Improved Separation and Quantification of Dioxin and Furan Congeners Using Novel Low-Bleed Capillary Gas Chromatography Columns and Mass Spectrometry

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The separation and quantitation of the dioxin and furan congeners is a very challenging analysis due to the similar structure of the various compounds. Congeners having chlorine substitution at terminal positions 2,3,7,and 8 are the most toxic, but in many cases, complete separation of these congeners from the less toxic or non-toxic other can be nearly impossible. This has resulted in the need for both primary and secondary column analysis even when using a high-resolution mass spectrometer. Most methods utilize a 5% diphenyl/95%dimethyl polysiloxane stationary phase for the primary column. These separations have a significant number of coelutions which bias the results. As a consequence, many methods use one of several cyanopropyl polysiloxane phases as a confirmatory analysis. While these columns resolve more of the congeners, they suffer from thermal limitations, and still leave some congeners unresolved.

The analysis of dioxins and furans using gas chromatography coupled to high-resolution mass spectrometry is a common environmental testing method. Dioxins and furans are monitored due to the toxicity that the congeners have when they have chlorine substitution at positions 2,3,7, and 8. In the US, the most common methods for the analysis of these compounds is either USEPA method 1613 or 8290, but this analysis is performed similarly in many countries. The overall goal of the testing methods is to accurately quantitate the 17 toxic dioxin and furan

congeners by separating them from the 136 total possible congeners with at least 4-chlorine substitution.

In order to achieve the separation requirements these methods generally require an initial analysis using a 5%-diphenyl/95%-dimethyl polysiloxane stationary phase. When this primary analysis detects the presence of 2,3,7,8-substituted congeners, most methods require a confirmatory analysis using a stationary phase that has been shown to separate these congeners from the less toxic congeners. While no single column has been universally agreed upon as the confirmation column, most laboratories use a high-cyano stationary phase like the Rtx-225, Rtx-2330, or others. While these columns yield a better separation of the 2,3,7,8-substituted congeners they all suffer from poor thermal stability, and decreased lifetime as compared to the 5-type columns used for the primary analysis. The difficulty with using the results from the 5-type column is that there are several known coelutions of environmentally-occurring non-2,3,7,8-substituted congeners with the toxic congeners. This causes false-high quantitation of the toxic congeners on the 5-type column, and results in the need for the confirmatory analysis.

Since many of the individual dioxin and furan congeners are not commercially available, analysis of flyash extracts is considered the test as to whether a column resolves the toxic congeners from the non-toxic congeners. Upon analyzing three flyash extracts that were part of a recent international round-robin study, the Rtx-Dioxin column was found to agree within 10 % of the “true” values for all 2,3,7,8-substituted congeners except for a single penta and hexa furan. This again demonstrates a significant improvement over the standard 5-type column for the primary analysis.

Overall, there is the potential need for two new stationary phases: A primary analysis column that has improved separation, and possibly higher thermal stability, and a confirmation column that has improved lifetime, and thermal stability. With these goals in mind, Restek has developed the Rtx-Dioxin2 capillary column. This column uses a new proprietary stationary phase that has a thermal stability in excess of 340C. This is an improvement over 5-type phases, as well as, the high cyano phases which have maximum operating temperatures of approximately 250C.

The Rtx-Dioxin2 capillary column has been demonstrated to separate all 17 of the toxic dioxin and furan congeners from each other, and also from all of the

environmentally-significant congeners found in the sample extracts. Using the conventional HRMS analysis, complete separation and unbiased quantification of the 17 TEF-congeners can be accomplished in about 30 minutes. Figure 1 demonstrates the excellent separation of the 2,3,7,8-tcdd congener from the others in the resolution check standard. Table 1 is comparison of the 2,3,7,8-tcdf values in several reference matrices for the results on the Rtx-Dioxin2, versus the DB-5 and DB-225.

Figure 1: Tetrachlorodibenzo-p-dioxin ion window for Rtx-Dioxin2

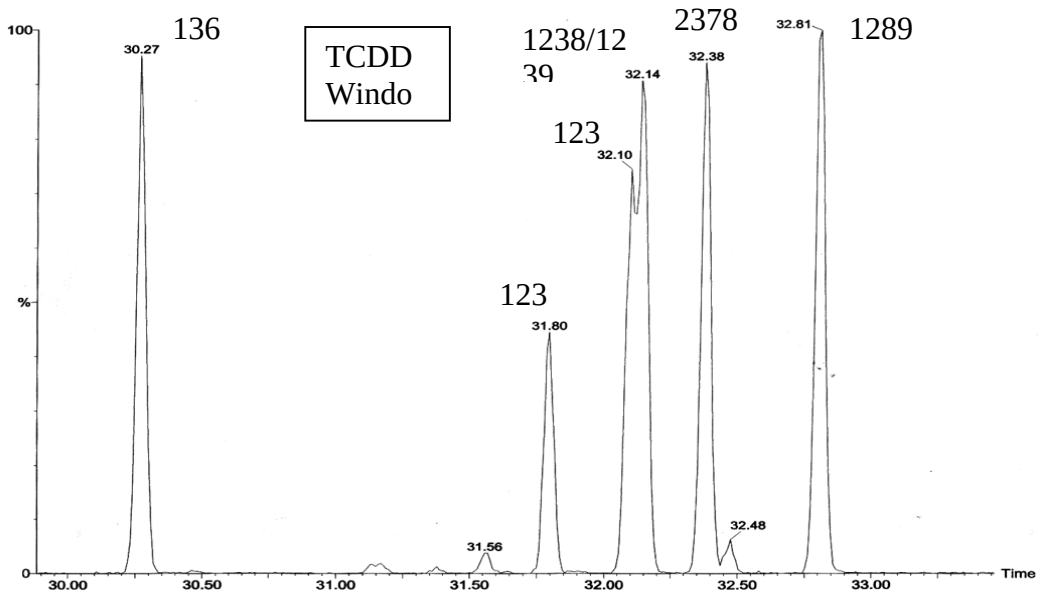

Table 1: 2,3,7,8-TCDF quantification values using the Rtx-Dioxin2

2,3,7,8-TCDF				Certified
	DB5	DB225	RTX-DIOXIN2	Value
Biota-1	1	1.3	0.8	
Biota-2	4.3	4.3	2.2	
Sediment	37	19	19	
Flyash	240	38	32	
EC-2 (DX-1)	88	n/a	37	89 (+-44)*
NIST 1974	4.7	n/a	3.3	
	All results reported as pg/g			
	* provisional (non 2378tcdf confirmed)			

This presentation will address the development of two new stationary phase chemistries that allow for improved separation of the toxic dioxin and furan congeners. Using conventional high-resolution mass spectrometry, it is possible to separate all of the congeners of interest in a single analysis on one column. Quantitation values from standard reference materials, fly ash, and previously characterized samples will be shown as evidence of how this separation is faster and more accurate than has previously been available. Finally results from comprehensive two-dimensional GC coupled to time-of-flight MS will be shown to demonstrate how this technique can rival the high-resolution method in terms of quality of information.