SEPARATION OF 2378 TCDD, 2378 TCDF, 23478 PECDF, AND OTHER 2378 PCDDS AND PCDFS ON A NEW HIGH-TEMPERATURE GC COLUMN

Cochran J[1]*, Misselwitz M[1], Reese S[1], Stricek R[2], Kolic T[2], MacPherson K[2], Reiner E[2]

[1]Restek Corporation, 110 Benner Circle, Bellefonte, Pennsylvania, USA; [2]Ontario Ministry of the Environment, Laboratory Services Branch, 125 Resources Road, Toronto, Ontario, Canada

Introduction

EPA Methods 1613 (Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS) and 8290a [Polychlorinated Dibenzodioxins(PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)] specify the use of a 60m 5% diphenyl 95% dimethyl polysiloxane GC column (e.g. DB-5, Rxi-5ms) for 2378 TCDD isomer specificity. This column does not separate 2378 TCDF or 23478 PeCDF, or even 123478 HxCDF. In a recent analysis of sediment, river clay, soil, and fly ash samples by the Ontario Ministry of Environment, these three furans summed represented 17 to 69% of the TEQ (dioxins/furans) depending on the sample. 23478 PeCDF contributed 9 (sediment) to 30% (fly ash) of the TEQ, but the value is biased high since there are multiple coelutions for 23478 PeCDF on 5-type columns (this includes silphenylene types such as DB-5MS and Rxi-5Sil MS) as reported by Slava Fishman with colleagues Greg Martin and Michael Wilken in their Chemosphere paper, "Retention time profiling of all 136 tetra- through octa- chlorinated dibenzo-p-dioxins and dibenzofurans on a variety of Si-Arylene gas chromatographic stationary phases"[1]. For 2378 TCDF, the EPA Method recommends a 225 or 2330 or 2331 GC column, high cyano content stationary phases that will also separate 23478 PeCDF and 123478 HxCDF. Unfortunately, these cyano columns all have very low maximum operating temperatures of 240-275°C, show high bleed, and are not rugged.

While 2378 TCDD and 2378 TCDF are perhaps the most important congeners because of their toxicity and presence in biota samples, 23478 PeCDF also has high toxicity (TEF = 0.3) and can dominate the overall toxicity of some samples, especially those where the contamination is from particular chloralkali processes, therefore its unbiased determination can be important. This paper describes the first GC separation of 23478 PeCDF from interfering congeners on a non-cyano stationary phase, the Rtx-Dioxin2, which has a thermal stability of 340°C. In addition, 2378 TCDD, 2378 TCDF, and other toxic congeners are separated with a short analysis time of less than 36 min. Quantification results for sediments, river clay, soil, and fly ash are presented.

Materials and methods

A 60m x 0.18mm x 0.10µm Rtx-Dioxin2 column from Restek (Bellefonte, PA, USA) was operated with helium carrier gas at a constant flow of 1 mL/min in an Agilent 6890 GC - Waters AutoSpec Ultima mass spectrometer using electron ionization at 40eV, a source temperature of 280°C, and a resolving power of 10,000. The GC oven was programmed as follows: 120°C (1 min), 35°C/min to 200°C, 4.5°C/min to 280°C (8 min), 20°C/min to 330°C (4.8 min). Quantification of sediment, river clay, soil, and fly ash extracts was by isotope dilution. The Rtx-Dioxin2 was previously mapped for elution orders of all 136 tetra- through octa- chlorinated dioxin and furan congeners with standards from Cambridge Isotope Laboratories (Andover, Massachusetts, USA)[2].

Results and discussion

2378 TCDD and 2378 TCDF separations on the 60m x 0.18mm x 0.10µm Rtx-Dioxin2 are shown in **Figure 1** for a fly ash extract. No cyano-based confirmatory column analysis is necessary for the TCDF congener, as it is unequivocally separated from other competing isobaric congeners. 2378 TCDD also has no coelutions. A chromatogram showing the 23478 PeCDF separation (and 12378 PeCDF, bias-free) on the 60m x 0.18mm x 0.10µm Rtx-Dioxin2 is presented in **Figure 2**. On a DB-5 or Rxi-5ms or other 5% diphenyl and other 5-type columns (including DB-5MS and Rxi-5Sil MS), 23478 PeCDF coelutes with 12369, 12489, and 12679 PeCDF congeners (at least one and maybe all three), leading to high quantification bias and false toxicity for the sample.

Figure 1. Both 2378 TCDF and 2378 TCDD are completely separated from other possible coeluting congeners on a 60m x 0.18mm x 0.10µm Rtx-Dioxin2 GC column.

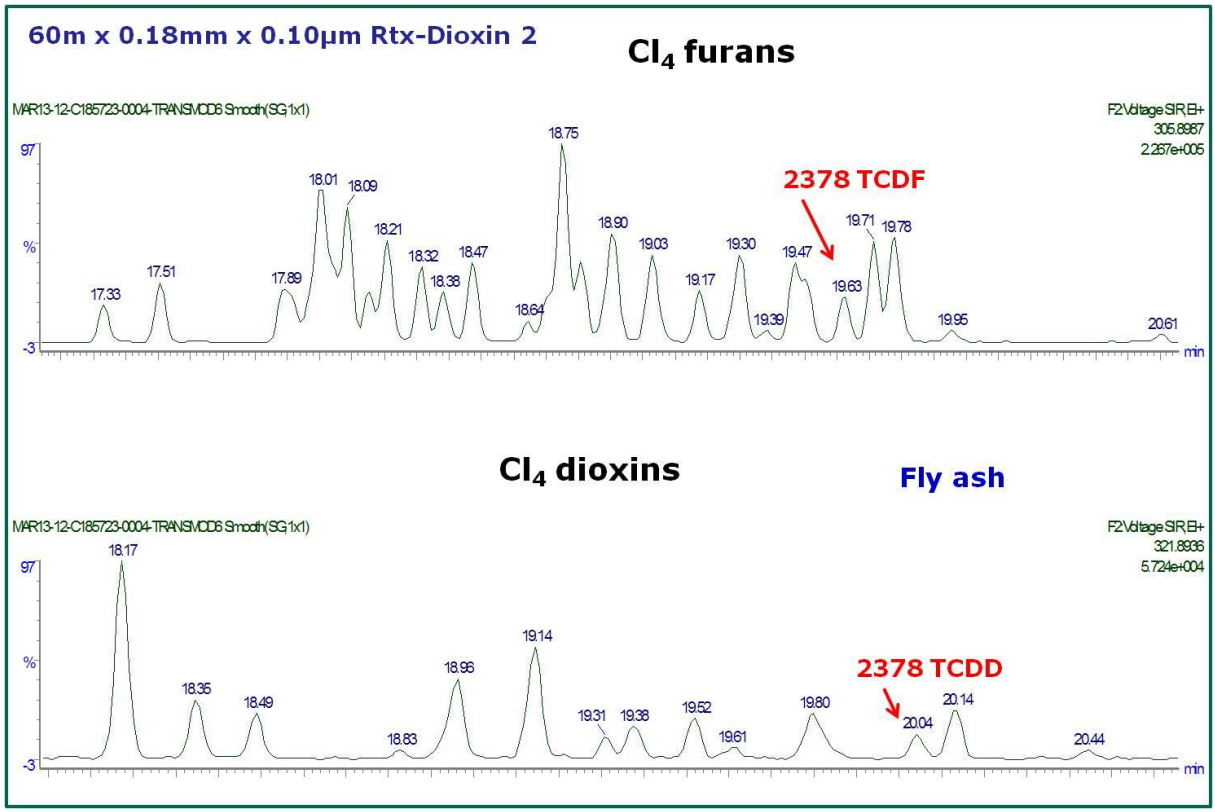


Figure 2. The toxic 23478 PeCDF congener is separated from other possible coeluting congeners, including 12349 PeCDF, on a 60m x 0.18mm x 0.10µm Rtx-Dioxin2 GC column.

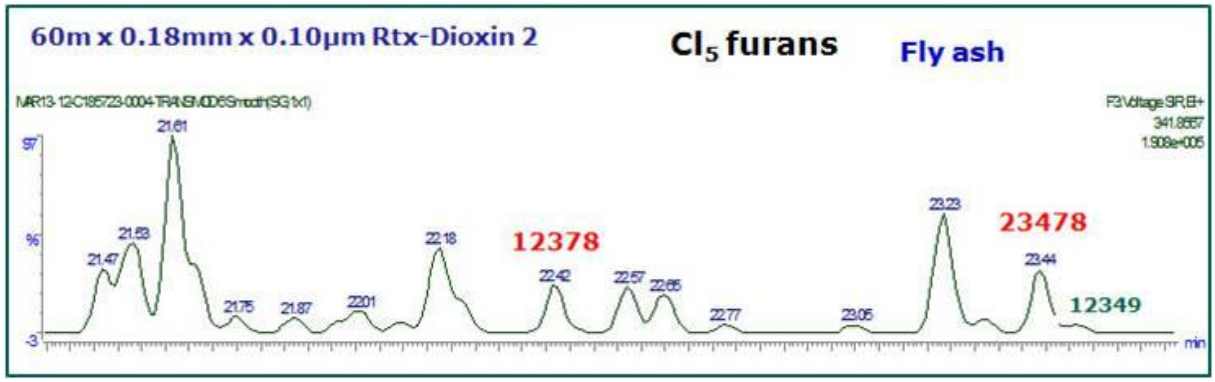


Table I demonstrates the problem with using only a 5% phenyl-type column for 23478 PeCDF quantification where the results can be biased quite high depending on the sample type. The Rtx-Dioxin2, however, allows accurate quantification since it resolves 23478 PeCDF from other possible coeluting PeCDFs. Just as importantly, it separates 2378 TCDF in the same run, eliminating the need for the non-rugged, high bleed cyano-based GC column.

Table I. Analysis of toxic furans, 2378 TCDF and 23478 PeCDF, with only a 5% phenyl-type GC column (DB-5) shows that some samples will have high quantification bias due to coelutions with non-toxic congeners. The Rtx-Dioxin2 (Dx2) separates 2378 TCDF, 23478 TCDF, and 123478 HxCDF from other congeners, providing more accurate results. Results are in pg/g.

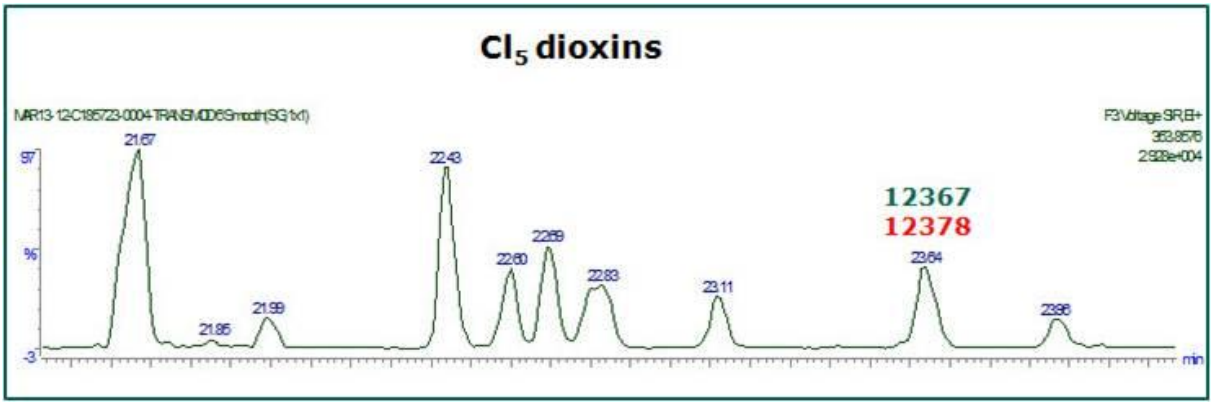
	2378		23478		123478	
Sample	**DB-5**	**Dx2**	**DB-5**	**Dx2**	**DB-5**	**Dx2**
Sediment 3	510	220	340	210	2200	2100
Sediment 4	10	9.2	11	6.5	30	25
Sediment 5	11	9.9	11	7.2	71	59
River clay	46	41	47	33	200	180
Soil	39	18	87	97	62	51
Fly ash 1	1200	270	400	180	300	240

60m x 0.25mm x 0.25µm DB-5

60m x 0.18mm x 0.18µm Rtx-Dioxin2

A previously noted coelution for 40m x 0.18mm x 0.18µm and 60m x 0.25mm x 0.25µm Rtx-Dioxin2 GC columns[2] continues on the higher-efficiency 60m x 0.18mm x 0.10µm version for the 12378 PeCDD congener (**Figure 3**), very important since its TEF is equivalent to that of 2378 TCDD. The extent of the bias can vary from sample to sample depending on the quantity of 12367 PeCDD, its coeluting congener, but previous work showed that 12378 PeCDD analyzed in sediment, soil, and fly ash reference materials using an Rtx-Dioxin2 fell within the certified ranges[3].

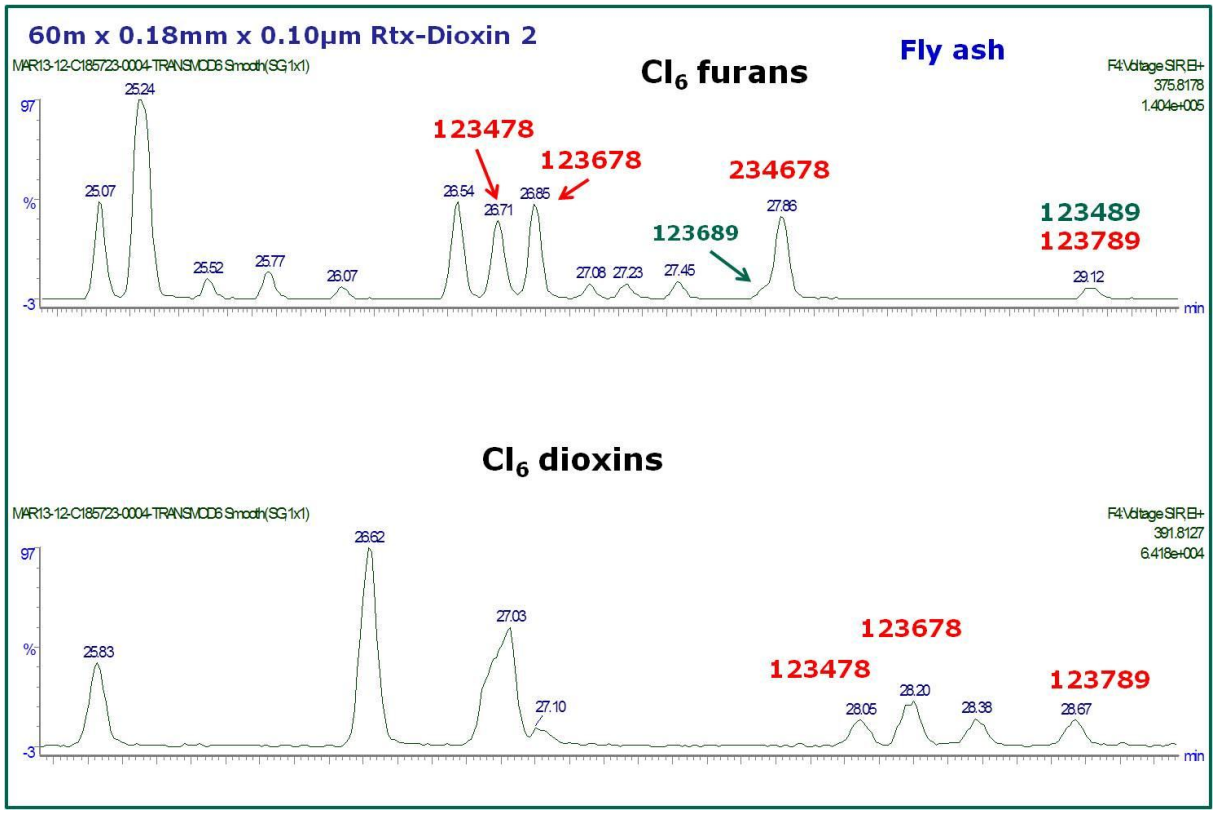
Figure 3. 12378 PeCDD shows a coelution on the 60m x 0.18mm x 0.10µm Rtx-Dioxin2, but quantification bias is typically small, including for fly ash samples such as this one.



The separation efficiency and selectivity for the Rtx-Dioxin2 extend to most of the hexa- chlorinated dioxin and furan congeners also, as seen in **Figure 4**, including for the previously mentioned 123478 HxCDF, a congener that is not resolved on DB-5 and may contribute greatly to the overall TEQ of a sample. Although a coelution exists for 123789 HxCDF, there is at least a partial separation for the 123689 and 234678 congeners. All of the 2378 hexachlorinated dioxins are easily separated.

In summary, the 60m x 0.18mm x 0.10µm Rtx-Dioxin2 column separates 15 of 17 2378 chlorine-substituted dioxins and furans, including 2378 TCDD, 2378 TCDF, 23478 PeCDF, and 123478 HxCDF. Its selectivity and high thermal stability at 340°C, and a fast analysis time of less than 36 min, make it an ideal primary and/or secondary column for analysis of PCDDs and PCDFs.

Figure 4. Hexachlorinated furans and dioxins on a 60m x 0.18mm x 0.10µm Rtx-Dioxin2 GC column.



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3. Robinson C, Blow P, Dorman F. (2004) *Organohalogen Compounds*. 66: 100-05