Separation of 2,3,7,8-substituted polychlorodibenzo-p-dioxins and polychlorodibenzofurans on a new mixed stationary phase.

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Introduction

The 2,3,7,8-substituted isomers of the polychlorinated dibenzo-*p*-dioxins and dibenzofurans are significant environmental pollutants and current interest among the 75 PCDDs and 135 PCDFs because of high toxicity. Therefore, accurate determination of the 2,3,7,8-substituted toxic isomers from all non-toxic ones is very important. [1-4]

Generally, the analysis of PCDDs/PCDFs is carried out by high resolution gas chromatography coupled with high resolution mass spectrometry(HRGC/HRMS). In order to separate all the isomers, many types of GC capillary columns with different compositions and polarities are commercially available. But these columns have several disadvantages such as unstability due to high column bleeding, coelutions with other non-toxic isomers which result in higher quantification values and losses of analytes due to abnormal adsorption process on a stationary phase in capillary column.

In the present work, a mixed nonpolar polysiloxane was prepared in our laboratory and used as the stationary phase in order to evaluate the separation ability. Separation of 17 toxic isomers with the columns prepared with two pure polysiloxanes was compared.

Materials and Methods

Deactivated empty fused silica capillaries were purchased from the Alltech Associates(IL 60015, USA). Fused silica columns(30m x 0.25mm i.d.) were statically coated with mixed phase, OV-1(100% methyl) : OV-17(50% phenyl-methyl), 1 : 4).[5] Separation was performed on a HP 6890 GC system(HP, USA) coupled with an Autospec-ultima(Micromass, Manchester, UK), operated in EI ionization(32eV) at 10,000 resolving power. The GC temperature was programmed at 120°C(held for 3 min), increased to 220 °C (held for 5 min) at 20 °C /min, increased to 260 °C (held for 25 min) at 4 °C /min. Injector temperature was 260 °C and injection was carried out on splitless mode(1min). Helium at a pressure of 20psi was used as carrier gas.

Results

According to the previously published papers, the separation abilities of commercially available columns for the analysis of PCDDs/PCDFs are summarized in Table 1. These columns do not provide specific separation of all of the 17 PCDDs/PCDFs toxic isomers. Separation of 2,3,7,8-

Table 1. Isomer specific separation of 2,3,7,8-class congeners on the various stationary phases (DB-1, DB-17, DB-5, SP-2331, DB-DIOXIN and DB-5ms).

Dioxins	DB-1	DB-5	DB-17	SP-2331	DB-DIOXIN	DB-5ms
2,3,7,8-TCDD	++	+	-	+	++	++
1,2,3,7,8-PeCDD	++	++	+	++	-	++
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	++	++	++	++	++	++

Furans						
2,3,7,8-TCDF	-	-	++	+	++	++
1,2,3,7,8-PeCDF	++	+	-	-	+	+
2,3,4,7,8-PeCDF	-	-	++	++	-	-
1,2,3,4,7,8-HxCDF	+	-	++	-	++	++
1,2,3,6,7,8-HxCDF	++	++	-	++	+	++
1,2,3,7,8,9-HxCDF	+	+	++	++	++	++
2,3,4,6,7,8-HxCDF	-	+	++	++	++	-
1,2,3,4,6,7,8-HpCDF	++	++	++	++	++	++
1,2,3,4,7,8,9-HpCDF	++	++	++	++	++	++
OCDF	++	++	++	++	++	++

++ baseline separated; + partially separated; - coelution with other congeners

Table 2. Comparison of Retention Order of 12 Congeners on DB-1, DB-17 and New Stationary Phase(OV-1 : OV-17 , 1 : 4(v:v)).

Congener	Elution Order(Retention Time(min.)) / separation factor(α)					
	DB-1		DB-17		New Column	
2,3,7,8-TCDD	2(22.60)		2(26.35)		2	
1,2,3,7,8-PeCDD	5(27.20)		4(31.50)		4(19.14)	
1,2,3,4,7,8-HxCDD	9(31.77)		8(35.70)		8(22.37)	
1,2,3,6,7,8-HxCDD	10(31.86)	1.0028	9(35.95)	1.0070	9(22.45)	1.0036
1,2,3,7,8,9-HxCDD	11(32.13)	1.0085	10(36.30)	1.0097	11(23.07)	1.0276
2,3,7,8-TCDF	1(22.00)		1(25.92)		1(15.22)	
1,2,3,7,8-PeCDF	3(25.97)		3(30.38)		3(18.17)	
2,3,4,7,8-PeCDF	4(26.75)	1.0300	5(31.70)	1.0434	4(19.14)	1.0534
1,2,3,4,7,8-HxCDF	6(30.65)		6(34.95)		6(21.44)	
1,2,3,6,7,8-HxCDF	7(30.82)	1.0055	7(35.25)	1.0086	7(21.51)	1.0033
1,2,3,7,8,9-HxCDF	8(31.50)	1.0221	11(36.82)	1.0445	10(22.46)	1.0442
2,3,4,6,7,8-HxCDF	12(32.72)	1.0387	12(38.50)	1.0456	12(23.45)	1.0441

substituted PCDDs/PCDFs was tried on a newly prepared column. This column is nonpolar polysiloxane phase composed of OV-1 and OV-17(1:4, w/w). DB-1 column can not resolve 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,7,8,9-HpCDD, 2,3,4,6,7,8-HpCDF, whereas DB-17 column can resolve these 4 isomers. Therefore, these two phases were chosen as a stationary phase and coated in a empty capillary column.

The separation factors and elution order for the toxic isomers measured on a newly prepared column are summarized in Table 2. Elution orders of 12 isomers on a newly prepared column are

compared with the results of related article.[1] The separation factors of 12 congeners on newly prepared column are similar to DB-1 and DB-17. But separation factor of 1,2,3,7,8-PeCDF having high i-TEF value is higher. This study is in progress to measure selectivities of all the PCDDs/PCDFs isomers for the better accurate quantitation.

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