RETENTION TIMES AND COELUTIONS FOR ALL 136 TETRA- THROUGH OCTA- CHLORINATED DIOXINS AND FURANS ON A UNIQUE, LOW-BLEED, THERMALLY-STABLE GAS CHROMATOGRAPHY COLUMN

Cochran J[1], Dorman F[1], Stidsen G[1], Reese S[1], MacPherson K[2], Kolic T[2], Reiner E[2], Ryan J[3], Bradley J[4], Craig D[4], Priest B[4]
[1]Restek Corporation, 110 Benner Circle, Bellefonte, Pennsylvania, 16823, USA
[2]Ontario Ministry of Environment, 125 Resources Road, Toronto, Ontario, M9P 3V6, Canada
[3]Health Canada, Banting 2203D, Ross Avenue, Ottawa, Ontario, K1A 0L2, Canada
[4]Cambridge Isotope Laboratories, Inc., 50 Frontage Road, Andover, Massachusetts, 01810, USA

Abstract
Historical standards for all 136 tetra- through octa- chlorinated dioxins and furans have been made available and were used to profile a gas chromatography column with unique selectivity.

Introduction
Ryan, Conacher, Panopio, Lau, Hardy, and Masuda[1] used individual standards of all 136 tetra- through octa- chlorinated dioxins and furans to characterize nine different GC stationary phases in 1991. We use the dioxins and furans from that study to determine retention times and coelutions for all tetra- through octa- chlorinated dioxins and furans under simple linear temperature programming conditions on a gas chromatography column with good selectivity for coplanar dioxins and furans. We note any 2378 congener coelutions.

Materials and Methods
Standards and Samples
Individual standards of all 49 tetra- through octa- chlorinated dibenzo-p-dioxins and all 87 tetra- through octa- chlorinated dibenzofurans were from Cambridge Isotope Laboratories, Inc. (USA). The full origin details for the materials for these standards are contained in the Ryan paper[1]. Eleven mixes of congeners were prepared for analysis. A Sample Fortification Solution (Cambridge Isotope Laboratories, Inc.) containing several ^{13}C-labeled chlorinated dioxins (2378, 12378, 123678, 1234678, 12346789) and furans (2378, 12378, 123478, 1234678) was added to each of the mixes prior to analysis to monitor any retention time drift and to use for relative retention time calculations.

GC-HRMS
The 40m x 0.18mm x 0.18µm Rtx-Dioxin2 GC column (Restek Corporation, USA) was installed in an Agilent 6890 GC (USA) connected to a Waters AutoSpec Ultima HRMS (UK). The mass spectrometer was operated at over 10,000 resolving power using electron ionization (40 eV) under selected ion recording conditions. The source temperature was at 280°C. One microliter splitless injections were performed at 280°C. The GC oven was held at 120°C for 1 min, programmed at 10°C/min to 160°C, and then programmed at 4°C/min to 320°C where it was held for 4 min. Helium carrier flow was constant at 1 mL/min.

Results and Discussion
The retention time and coelution results for all tetra- through octa- chlorinated dioxins and furans on the Rtx-Dioxin2 column are shown in **Tables 1 and 2**. While a difference in retention times of at least 3 sec was used to describe a separation, it is important to note that peaks would not be baseline separated using this criterion. Extreme concentration differentials in closely eluting congeners could also invalidate the choice of the 3 sec criterion. However, baseline separation of 2378 TCDD and 2378 TCDF from other closely eluting congeners is not a requirement for columns listed to be specific for TCDD and TCDF in EPA Methods[2,3]. The separation for TCDD and TCDF congeners in a fly ash sample under the GC conditions listed here are shown in another contribution for Dioxin 2007[4].

Even with the coelutions, the Rtx-Dioxin2 can be considered a valuable column for dioxin and furan analysis, especially because of its specificity for 2378 TCDD and 2378 TCDF.

References

1. Ryan J, Conacher H, Panopio L, Lau B, Hardy B, Masuda Y. *J Chromatogr* 1991; 541:131.
2. United States Environmental Protection Agency. "Method 1613 – Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS", October 1994.
3. United States Environmental Protection Agency. "Method 8290A – Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)", January 1998.
4. Cochran J, Dorman F, Stidsen G, Reese S, MacPherson K, Kolic T, Reiner E, Ryan J, Bradley J, Craig D, Priest B, Dioxin 2007, Tokyo, Japan, September 2-7, 2007.

Table 1. Retention times (RT) and relative retention times (RRT) for all tetra- through octa- chlorinated dioxins (D) on an Rtx-Dioxin2 GC column using linear oven temperature programming. The RRTs were calculated versus 12378 ^{13}C-labeled dioxin. Boxes indicate coeluting congeners and the congeners highlighted in red are 2378 chlorine substituted.

Congener	RT (min)	RRT (min)	Congener	RT (min)	RRT (min)
1368 D	29.43	0.8198	12468 D	33.75	0.9401
1379 D	29.64	0.8256	12479 D	33.80	0.9415
1369 D	29.84	0.8312	12469 D	34.17	0.9515
1469 D	30.25	0.8424	12368 D	34.67	0.9657
1246 D	30.38	0.8462	12478 D	34.83	0.9702
1249 D	30.42	0.8474	12379 D	34.92	0.9727
1247 D	30.43	0.8476	12467 D	35.02	0.9755
1248 D	30.44	0.8479	12369 D	35.08	0.9769
1378 D	30.64	0.8535	12489 D	35.08	0.9772
1268 D	30.68	0.8546	12346 D	35.36	0.9850
1478 D	30.88	0.8599	12347 D	35.40	0.9858
1279 D	30.95	0.8621	12367 D	35.89	0.9997
1269 D	31.12	0.8669	12378 D	35.91	1.0003
1234 D	31.15	0.8677	12389 D	36.21	1.0086
1236 D	31.25	0.8705			
1237 D	31.47	0.8766	124679 D	37.89	1.0554
1238 D	31.50	0.8774	124689 D	37.89	1.0554
1239 D	31.51	0.8777	123468 D	38.53	1.0730
2378 D	31.79	0.8855	123679 D	38.79	1.0805
1278 D	31.90	0.8883	123689 D	38.82	1.0813
1267 D	31.90	0.8886	123469 D	38.90	1.0833
1289 D	32.27	0.8989	123478 D	39.55	1.1017
			123678 D	39.66	1.1047
			123467 D	39.78	1.1081
			123789 D	39.98	1.1136
			1234679 D	42.44	1.1822
			1234678 D	43.34	1.2072
			12346789 D	46.93	1.3069

Table 2. Retention times (RT) and relative retention times (RRT) for all tetra- through octa- chlorinated furans (F) on an Rtx-Dioxin2 GC column using linear oven temperature programming. The RRTs were calculated versus 12378 ^{13}C-labeled furan. Boxes indicate coeluting congeners and the congeners highlighted in red are 2378 chlorine substituted.

Congener	RT (min)	RRT (min)	Congener	RT (min)	RRT (min)
1368 F	28.29	0.8181	13468 F	32.38	0.9364
1468 F	28.52	0.8243	12468 F	32.44	0.9378
2468 F	29.03	0.8393	13678 F	33.53	0.9694
1346 F	29.03	0.8393	13467 F	33.58	0.9705
1246 F	29.11	0.8413	12467 F	33.61	0.9717
1378 F	29.15	0.8427	14678 F	33.70	0.9717
1347 F	29.19	0.8441	13478 F	33.69	0.9743
1247 F	29.26	0.8459	12368 F	33.71	0.9746
1348 F	29.27	0.8459	12478 F	33.76	0.9760
1248 F	29.35	0.8485	13479 F	33.85	0.9783
1379 F	29.40	0.8497	13469 F	34.00	0.9829
1367 F	29.42	0.8503	12479 F	34.09	0.9858
1268 F	29.56	0.8546	12346 F	34.14	0.9870
1467 F	29.64	0.8569	12469 F	34.25	0.9902
1478 F	29.76	0.8604	23468 F	34.35	0.9928
1369 F	29.97	0.8664	12347 F	34.36	0.9931
1237 F	30.03	0.8684	12348 F	34.39	0.9945
1678 F	30.10	0.8702	12378 F	34.61	1.0006
2467 F	30.14	0.8714	12678 F	34.85	1.0075
1234 F	30.16	0.8719	12367 F	34.86	1.0075
1238 F	30.18	0.8725	12379 F	34.99	1.0116
1469 F	30.19	0.8725	12679 F	35.27	1.0197
1236 F	30.27	0.8754	23467 F	35.48	1.0257
2368 F	30.35	0.8772	12369 F	35.51	1.0266
1278 F	30.45	0.8803	12489 F	35.56	1.0277
1349 F	30.48	0.8812	23478 F	35.68	1.0318
1267 F	30.66	0.8864	12349 F	35.74	1.0335
1249 F	30.78	0.8864	12389 F	36.47	1.0544
2346 F	30.83	0.8910			
1279 F	30.89	0.8930			
2347 F	31.03	0.8968			
2348 F	31.10	0.8991			
2378 F	31.22	0.9028			
3467 F	31.33	0.9058			
2367 F	31.41	0.9081			
1269 F	31.44	0.9089			
1239 F	31.61	0.9141			
1289 F	32.43	0.9376			

Table 2 (continued). Retention times (RT) and relative retention times (RRT) for all tetra- through octa-chlorinated furans (F) on an Rtx-Dioxin2 GC column using linear oven temperature programming. The RRTs were calculated versus 12378 ^{13}C-labeled furan. Boxes indicate coeluting congeners and the congeners highlighted in red are 2378 chlorine substituted.

Congener	RT (min)	RRT (min)		Congener	RT (min)	RRT (min)
123468 F	37.23	1.0766		1234678 F	41.99	1.2143
134678 F	37.38	1.0807		1234679 F	42.36	1.2243
124678 F	37.40	1.0812		1234689 F	42.60	1.2319
134679 F	37.62	1.0873		1234789 F	43.92	1.2697
124679 F	37.83	1.0876				
124689 F	38.08	1.1009		12346789 F	47.07	1.3604
123467 F	38.45	1.1116				
123478 F	38.58	1.1154				
123678 F	38.70	1.1191				
123479 F	38.86	1.1234				
123469 F	38.96	1.1263				
123679 F	39.14	1.1315				
123689 F	39.40	1.1387				
234678 F	39.42	1.1400				
123489 F	40.29	1.1651				
123789 F	40.31	1.1654				