RESTEK environmental

Applicationsnote

Fast Analysis of Dioxin and Related Compounds Using an Rtx^{fi}-5MS Column

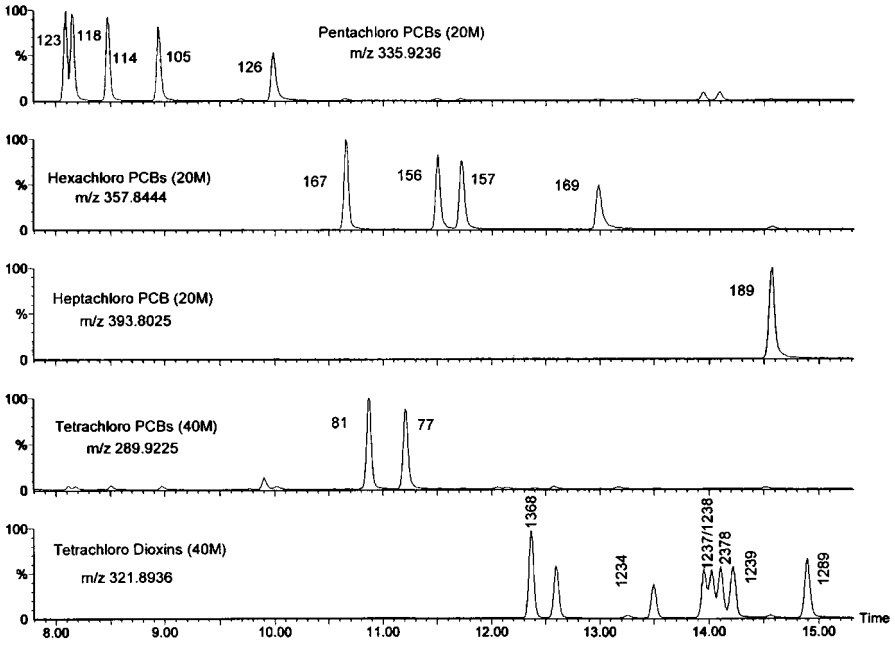
Dioxin and furan testing can be very time consuming and costly. Total analyses times can easily exceed one hour per sample, and instrument time on high-resolution mass spectrometers (MS) is quite valuable. In addition, many samples analyzed for dioxins and furans require analysis for polychlorinated biphenyls (PCBs) as well. Researchers at the Ontario Ministry of the Environment (MOE) and Restek have recently developed a method for more rapid dioxin, furan, and PCB analysis.

Historically, chlorinated dioxins and furans have been analyzed by gas chromatography (GC) separately from PCBs. In 1998, the World Health Organization (WHO) reported toxic equivalent factors (TEFs) for the 12 dioxin-like PCB congeners.[1] This enabled concentrations of PCBs to be expressed in terms of 2,3,7,8-TCDD, the most toxic form of dioxin. Using similar methods to analyze dioxins and PCBs allows detection limits up to three orders of magnitude lower than that of conventional PCB congener methods. The toxicity of a single sample now can be reported in toxic equivalents of 2,3,7,8,-TCDD (i.e., toxic equivalent quantities [TEQ]) by summing the toxic equivalents of each of the 17 toxic dioxin congeners and 12 dioxin-like PCB congeners.

Extracts were prepared according to Canada's MOE Method 3418, which is similar to the combination of US Environmental Protection Agency (EPA) Methods 1613 and 1668. The extracts are further cleaned using activated carbon.[2] This allows for the collection of two sample extract fractions: one containing the dioxins, furans, and coplanar PCBs; and the other containing the remaining PCBs, chlorinated and brominated diphenyl ethers, and other non-planar organic compounds. The chlorinated diphenyl ethers interfere with the furans and, therefore, they need to be analyzed separately. Normally, dioxins and furans, and PCBs (congeners) are analyzed separately on a 60m analytical column using GC/high resolution mass spectrometry (GC/HRMS) with analysis times of 50 to 90 minutes each.

Figure 1

The Rtx^{fi}-5MS column and a combined system can separate dioxin-like PCBs and dioxins/furans within 30 minutes.



GC_EV00392

Inj. temp.: 280°C; **Carrier gas:** helium; **Det.:** Agilent 6890 GC coupled to a Micromass Ultima HRMS @10,000RP.

20m, 0.1mm ID, 0.1µm Rtx®-5MS (custom cat.# 58136). **Column head pressure:** 100psi; **Oven program:** 100°C (hold 1 min.) to 200°C @ 100°C/min, to 235°C @ 13°C/min., to 300°C @ 27°C/min. (hold 4 min.); **Inj. volume:** 0.2mL

40m, 0.18mm ID, 0.18µm Rtx®-5MS (custom cat.# 550590). **Column head pressure:** 61psi; **Oven program:** 100°C (hold 0.62 min.) to 200°C @ 64.5°C/min, to 235°C @ 4.8°C/min. (hold 6.2 min.), to 300°C @ 9.7°C/min.(hold 5.6 min.); **Inj. volume:** 1.0mL

Table I

Mass windows used for parallel column system.

Mass Group	M/Z	Species	Fraction	Column (m)
1	289.9225,291.9195*	Cl_4CB	PCDD/F/COP	40
	301.9626,303.9598*	$13C_{12}$- Cl_4CB	PCDD/F/COP	40
	323.8834,325.8805*	Cl_5CB	MONO-ORTHO	20
	330.9792,330.9792	PFK Lock Mass, Lockmass Check		
	335.9236,337.9207*	$13C_{12}$- Cl_5CB	MONO-ORTHO	20
	357.8444,359.8415*	Cl_6CB	MONO-ORTHO	20
	371.8817*,373.8788	$13C_{12}$- Cl_6CB	MONO-ORTHO	20
	393.8025*,395.7996	Cl_7CB	MONO-ORTHO	20
2	303.9016,305.8987*	Cl_4CDF	PCDD/F/COP	40
	315.9419,317.9389*	$13C_{12}$- Cl_4CDF	PCDD/F/COP	40
	318.9792,318.9792	PFK Lock Mass, Lockmass Check		
	319.8965,321.8936*	Cl_4CDD	PCDD/F/COP	40
	327.8847	$^{37}Cl_4CDD$	PCDD/F/COP	40
	331.9368,333.9339*	$13C_{12}$- Cl_4CDD	PCDD/F/COP	40
	323.8834,325.8805*	Cl_5CB	PCDD/F/COP	40
	335.9236,337.9207*	$13C_{12}$- Cl_5CB	PCDD/F/COP	40
	357.8444*,359.8415	Cl_6CB	PCDD/F/COP	40
	371.8817*,373.8788	$13C_{12}$- Cl_6CB	PCDD/F/COP	40
	393.8025*,395.7996	Cl_7CB	MONO-ORTHO	20
	375.8364	Cl_6DPE	MONO-ORTHO	20
	405.8428*,407.8398	$13C_{12}$- Cl_7CB	MONO-ORTHO	20
3	339.8597*,341.8567	Cl_5CDF	PCDD/F/COP	40
	351.9000*,353.8970	$13C_{12}$- Cl_5CDF	PCDD/F/COP	40
	366.9792,366.9792	PFK Lock Mass, Lockmass Check		
	353.8576,355.8546*,357.8517	Cl_5CDD	PCDD/F/COP	40
	357.8444,359.8415*,361.8385	Cl_6CB	PCDD/F/COP	40
	367.8949*,369.8919	$13C_{12}$- Cl_5CDD	PCDD/F/COP	40
	371.881*,373.8788	$13C_{12}$- Cl_6CB	PCDD/F/COP	40
	405.8428*,407.8398	$13C_{12}$- Cl_7CB	PCDD/F/COP	40
	409.7974	Cl_7DPE	PCDD/F/COP	40
	427.7635	Cl_8CB	PCDD/F/COP	40
4	373.8208*,375.8178	Cl_6CDF	PCDD/F/COP	40
	383.8639,385.8610*	$13C_{12}$- Cl_6CDF	PCDD/F/COP	40
	389.8157*,391.8127	Cl_6CDD	PCDD/F/COP	40
	380.976,380.976	PFK Lock Mass, Lockmass Check		
	401.8559*,403.8829	$13C_{12}$- Cl_6CDD	PCDD/F/COP	40
	445.7555	Cl_8DPE	PCDD/F/COP	40
5	407.7818*,409.7789	Cl_7CDF	PCDD/F/COP	40
	417.8250,419.8220*	$13C_{12}$- Cl_7CDF	PCDD/F/COP	40
	423.7766*,425.7737	Cl_7CDD	PCDD/F/COP	40
	435.8169*,437.8140	$13C_{12}$- Cl_7CDD	PCDD/F/COP	40
	430.9728,430.9728	PFK Lock Mass, Lockmass Check		
	479.7165	Cl_9DPE	PCDD/F/COP	40
6	441.7428,443.7400*	Cl_8CDF	PCDD/F/COP	40
	457.7377,459.7348*	Cl_8CDD	PCDD/F/COP	40
	469.7779,471.7750*	$13C_{12}$-O_8CDD	PCDD/F/COP	40
	454.9728,454.9728	PFK Lock Mass, Lockmass Check		

* - ion occurs at 100% intensity in molecular ion cluster. All ions (m/z) monitored for detection of native species had a dwell time of 50ms. Detection of corresponding $13C_{12}$-labelled specie ions had dwell times of 25ms. Delay times were set at 10ms.

Because an MS is used for detection, many analysts want a column with the lowest bleed possible. Some laboratories may use silarylene columns (e.g., Rtx®-5Sil MS or DB-5MS® columns) due to their low bleed feature. However, these columns yield a coelution between 2,3,7,8-TCDD and 1,2,3,9-TCDD; and their elution orders and retention times will differ from the phase for which the window performance mixtures were designed. The Rtx®-5MS (5% diphenyl/95% dimethyl polysiloxane) column is better suited to meet the performance standards for this analysis. It separates all of the important compounds within 30 minutes, and each one is individually tested to provide low bleed levels for MS detection.

Chromatographic resolution and analysis time also are dependent on column dimensions (i.e., length, ID, phase thickness). Experimentally, we have found 175,000 plates are required to obtain separation of 2,3,7,8-TCDD from its nearest neighbors (1,2,3,7- and 1,2,3,8-TCDD the unresolved pair eluting before; and 1,2,3,9-TCDD the compound eluting after).[3] A 40m, 0.18mm ID, 0.18 m Rtx®-5MS column meets this criteria, and can complete the analysis in approximately half as much time as a 60m column. A 20m, 0.10mm ID, 0.10 m Rtx®-5MS column is capable of meeting these requirements in about one-quarter the time of a 60m column; however, there is little tubing length available for trimming to maintain column performance. Therefore, we suggest using a 40m column.

To minimize the number of ions that must be monitored simultaneously, elute the bulk of PCB compounds prior to eluting dioxin and furan compounds. Accomplish this by injecting the non-coplanar PCB fraction into a 20m Rtx®-5MS column that is set up parallel (i.e., two separate injectors) to a 40m Rtx®-5MS column, which is used for the separation of the dioxin/furan/coplanar PCB fraction. Both fractions are injected simultaneously. The columns are installed into the MS ion source in parallel. The resulting analysis time is less than that for a single fraction on a conventional 60m column (Figure 1). Table I summarizes the high resolution MS conditions and which masses are monitored for which compound.

For the analysis of dioxin-like PCBs and dioxins/furans, method consolidation and throughput increase is possible when using a parallel, dual-column system with GC/HRMS. This method allows the combination of several different analytical methods to a single system, and results in a total analysis time of less than 30 minutes for elution of octachlorodibenzodioxin.

References

1. Berg, M. V., L. Birnbaum, A.T.C. Bosveld, B. Brunstrom, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X.R. Leeuwen, A.K.D. Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, and T. Zacharewski, Environmental Health Perspectives, 106 (1998), p. 775.
2. Kolic T.M., K. A. MacPherson, E.J. Reiner, T. Gobran, and A. Hayton, Organohalogen Compounds, 46 (2000), p. 562.
3. Reiner E.J., K.A. MacPherson, R. Brunato, T. Chen, M.A. Bogard, A.R. Boden, and G. Ladwig, Organohalogen Compounds, 45 (2000), p. 17.

Product Listing

Rtx®-5MS Columns				
ID	**df (m)**	**temp. limits**	**20-Meter**	**40-Meter**
0.10mm	0.10	-60 to 330/350 C	58136	
0.18mm	0.18	-60 to 330/350 C		550590

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