GCxGC-TOFMS of Chlorinated Dioxins and Furans in Environmental Samples

Jack Cochran[1], Jean-Francois Focant[2], Andreas Sjödin[2], Donald Patterson, Jr.[2], Eric Reiner[3], Karen MacPherson[3], Terry Kolic[3], Frank Dorman[4], Shawn Reese[5]

[1]LECO Corporation, Las Vegas
[2]Centers for Disease Control, Atlanta
[3]Ministry of Environment, Toronto
[4]Restek Corporation, Bellefonte
[5]Folsom Lake College, Folsom

Introduction

Chlorinated dioxins and furans are toxic organic compounds found in the environment, usually at relatively low levels. The typical instrumental approach to their determination, after sample extraction and cleanup, is high resolution GC – high resolution MS (HRGC-HRMS). The United States Environmental Protection Agency (EPA) methods 1613[1] and 8290A[2] specify HRGC-HRMS (with selected ion recording) to meet the sensitivity and selectivity necessary for dioxin analysis. One of the challenges is to not only separate the dioxins and furans from other interferences (either through chromatography or HRMS) that can be at higher concentration levels, but also to separate the most toxic congeners from each other within their respective homolog groups. For individual quantification of isomers, chromatographic separation is mandatory.

An alternate way to approach the dioxin and furan separation problem is to use comprehensive two-dimensional GC (GCxGC)[3]. GCxGC increases peak capacity by applying two independent separations to a sample in one analysis. Typically, GCxGC involves press-fitted serial columns (differing phases) separated by a thermal modulator. One separation is performed on the first column, and its effluent is continually focused and "injected" onto the second column, where another separation occurs. By keeping the second column short a series of high-speed chromatograms are generated, and the first column separation is maintained. Separation results are plotted as a retention plane (column 1 time x column 2 time), which is also known as a contour plot.

The focusing process of GCxGC leads to peaks on the order of 50 to 500 ms wide, so a fast detector is required. When MS is used, only time-of-flight (TOF) has the necessary acquisition rates (hundreds of spectra/sec). Even though a fast TOF is a low resolution MS, the separating power of GCxGC gives the potential to provide selectivity for dioxin and furan analysis. The focusing effect of GCxGC enhances sensitivity, so that sub- to low pg levels can be determined.

This work describes preliminary results obtained using GCxGC-TOFMS with isotope dilution quantification for the determination of chlorinated dioxins and furans in a variety of environmental and biological matrices.

Methods and Materials

Standards and Samples: The EPA-1613CVS dioxin and furan calibration solutions were from Wellington Laboratories (Canada) and contained native compound concentrations ranging from 0.5 to 2000 pg/µL, depending on the congener. ^{13}C-labeled internal standards were present at 100 and 200 pg/µL. Fly ash, sediment, fish, and vegetation extracts were prepared according to previously published methodology[3].

GCxGC-TOFMS: A Pegasus 4D GCxGC-TOFMS (LECO Corporation, USA), which can acquire up to 500 full-range mass spectra per second, was used with electron ionization at 70eV and an MS source temperature of 250°C. The acquired mass range was 160 to 520u at 100 spectra/sec. The detector was set at 1800V. The acquisition rate was chosen to define the extremely narrow peaks (~150 ms) generated under the GCxGC conditions described below, and to allow spectral deconvolution of closely eluting peaks.

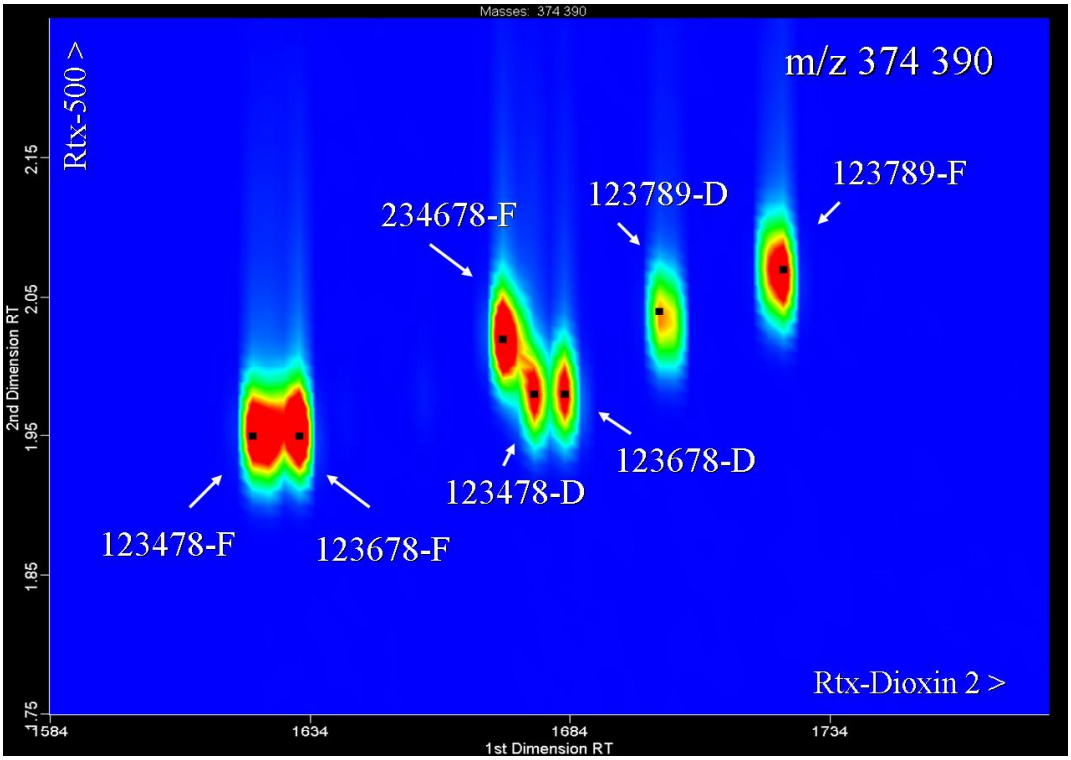
The primary (first dimension) GC column was a 60m x 0.25mm x 0.25µm Rtx-Dioxin 2 (Restek Corporation, USA) connected by a press-fit to a secondary GC column that was a 2.5m x 0.18mm x 0.10µm Rtx-500 (Restek). The secondary column was installed in its own oven. This column combination was operated with helium carrier at an approximate constant flow of 2.5 mL/minute. One microliter direct injections were performed by hand into a 4mm Uniliner (Restek) at 275°C. Standards and samples were analyzed under the following GC oven program: The primary oven was held at 130°C for one minute, programmed at 40°/min to 210°, and then programmed at 4°/min to 330° where it was held for five min. The secondary oven was programmed at a positive 20°C offset from the primary oven. A quad jet, dual-stage modulator was used with a temperature offset of 60°C and a modulation time of 3 sec. Modulation occurred on the secondary column. The total run time was 38 minutes.

LECO ChromaTOF software, the built-in control, acquisition, and data manipulation platform for the Pegasus 4D GCxGC-TOFMS system, was used for data processing, including automated peak find and spectral deconvolution, and isotope dilution quantification.

Results and Discussion

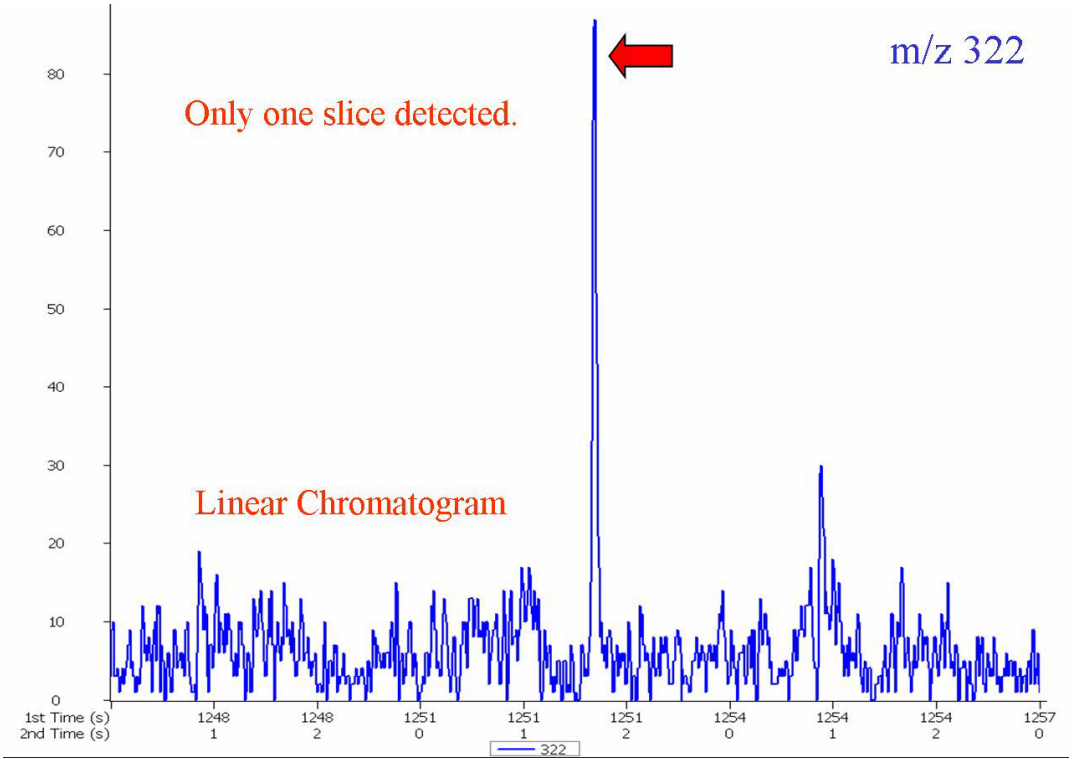
The Rtx-Dioxin 2 has tentatively been shown to provide separation of the 17 toxic dioxins and furans from each other and additional congeners that could act as interferences. Figure 1 is a contour plot of some of the hexachlorinated dioxins and furans from a calibration solution, and indicates several of the most critical separations achieved by the Rtx-Dioxin 2 column (the first dimension), including that of 1,2,3,4,7,8- and 1,2,3,6,7,8-hexachlorinated dibenzofurans (HxCDFs).

Figure 1: GCxGC-TOFMS contour plot of hexachlorinated dioxins and furans.



The GCxGC-TOFMS calibration curve correlation coefficients for the seventeen dioxins and furans specified in the EPA Methods were 0.995 or greater. The most intense molecular ion in the chlorinated cluster was always used for calibration and quantification purposes. A linear chromatogram from the analysis of the 0.5 pg/µL standard of 2,3,7,8-tetrachlorodibenzodioxin (TCDD) is illustrated in Figure 2. For a more concentrated standard, a total of three "slices" would have been noted in the linear chromatogram, due to the modulation of the original one-dimensional peak. But in this case, only one slice is seen due to the low concentration of the TCDD, and its proximity to the detection limit of the TOFMS.

Figure 2: Linear chromatogram of 0.5 pg of 2,3,7,8-tetrachlorodibenzodioxin analyzed with GCxGC-TOFMS.



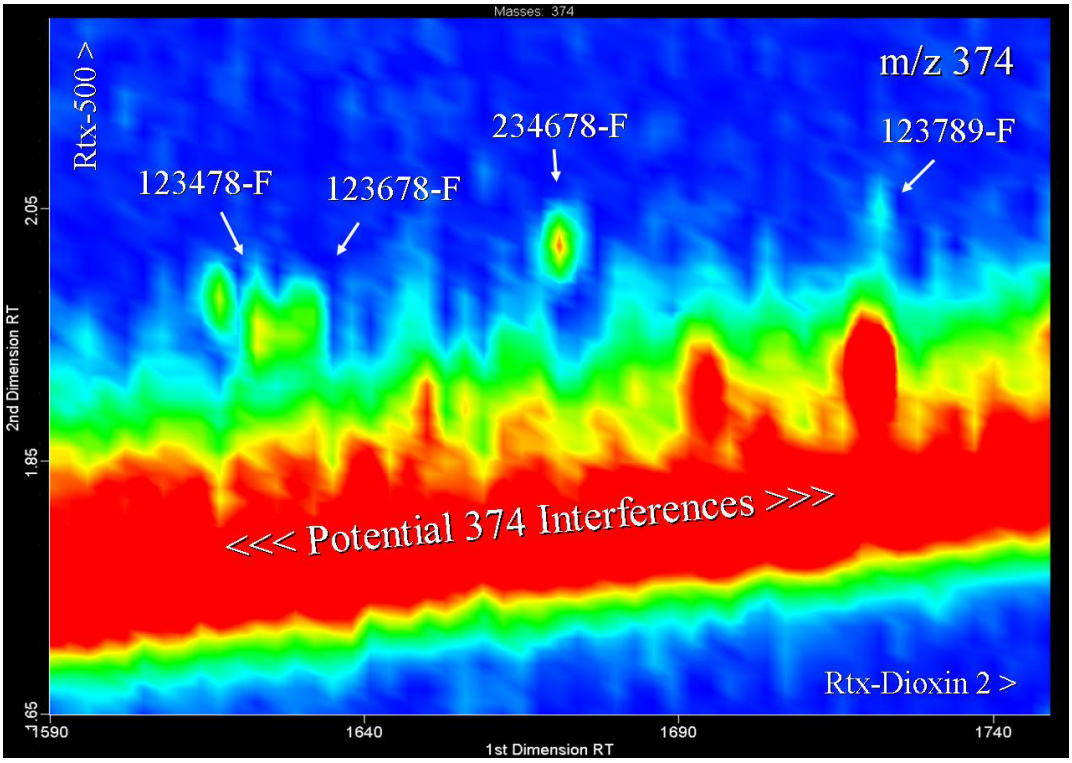
Quantitative results are presented in Table 1 and demonstrate the viability of using GCxGC-TOFMS by comparing those values to HRGC-HRMS results. In most cases, the HRGC-HRMS and GCxGC-TOFMS numbers show good agreement. Obvious exceptions are the octachlorodibenzofuran (OCDF) and octachlorodibenzodioxin (OCDD) for the fish sample, where a known syringe contamination occurred from a previous high-level sample.

Table 1: Comparison of HRGC-HRMS and GCxGC-TOFMS values for chlorinated dioxins and furans in several matrices. ND = not detected.

	Sediment			Fish			Fly Ash	
Compound	**HR**	**TOF**		**HR**	**TOF**		**HR**	**TOF**
Furans								
2378	60	71		30	17		38	38
12378	23	18		6.6	11		72	80
23478	570	510		7.3	9.4		170	150
123478	490	360		3.6	4.1		570	250
123678	26	26		2.7	6.1		260	210
234678	13	18		3.7	2.8		440	480
123789	1.5	13		< 0.5	1.0		22	42
1234678	210	210		< 2.0	9.9		2300	2700
1234789	16	13		< 0.50	ND		180	190
OCDF	490	360		< 1.0	7.0		1600	1500
Dioxins								
2378	170	170		7.4	19		5.6	2.0
12378	4.4	13		1.3	ND		25	46
123478	12	15		< 0.70	ND		40	41
123678	21	17		4.6	1.7		78	61
123789	15	23		< 2.0	1.8		40	51
1234678	230	230		5.8	4.2		750	800
OCDD	1400	1200		< 7.0	22		4600	4300

The importance of the Rtx-500 column (second dimension) in the GCxGC separation of the analytes of interest from matrix components in a fish sample is demonstrated in Figure 3. With only a nominal mass instrument, such as the TOFMS employed for this work, a one-dimensional GC analysis would be impossible for the hexachlorinated dibenzofurans (HxCDFs) due to the m/z 374 interferences from the sample matrix. A review of the Table 1 data for the HxCDFs in fish show that the TOFMS values and HRMS values are in relatively good agreement.

Figure 3: Contour plot showing separation of hexachlorinated dibenzofurans from matrix interferences in a fish extract. The molecular ion used for quantification, 374, is plotted.



References

1 United States Environmental Protection Agency. "Method 1613 - Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS", October 1994.

2 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.

3 Focant J-F., Reiner E.J., MacPherson K., Kolic T., Sjödin A., Patterson, Jr. D.G., Reese S.L., Dorman F.L., and Cochran J. (2004) Talanta (in press).