-HxCDF (^{13}C)	I-TEF	44:42	1.01	1.03	0.97	0.99	1.02	1.04
1,2,3,4,8,9-HxCDF	Window	44:52	1.01	1.03	0.98	0.98	1.02	1.03
1,2,3,4,6,7,8-HpCDF	Window/I-TEF	47:05	1.01	1.03	0.98	0.98	1.01	1.03
1,2,3,4,6,7,8-HpCDF (^{13}C)	Window/I-TEF	47:04	1.01	1.03	0.98	0.98	1.01	1.03
1,2,3,4,7,8,9-HpCDF	Window/I-TEF	49:03	1.01	1.03	0.98	0.99	1.02	1.04
1,2,3,4,7,8,9-HpCDF (^{13}C)	Window/I-TEF	49:02	1.01	1.03	0.98	0.99	1.02	1.04
OCDF	I-TEF	53:12	1.01	1.03	0.97	0.98	1.02	1.04
OCDF (^{13}C)	I-TEF	53:11	1.01	1.03	0.97	0.98	1.02	1.04

Retention times on DB-5 column are in minutes.

3.1. TCDD column performance

All columns tested showed good separation of 2,3,7,8-TCDD from other co-eluting isomers. We observed differences in the elution order of 2,3,7,8-TCDD with respect to closely eluting isomers: 1,2,3,7/1,2,3,8-TCDD and 1,2,3,9-TCDD as shown in Fig. 2. The data on DB-5 and DB-5MS columns agreed well with previously reported observations [8–11].

3.2. PnCDD column performance

"Conventional" columns showed separation of 1,2,3,7,8-PnCDD (pentachlorodibenzo-*p*-dioxin) from its closest eluting isomer of 1,2,3,6,7-PnCDD with a peak resolution of $R = 1.9$ (Fig. 3) (typically for our mass chromatograms peak resolution of $R = 1.4$ and more represents "baseline separation", $R = 1$ corresponds to "near baseline" with 90% separation completed, and $R = 0.8$ in most cases allows us to

Table 4
Comparison of calculated mass in nanograms for 2,3,7,8-substituted PCCDs/PCDFs and homolog totals based on 1 g sample (1 ppb) (Sample No. 2)

PCDD/PCDF	DB-5 HP-5MS Rtx-5MS Equity-5	DB-5MS	ZB-5UMS	CP-Sil 8 CB/MS
Total-TCDD	0.26 (±0.05)[a]	0.25	0.44	0.37
2,3,7,8-TCDD	ND (0.04)[b]	ND (0.03)[c]	ND (0.03)[c]	ND (0.02)[c]
Total-PnCDD	1.44 (±0.05)	1.4	1.2	1.34
1,2,3,7,8-PnCDD	0.24 (±0.02)	0.24	0.28	0.22
Total-HxCDD	5.4 (±0.41)	5.61	4.96	4.92
1,2,3,4,7,8-/1,2,3,6,7,8-HxCDD	1.36 (±0.12)	1.37	1.26	1.22
1,2,3,7,8,9-HxCDD	0.93 (±0.03)	0.45	0.48	0.45
Total-HpCDD	24.79 (±2.08)	23.11	24.69	23.14
1,2,3,4,6,7,8-HpCDD	15.14 (±1.38)	13.83	15.24	14.11
OCDD	54.62 (±3.99)	46.66	55.18	50.15
Total-TCDF	4.09 (±0.19)	3.77	3.89	3.53
2,3,7,8-TCDF	1.13 (±0.12)	0.71	0.72	0.66
Total-PnCDF	8.57 (±0.62)	8.35	7.47	7.49
1,2,3,7,8-PnCDF	1.44 (±0.08)	1.49	1.38	1.34
2,3,4,7,8-PnCDF	1.07 (±0.07)	1.29	1.22	0.82
Total-HxCDF	24.75 (±1.83)	25.04	25.13	22.32
1,2,3,4,7,8-/1,2,3,6,7,8-HxCDF	11.49 (±0.88)	8.98	9.24	7.96
2,3,4,6,7,8-HxCDF	2.41 (±0.09)	3.17	3.24	3.03
1,2,3,7,8,9-HxCDF	0.55 (±0.04)	2.23	2.17	1.99
Total-HpCDF	86.21 (±6.21)	80.23	85.21	83.55
1,2,3,4,6,7,8-HpCDF	46.14 (±2.81)	43.27	45.39	44.85
1,2,3,4,7,8,9-HpCDF	15.58 (±0.28)	14.63	15.7	14.52
OCDF	416.51 (±12.91)	378.81	397.07	386.3

[a] Average concentration with standard deviation of four GC columns tested.
[b] Average limit of detection of four GC columns tested.
[c] Absolute limit of detection of corresponding GC column tested.

do “quantifiable” measurements with ±10% accuracy). The elution order for our DB-5 GC column is very similar to that described previously in the literature [8,11]. DB-5MS and CP-Sil 8 CB LowBleed/MS with resolutions of $R = 0.9$ and 1.0 correspondingly, yield results with nearly baseline separations of the peaks mentioned above. The elution order for DB-5MS is identical to that observed by Abad and Rivera [10], with better separation of 1,2,3,7,8-PnCDD and 1,2,3,6,7-PnCDD isomers. The difference in this separation may be due to differences in manufacturing practices since the work of Abad and Rivera. The ZB-5UMS column shows no separation between the two peaks described above. We consider this as a major drawback for this column compared to other Si-arylene based columns, see below.

3.3. HxCDD column performance

All Si-arylene based GC columns demonstrate better performance compared to “conventional” columns in separation of 1,2,3,7,8,9-HxCDD from the closely eluting

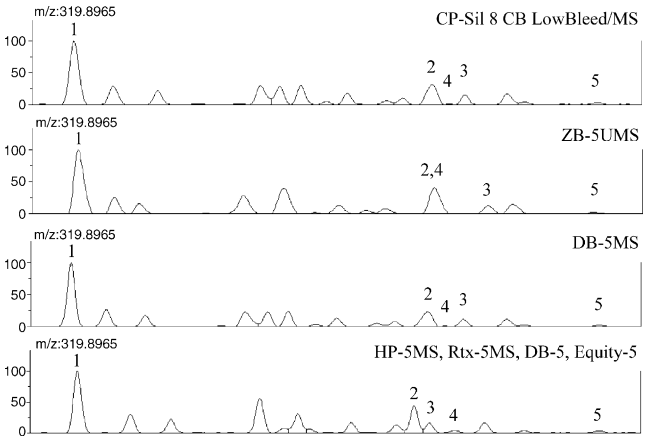


Fig. 2. GC high-resolution mass chromatograms of TCDD obtained using a variety of Series 5 fused-silica bonded phase capillary columns: (1) 1,3,6,8-TCDD; (2) 1,2,3,7/1,2,3,8-TCDD; (3) 2,3,7,8-TCDD; (4) 1,2,3,9-TCDD; (5) 1,2,8,9-TCDD.

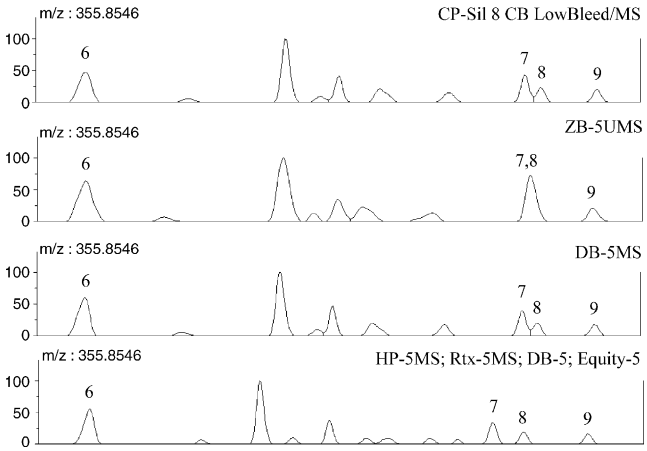


Fig. 3. GC high-resolution mass chromatograms of PnCDD obtained using a variety of Series 5 fused-silica bonded phase capillary columns: (6) 1,2,4,6,8/1,2,4,7,9-PnCDD; (7) 1,2,3,7,8-PnCDD; (8) 1,2,3,6,7-PnCDD; (9) 1,2,3,8,9-PnCDD.

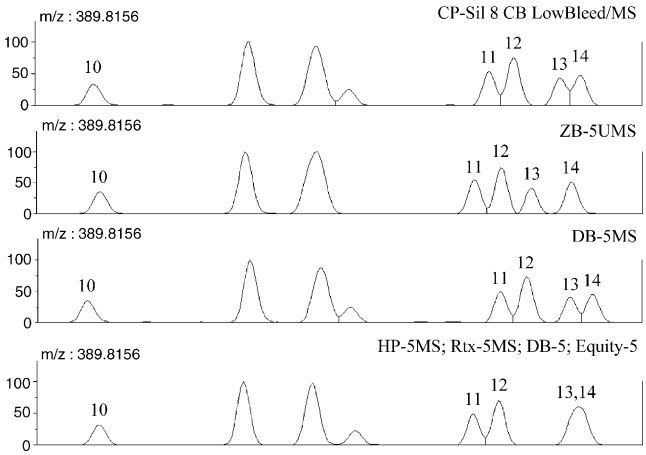


Fig. 4. GC high-resolution mass chromatograms of HxCDD obtained using a variety of Series 5 fused-silica bonded phase capillary columns: (10) 1,2,4,6,7,9/1,2,4,6,8,9-HxCDD; (11) 1,2,3,4,7,8-HxCDD; (12) 1,2,3,6,7,8-HxCDD; (13) 1,2,3,4,6,7-HxCDD; (14) 1,2,3,7,8,9-HxCDD.

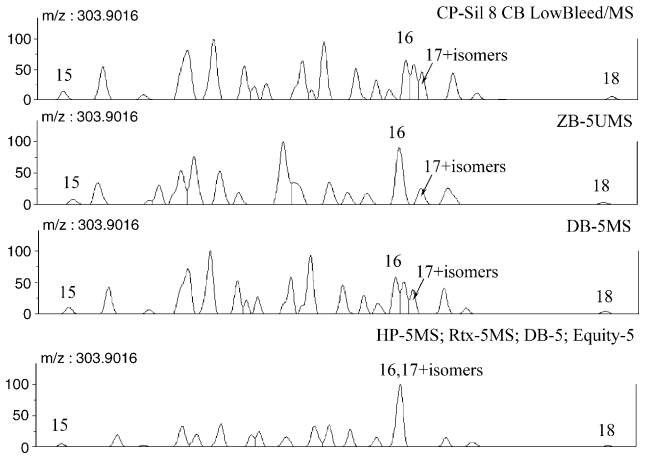


Fig. 5. GC high-resolution mass chromatograms of TCDF obtained using a variety of Series 5 fused-silica bonded phase capillary columns: (15) 1,3,6,8-TCDF; (16) 2,3,4,7-TCDF; (17) 2,3,7,8-TCDF co-elution with another isomers is suspected in this case; (18) 1,2,8,9-TCDF.

isomer of 1,2,3,4,6,7-HxCDD. ZB-5UMS shows baseline separation ($R = 1.8$) while DB-5MS and CP-Sil 8 CB LowBleed/MS exhibit sufficient separation ($R = 0.9$ in both cases) to allow accurate quantification (Fig. 4). For those three Si-arylene based MS columns, it is worth mentioning that the I-TEF isomer of 1,2,3,7,8,9-HxCDD elutes after its window-defining standard required by EPA method to demonstrate column performance [5]. Our data agree very well with previously published results on DB-5MS [9,10] and DB-5 columns [8,9,11]. Korhonen and Mantykoski [28] studied separation of some PCDDs/PCDFs based on HP-5 column performance. Interestingly, their data showed that 1,2,3,7,8,9-HxCDD and 1,2,3,4,6,7-HxCDD co-elute in a manner similar to the "conventional" columns [8,9,11].

3.4. TCDF column performance

One of the most important advantages of all Si-arylene columns compared to "conventional" columns is the improvement of the separation of 2,3,7,8-TCDF from other, at least two, closely eluting isomers (Fig. 5). For DB-5 GC column Ryan et al. [8] have shown five isomers co-elution and Ballschmiter and Bacher [11] observed that six isomers co-elute with 2,3,7,8-TCDF. Our TCDF mass chromatograms for DB-5 and DB-5MS columns are very similar to others [8–11], however, it is not clear from our data and from the prior published data [9,10] how many isomers co-elute with 2,3,7,8-TCDF on "non-conventional" columns. Some confusion arises from EPA method 1613b [5], particularly from Fig. 7 on page 82 where we believe there are two misprints. On page 68, the method suggests using 2,3,4,7-TCDF, 2,3,7,8-TCDF, and 1,2,3,9-TCDF as a column performance mixture for DB-225 column. However, the Fig. 7 caption states "Isomer-specific separation of 2,3,7,8-TCDF on DB-5 column" and there is no 2,3,7,8-isomer on this picture. The caption should read "Isomer-specific separation of 2,3,7,8-TCDF on DB-225 column" and the peak labeled 2,3,4,8-TCDF should be labeled 2,3,7,8-TCDF. We believe that based on this information the CIL EDF-4147 PCDD/PCDF Window Defining and Isomer Specificity Mix (DB-5) for column performance check should be used to confirm 2,3,7,8-TCDD separation on a DB-5 column and 2,3,7,8-TCDF on a DB-225 column [8]. However, as stated in Method 1613b, the DB-5 column cannot separate all TCDF isomers from 2,3,7,8-TCDF and therefore should be used with caution when analyzing for that compound. Nevertheless, Si-arylene columns appear to exhibit the least amount of interference and therefore a significantly lower concentration value for this isomer (see Table 4) compared to "conventional" columns tested.

3.5. PnCDF column performance

All Si-arylene based columns demonstrated baseline separation ($R > 1.5$) of 1,2,3,7,8-PnCDF, on the other hand, "conventional" columns showed only "quantifiable" results ($R = 0.9$) as shown in Fig. 6. The most challenging aspect for all Series 5 columns is the separation of 2,3,4,7,8-PnCDF from other closely eluting isomers, presumably 1,2,4,8,9-PnCDF, 1,2,6,7,9-PnCDF and 1,2,3,6,9-PnCDF [8,11]. None of the columns tested was successful in this matter, however, Varian CP-Sil 8 CB LowBleed/MS column gave the lowest concentration value for this isomer as reported in Table 4. An unique feature observed for the Phenomenex ZB-5UMS column is that it can distinguish the 1,3,4,6,8-PnCDF from 1,2,4,6,8-PnCDF isomers with peak resolution of $R = 0.83$ (Fig. 6) [8,11]. Here 1,3,4,6,8-PnCDF serves as a "window-defining standard" based on the standard 1613b EPA method [5].

3.6. HxCDF column performance

We observed a large amount of discrepancy in the separation of HxCDF isomers between Si-arylene and "conven-

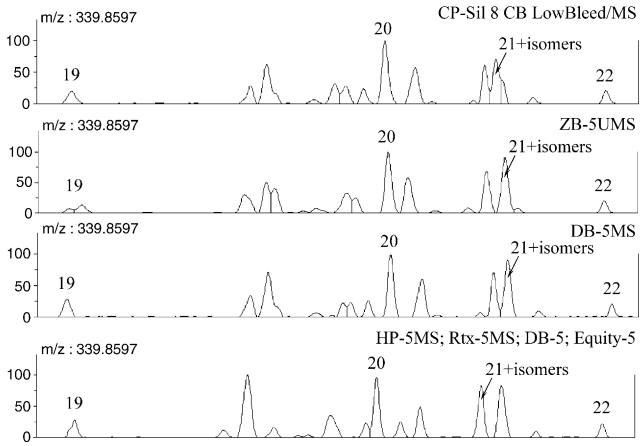


Fig. 6. GC high-resolution mass chromatograms of PnCDF obtained using a variety of Series 5 fused-silica bonded phase capillary columns: (19) 1,3,4,6,8/1,2,4,6,8-PnCDF; (20) 1,2,3,7,8-PnCDF; (21) 2,3,4,7,8-PnCDF co-elution with another isomers is suspected in this case; (22) 1,2,3,8,9-PnCDF.

tional" columns as shown in Fig. 7. Our data agree well with previously published separation by some authors [8,9,11] and somewhat in contradiction with Abad and Rivera [10] on the DB-5 column elution order for 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF.

DB-5, HP-5MS, Rtx-5MS, and Equity-5 GC columns could not separate 1,2,3,4,7,8-HxCDF from its closely eluted isomer of 1,2,3,4,6,7-HxCDF, while DB-5MS and CP-Sil 8 CB LowBleed/MS columns exhibited near baseline separation with peak resolutions of $R = 1.3$ and 1.1 correspondingly; and, in the case of ZB-5UMS, it achieved baseline separation (R = 1.5) of the aforementioned isomers. On the other hand, "conventional" columns could quantitatively ($R = 0.9$) and near baseline ($R = 1.1$) resolve 2,3,4,6,7,8-HxCDF from 1,2,3,6,8,9-HxCDF and 1,2,3,7,8,9-HxCDF

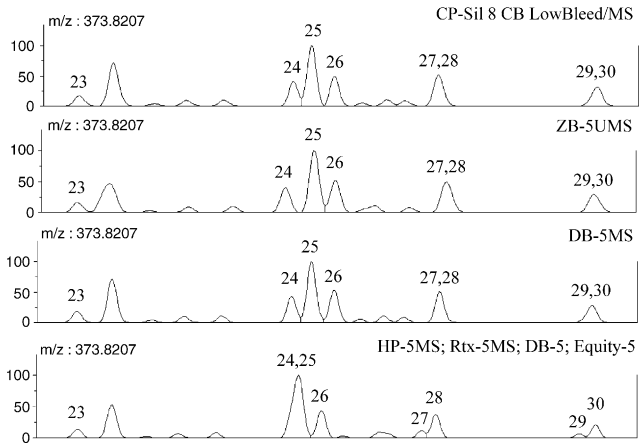


Fig. 7. GC high-resolution mass chromatograms of HxCDF obtained using a variety of Series 5 fused-silica bonded phase capillary columns: (23) 1,2,3,4,6,8-HxCDF; (24) 1,2,3,4,6,7-HxCDF; (25) 1,2,3,4,7,8-HxCDF; (26) 1,2,3,6,7,8-HxCDF; (27) 1,2,3,6,8,9-HxCDF; (28) 2,3,4,6,7,8-HxCDF; (29) 1,2,3,7,8,9-HxCDF; (30) 1,2,3,4,8,9-HxCDF.

from 1,2,3,4,8,9-HxCDF, correspondingly, while Si-arylene columns showed clear signs of co-elution (Fig. 7).

3.7. HpCDD, HpCDF, OCDD, and OCDF column performance

All columns tested were capable of base line chromatographic separation of all HpCDD, HpCDF congeners. We have found it very helpful in our laboratory to use ^{13}C-labeled standard for quantitative measurements of OCDF. The real challenge in using this standard is that it requires over 10,000 of resolving power to separate some of the ^{13}C-OCDF isotopes from native OCDD (m/z 457.7771 versus 457.7377, m/z 459.7742 versus 459.7347, etc.). However, using a proper GC program allows one to resolve chromatographically OCDD and OCDF as seen in Table 3.

3.8. Concentrations, total mass 17 (TM 17), and toxic equivalence (TEQ)

Figs. 2–7 demonstrates that none of the columns tested in this study were able to separate all 2,3,7,8-substituted isomers without co-elution with others. This means that for any Series 5 GC column, the Total TEQ value will always be biased high. We think that the best way to compare GC column performances with respect to separation of 2,3,7,8-substituted isomers is to compare them using their Total TEQs. The column with the least amount of co-elution of I-TEFs with other closely eluted isomers should give the lowest Total TEQ value. Table 5 represents the TEQ values for all six samples analyzed in this study. Similar to Table 4, we combined "conventional" column results because of their identical gas chromatographic separation performances. The major discrepancies in Total TEQ values come from differences in concentrations of 1,2,3,7,8-PnCDD, 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PnCDF, 1,2,3,4,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,7,8,9-HxCDF as their elution/co-elution order change from one column to another. As Table 2 shows, the I-TEFs with the largest potential to contribute to the Total TEQ value are 2,3,7,8-TCDD, 1,2,3,7,8-PnCDD, 1,2,3,7,8-PnCDF, 2,3,4,7,8-PnCDF. Hence, it is important that a GC column should primarily be able to resolve these isomers in a first place. For example, as seen in the PnCDD mass chromatograms (Fig. 3) there is a co-elution between the 1,2,3,7,8-PnCDD and 1,2,3,6,7-PnCDD isomers for the ZB-5UMS column and hence the Total TEQ values for this column are higher than for DB-5MS and CP-Sil 8 CB LowBleed/MS columns and somewhat close to "conventional" columns. However, the ZB-5UMS column better separates 2,3,7,8-TCDD, 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF + isomer(s), and 1,2,3,4,7,8-HxCDF than any other column tested.

3.9. Limit of detection

There are no standard methods to compare the (LoD = 2.5 × noise) from one column to another. It has been

Table 5
Comparison of total dioxin and furan masses, total mass 17 (I-TEFs) and Total TEQ (0.5)[a] values in picograms for variety GC columns tested

PCDD/PCDF	DB-5 HP-5MS Rtx-5MS Equity-5	DB-5MS	ZB-5UMS	CP-Sil 8 CB/MS
Sample No. 1				
Total dioxin	10.95 (±0.59)[b]	10.97	10.64	11.53
Total furans	28.49 (±0.8)	29.44	27.04	29.03
Total mass 17	24.98 (±1.15)	24.2	23.97	25.94
Total TEQ (0.5)	1.1 (±0.03)	1.11	1.09	1.09
Sample No. 2				
Total dioxin	86.51 (±6.06)	77.03	86.47	79.92
Total furans	540.13 (±20.52)	496.2	518.77	503.19
Total mass 17	568.61 (±21.61)	517.13	548.57	527.62
Total TEQ (0.5)	3.75 (±0.21)	3.67	3.75	3.29
Sample No. 3				
Total dioxin	13.78 (±0.51)	13.4	14.85	13.5
Total furans	152.73 (±7.48)	146.18	160.1	149.54
Total mass 17	124.81 (±5.24)	115.12	129.19	116.57
Total TEQ (0.5)	2.17 (±0.13)	1.88	2.01	1.88
Sample No. 4				
Total dioxin	5552.9 (±360.94)	5121.72	5428.19	5321.77
Total furans	4587.5 (±330.3)	4358.69	4590.22	4436.33
Total mass 17	7976.43 (±207.39)	7522.11	8063.10	7694.95
Total TEQ (0.5)	36.84 (±1.73)	33.5	37.13	34.72
Sample No. 5				
Total dioxin	31.73 (±1.71)	30.63	30.84	29.46
Total furans	33.18 (±1.69)	33.67	33.29	30.75
Total mass 17	36.34 (±1.64)	33.7	34.31	32.27
Total TEQ (0.5)	5.82 (±0.37)	5.45	5.75	5.45
Sample No. 6[c]				
Total dioxin	213.91 (±7.91)	204.84	221.44	194.57
Total furans	6322.34 (±31.61)	5777.85	6416.67	5941.21
Total mass 17	2738.64 (±54.77)	2349.82	2658.7	2442.79
Total TEQ (0.5)	257.88 (±0.52)	239.75	260.92	206.37

[a] Non-detected species are assumed to be present at 0.5 × LoD for calculation purposes.
[b] Average values with standard deviation of four GC columns tested.
[c] Sample No. 6 was not available for columns Equity-5 and Rtx-5MS at the time tested. Data represent only average of two experimental values (DB-5 and HP-5MS).

observed in our laboratory that the LoD might significantly change on a day-to-day basis due to the instrument operating conditions. For example, changing the spectrometer tuning parameters, ion volume/ion source cleaning or replacement, etc. can significantly affect the LoD by causing changes in the noise level. Therefore, we decided to compare the LoD of a GC column tested by injecting a known amount of the Sample No. 5 into the instrument. The assumption is that any mass spectrometer operation changes will equally affect both instrument noise and analyte signal and therefore it will have no effect on the signal-to-noise ratio for the given column. This approach allows us to calculate the LoD from mass chromatograms in which only a known amount of congeners are present. The LoD values have been normalized for the injected amount of each column tested. For PCDD and PCDF analysis, we considered this approach to be the most informative because we do not have interferences from the major polysiloxane fragments coming off the column (*m*/*z* 73, *m*/*z* 147, *m*/*z* 207, *m*/*z* 221, *m*/*z* 281, *m*/*z* 355, *m*/*z* 429, etc.) due to combination of HRMS and SIM mode. Values for "conventional" and "non-conventional" GC columns were grouped together. The results indicate that LoD values are experimentally indistinguishable (all within error bars) between "conventional" and "non-conventional" columns for most of 2,3,7,8-substituted isomers. One exception, 1,2,3,7,8-PnCDF shows slightly better detection limit using Si-arylene type columns. In our case, it is very difficult to make comments about durability of GC columns tested, simply because these columns were installed for experimental use only and for a short period of time. However, our general experience is that the lifetime of GC column dramatically decreases after injection of some unknown aggressive compound(s) that could be present in the sample extract. Optimizing HRGC–HRMS parameters for the best sensitivity and taking a smaller amount of the sample for the extraction makes cleanup more efficient and prolongs the lifetime of the GC column and ion source components.

Because of the possible variability in the LoD values from day-to-day operation, we use limit of quantification (LoQ = 10 × noise) to determine our "true" concentration values. In

Table 6
Isomeric specific separation of 2,3,7,8-substituted PCDDs/PCDFs on GC columns

PCDD/PCDF	DB-5 HP-5MS Rtx-5MS Equity-5	DB-5MS	ZB-5UMS	CP-Sil 8 CB/MS
2,3,7,8-TCDD	+ +	+ +	+ +	+ –
1,2,3,7,8-PnCDD	+ +	+ –	– –	+ –
1,2,3,4,7,8-HxCDD	+ +	+ +	+ +	+ +
1,2,3,6,7,8-HxCDD	+ +	+ +	+ +	+ +
1,2,3,7,8,9-HxCDD	– –	+ –	+ +	+ –
1,2,3,4,6,7,8-HpCDD	+ +	+ +	+ +	+ +
OCDD	+ +	+ +	+ +	+ +
2,3,7,8-TCDF	– –	– –[a]	– –[a]	– –[a]
1,2,3,7,8-PnCDF	+ +	+ +	+ +	+ +
2,3,4,7,8-PnCDF	– –	– –	– –	– –
1,2,3,4,7,8-HxCDF	– –	+ +	+ +	+ +
1,2,3,6,7,8-HxCDF	+ +	+ +	+ +	+ +
2,3,4,6,7,8-HxCDF	+ –	– –	– –	– –
1,2,3,7,8,9-HxCDF	+ +	– –	– –	– –
1,2,3,4,6,7,8-HpCDF	+ +	+ +	+ +	+ +
1,2,3,4,7,8,9-HpCDF	+ +	+ +	+ +	+ +
OCDF	+ +	+ +	+ +	+ +

++: Baseline separation or at least 10% valley. Peak resolution, $R > 1$; + –: quantifiable result (separation that allows peak area measurement with ±10% of each peak and typically correspond to at least 50% valley of equal peaks on GC mass chromatogram. Corresponded to peak resolution of $R \sim 0.8$); – –: interference present.

[a] DB-5MS, ZB-5UMS, and CP-Sil 8 CB LowBleed/MS appear to exhibit the least amount of interference compared to "conventional" columns (see text for details).

general, LoQ are used by our laboratory for the reporting of PCDD/PCDF concentrations into the Government (EPA) and Local Environmental Agencies.

4. Conclusion

All seven GC columns tested for this study can be used for PCDD/PCDF analysis. The relative performances of these columns were compared on the basis of separation of 2,3,7,8-substituted isomers of PCDDs/PDCFs and summarized in Table 6. HP-5MS, Rtx-5MS, and Equity-5 columns have isomer elution orders identical to "conventional" DB-5 column performance. DB-5MS, CP-Sil 8 CB LowBleed/MS, and ZB-5UMS show differences in isomer resolution compared to DB-5 type columns as well as with respect to each other. For example, DB-5, HP-5MS, Rtx-5MS, and Equity-5 columns could separate most of I-TEF isomers excluding 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PnCDF, and 1,2,3,4,7,8-HxCDF from the other closely eluting isomers tested. On another hand, DB-5MS, CP-Sil 8 CB LowBleed/MS, and ZB-5UMS columns could not resolve 2,3,4,7,8-PnCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,7,8,9-HxCDF from other non-toxic isomers. The ZB-5UMS column could not separate 1,2,3,7,8-PnCDD from 1,2,3,6,7-PnCDD. For those three MS columns, it is worth mentioning that the I-TEF isomer of 1,2,3,7,8,9-HxCDD elutes after its "window-defining standard" required by 1613b EPA methods to demonstrate column performance. In comparing isomeric data from different analytical GC Series 5 columns, care should be taken to insure that subtle differences in isomeric separation are taken into account. None of the columns tested were able to separate all 17 I-TEFs from other co-eluting isomers, which therefore leads to the overestimation of the TEQ value reported. Calculated total mass 17 and consequently TEQ values were lower when using the DB-5MS and CP-Sil 8 CB LowBleed/MS columns compared to "conventional" GC columns (see Table 4).

The combination of "conventional" (DB-5, HP-5MS, Rtx-5MS, Equity-5) and DB-225 columns made possible separation of all 2,3,7,8-substituted PCDDs/PCDFs [8]. However, if a laboratory is using a Series 5 column in most applications and using a DB-225 column only as complimentary equipment they probably should choose the Series 5 column based on the "common" congener concentrations, i.e. to ensure that the I-TEFs that significantly contribute to their TEQ value are separated from other closely eluting isomers. In the examples presented here, Si-arylene based columns such as DB-5MS, ZB-5UMS, CP-Sil 8 CB LowBleed/MS are better choice for analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in spite of some co-elutions.

Although the quantitative comparison of the TEQ values calculated on identical sample extracts analyzed on the different columns tested in this study showed relatively small differences, a greater concern would be the possible implications of using I-TEF isomer data obtained on different types of columns for comparison of "isomer fingerprints". Frequently, relative isomer concentrations are used for principal component analysis (PCA) or similar type of data assessment to make judgments about the source of PCDDs/PCDFs in particular samples. In this type of application, care should be exercised to insure that the isomer profiles being compared

have been obtained under conditions that are truly comparable. If data from different column types are interchanged, possible isomer interferences with one analytical column may be interpreted as a different isomer concentration and result in incorrect conclusions regarding the isomer profile.

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