

Improved Resolution of Dioxins and Furans by GC-High-Resolution Mass Spectrometry, Using an Rtx®-Dioxin Capillary Column

By Frank L. Dorman, Ph.D., Director of Technical Development

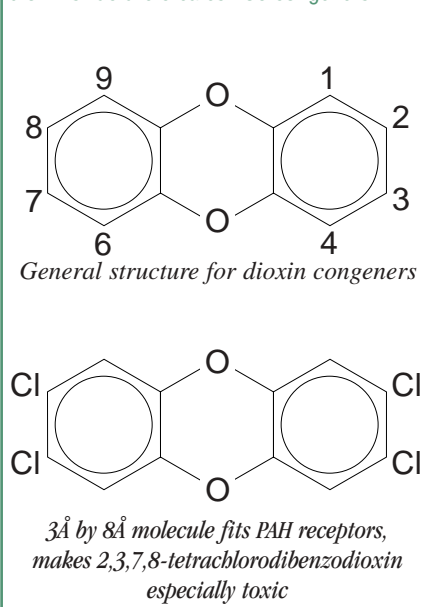
- ✓ Improved separation of dioxin and furan congeners, compared to 5% diphenyl columns.
- ✓ Greater thermal stability than 5% diphenyl columns or high-cyano confirmation columns.
- ✓ May eliminate confirmation analysis.

Gas chromatographic analysis coupled to high-resolution mass spectrometry is a common method of evaluating environmental samples for dioxins and furans. Dioxins and furans are monitored due to the toxicity of congeners that have chlorine substitution at positions 2, 3, 7, and/or 8 (Figure 1). In the US, the most common analysis methods for these compounds are USEPA methods 1613 and 8290, but the analysis is performed similarly in many countries. The overall goal of the analysis is to accurately quantify the 17 toxic dioxin and furan congeners by separating them from 119 other congeners.

In order to achieve the desired separation, most methods describe an initial analysis on a 5% diphenyl/95% dimethyl polysiloxane stationary phase. If 2-, 3-, 7-, and/or 8-substituted congeners are detected in this analysis, most methods require a confirmatory analysis on a stationary phase that separates these congeners from the less toxic congeners. While no single column has been universally agreed upon as the best confirmation column, most analysts use a high-cyano stationary phase. While these columns offer better separation of the 2-, 3-, 7-, 8-substituted congeners, analysts using any of them must contend with poor thermal stability (maximum operating temperatures of approximately 250°C) and poor column lifetimes, compared to 5% diphenyl-type columns used for the primary analysis. The difficulty with using the results from 5% diphenyl columns is that there are several known coelutions of environmentally-occurring 2-, 3-, 7-, 8-substituted congeners with less toxic congeners. This leads to falsely high values for the toxic congeners on the 5% diphenyl column, and to unnecessary confirmatory analysis.

An ideal stationary phase for this application would combine excellent separation, high thermal stability and, thereby, long column lifetime. With these goals in mind, Restek has developed the Rtx®-Dioxin column. The new, proprietary stationary phase, specifically developed for dioxins/furans analysis, is stable to temperatures above 425°C. When coated onto high-temperature fused silica tubing, the thermal limit of the column is a function of the polyimide outer coating: 380°C. Not only is this a major improvement over the thermal stability of high-cyano phases, it is an improvement over the capabilities of 5% diphenyl phases as well.

Figure 1 — Chlorine substitution in the basic dioxin structure creates 136 congeners.



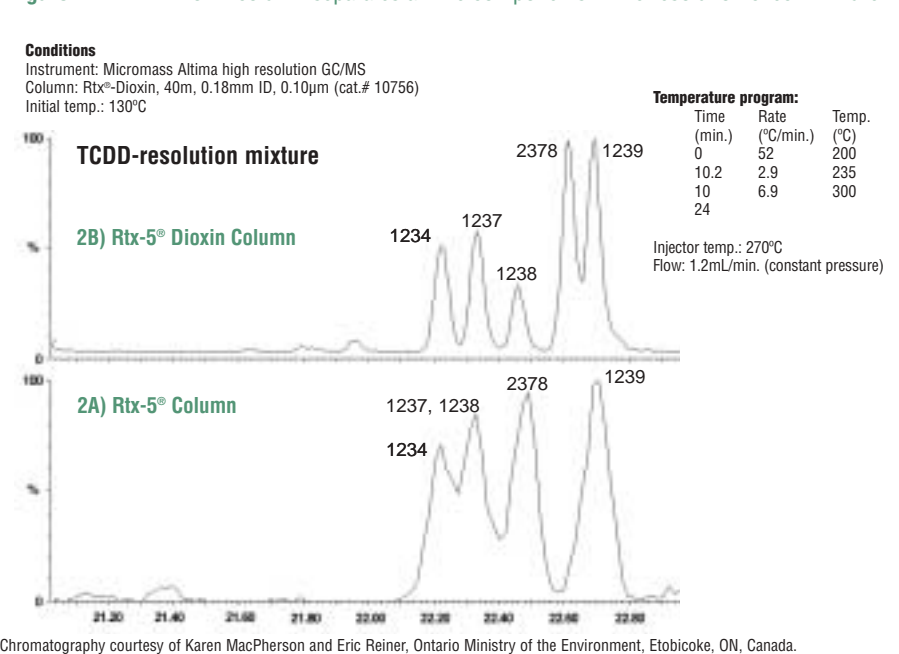
An Rtx®-Dioxin column better separates the dioxin and furan congeners, compared to 5% diphenyl columns. Most analysts experienced with dioxin and furan separations are familiar with the 4-peak tetrachlorodibenzodioxin mass pattern from a 5% diphenyl column, as shown in Figure 2A. An Rtx®-Dioxin column separates all five components in the resolution check mixture for this mass window—a significant improvement (Figure 2B). Note that 1,2,3,7- TCDD and 1,2,3,8-TCDD are tentatively identified; reference materials for individual congeners are not available.

Because few of the individual dioxin and furan congeners are available as reference materials, analysis of fly ash extracts is the accepted test of whether a column resolves the toxic congeners from the non-toxic congeners. In analyses of three fly ash extracts used in a recent international round-robin study, data from an Rtx®-Dioxin column agreed to within ±10% of the “true” values for all 2-, 3-, 7-, 8-substituted congeners, except for one penta- and one hexa-furan. This also is a significant improvement over 5% diphenyl column performance for the primary analysis. Table 1 (page 7) summarizes data for 2,3,7,8-tetrachlorodibenzofuran from an Rtx®-Dioxin column, a 5% diphenyl column, and a high-cyano column, compared to median and mean from an international round-robin study. Excellent agreement between the median and the mean, and between the Rtx®-Dioxin column and the study data, gives confidence in the proximity to the “true” value. Further work toward optimizing flow and oven temperature is in progress, to determine if the Rtx®-Dioxin column could eliminate the need for high-cyano phases for confirmation.

In summary, the new Rtx®-Dioxin column is a significant improvement over 5% diphenyl columns commonly used in the primary analysis for dioxins and

Continued on page 7

Figure 2 — Rtx®-Dioxin column separates all five components in the resolution check mixture.



Dioxins and Furans by GC-High Resolution MS... Continued from page 6

furans. The column also shows potential as a replacement for high-cyano confirmation phases with poor thermal stability and short lifetimes. We continue to work to optimize a temperature program that resolves all of the toxic congeners, with a goal of eliminating the need for confirmation.

If you are involved in the analysis of dioxins and furans, and would like additional information about Rtx®-Dioxin columns, please contact Frank Dorman at 1-800-356-1688, ext. 2186, or by e-mail at frank@restekcorp.com

Acknowledgements

Chromatography courtesy of Karen MacPherson and Eric Reiner, Ontario Ministry of the Environment, Etobicoke, ON, Canada. Reference materials courtesy of Brock Chittam, Wellington Laboratories, Guelph, ON, Canada.

Table 1 — Excellent agreement between Rtx®-Dioxin column and round-robin study data.

Sample	Column / 2,3,7,8-tetrachlorodibenzofuran (pg/g)				
	DB-5*	DB-225**	Rtx®-Dioxin	Median***	Mean***
Fly Ash A	250	21	30	28	32
Fly Ash B	2100	300	378	390	390
Fly Ash C	170	19	28	27	32

*5% diphenyl column.

**high-cyano column.

***n > 110 laboratories.

Ordering Information | Rtx®-Dioxin Columns

ID	df (µm)	temp. limits	40-Meter	60-Meter
0.18mm	0.10	-60°C to 380°C	10756	—
0.25mm	0.15	-60°C to 380°C	—	10755

New Books Available from Restek

Mass Spectrometry Basics

C. G. Herbert and R. A. W. Johnstone
CRC Press, 2002, 496 pp.
ISBN 0-8493-1354-6
cat.# 21461

Liquid Chromatography-Mass Spectrometry: An Introduction

B. Ardrey
John Wiley, 2003, 296 pp.
ISBN 0-471-49799-1
cat.# 21462

DNA Chromatography

D. T. Gjerde, C. P. Hanna and D. Hornby
Wiley-VCH, 2002, 244 pp.
ISBN 3-527-30244-1
cat.# 21463

Chromatography and Separation Science

S. Ahuja
Academic Press, 2002, 250 pp.
ISBN 0-12-044981-1
cat.# 21464

Flavor, Fragrance, and Odor Analysis

R. Marsili
Marcel Dekker, 2001, 440 pp.
ISBN 0-8247-0627-7
cat.# 21465

Solid Phase Microextraction. A Practical Guide

S. A. Schepers Wercinski
Marcel Dekker, 1999, 264 pp.
ISBN 0-8247-7058-7
cat.# 21466

Advances in Chromatography, Volume 42

P. R. Brown and E. Grushka
Marcel Dekker, 2003, 448 pp.
ISBN 0-8247-0950-0
cat.# 21467

Dioxin 2003

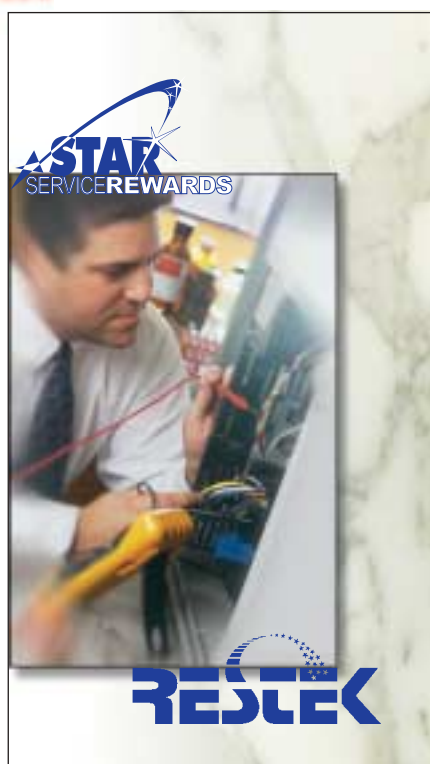
The annual meeting of world experts on these important and controversial materials, the 23rd International Symposium on Halogenated Organic Pollutants and Persistent Organic Pollutants, will be held at the Westin Copley Place Hotel, Boston, MA, August 24-29, 2003.

Specialists in dioxin research will make more than 500 presentations and discuss current knowledge. "Hot topics" sessions will focus on endocrine disrupters, Arctic POPs, neurotoxicity, ultimate trace method, and more.

For details, visit www.dioxin2003.org or contact Laura Biringer, 617-262-3424 / Lbiringer@mpwi.org

Dioxin 2003

new!



STAR Service Rewards Program

Restek Corporation has formed an alliance with some of the premiere independent instrument service providers in the United States, with a goal of bringing you the finest chromatography operating supplies, equipment service, and applications support available.

We are pleased to introduce a new program that pays you for using Restek products, by reducing your costs for quality instrument service: STAR Service Rewards. Similar to our popular Restek Wizard Dollar program, STAR Service Rewards pays you one STAR Point for every \$50 of Restek products you purchase. Redeem STAR Points with participating STAR member service providers for selected service, equipment, and training products. You get the finest chromatography operating supplies from Restek and high quality instrument service from your preferred service provider. STAR Service Rewards is one more example of why Restek is the company chromatographers trust for complete chromatography support.

STAR, the Service and Technology Alliance by Restek, is an affiliation of independent instrument service providers, original equipment manufacturers, and instrument remanufacturers, working with Restek to provide chromatographers with the most complete level of support available in the industry.

For more information about the STAR Service Rewards Program, to view the list of member service providers, or to register your lab;

- Call Restek Customer Service at **800-356-1688 ext.3**, or
- Go to the Restek web site—
<http://www.restekcorp.com/star>

