Selectivity of PCBs at Low Level With High Precision Using Triple Quadrupole GC-MS/MS

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Overview

Purpose: To demonstrate the ability of the Thermo Scientific TSQ Quantum XLS Series Triple Quadrupole GC-MS/MS to analyze the 209 PCB congeners listed in EPA Method 1668A at low levels with high precision and can be used for screening of PCBs even in difficult matrices.

Methods: Retention times were determined in full scan mode and then a timed-SRM method was developed. Standards were analyzed at concentrations as low as 20 fg on-column, and precision was determined at 100 – 300 fg. A variety of matrices were spiked at low levels.

Results: Individual compound %RSDs ranged from 5 to 32 analyzing 9 replicate samples with an average for all 209 congeners of 13%. Low level matrix spikes demonstrated the selectivity of the instrument.

Introduction

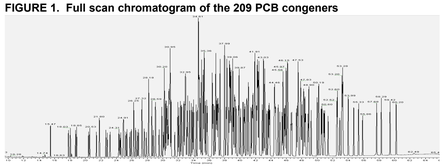
This application details a fast, reliable and highly selective trace level screening method for the quantitation of PCBs in environmental, food and biological samples, using triple stage quadrupole mass spectrometry with the TSQ Quantum™ XLS Series Triple Quadrupole Mass Spectrometer. The analytical strategy is analogous to the well-established United States Environmental Protection Agency (USEPA) Method 1668A.[1]

Methods

Sample Preparation

Standards were purchased from the AccuStandard® Catalogue (#M-1668-1-0.01X) and included 5 vials containing the 209 PCB congeners. The five mixes were analyzed in full scan to determine retention times, then combined to provide a standard mix with all 209 PCB congeners. Figure 1 is a full scan chromatogram of all 209 PCB congeners. Serial dilutions were performed to provide a concentration range of 0.020 to 1500 pg/µL.

FIGURE 1. Full scan chromatogram of the 209 PCB congeners



Separation was performed on a Thermo Scientific TRACE GC Ultra using a Thermo Scientific TRACE TR-PCB 8MS column. GC parameters are provided in Table 1.

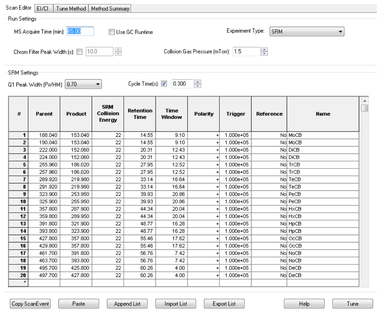
TABLE 1. GC Parameters

Oven	Ramp	Temp	Hold
		75°C	2 min
	15° C/min	150°C	0 min
	2.5° C/min	290°C	2.5 min
SSL inlet			
Temp	270°C		
Split Flow	50ml/min		
Splitless Time	1.00 min		
Stop Purge Time	1.00 min		
Carrier	1.2 ml/min		
Transferline Temp	290°C		

Mass Spectrometry

Analysis of the 209 PCB congeners was performed on the TSQ Quantum XLS Series GC-MS/MS with the source temperature at 290 °C and emission current set to 50 µA. The remaining parameters are displayed in Figure 2. The timed-SRM function was used to provide overlapping transitions for the differing levels of chlorination.

FIGURE 2. List of MS parameters from Thermo Scientific Xcalibur software



Data Analysis

An Xcalibur™ instrument method was used for controlling the GC and MS during data collection. Thermo Scientific QuanLab Forms software was used to process the data.

Results

20 fg Injection

The lowest standard injected contained 20 -60 fg/µL. Even at such a low level, good peak shapes and the number of scans across the peak were very good for most of the compounds as shown in Figures 3 and 4.

FIGURE 3. Xcalibur software showing the number of scans across the peaks of 2,3,5-TrCB, 2',3,5-TrCB, and 2,4,5-TrCB at 20 fg/µL

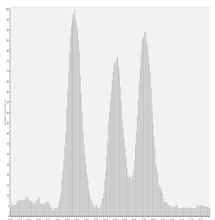
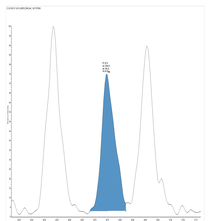


FIGURE 4. QuanLab™ Forms showing the peak shapes of the same three Tri-Chlorinated PCBs at 20 fg/µL



Precision at 100 - 300 fg/µL

The standard containing 100 – 300 fg/µL was injected nine times to provide data for precision of the instrument. These calculations are based on the areas of each compound and not the concentration using internal standard calibration. The average % RSD for all compounds was 13 %. Table 2 shows the average % RSDs for each level of chlorination and the concentration of the standard. The % RSDs for each of the toxics are exhibited Table 3.

TABLE 3. Average % RSD for each level of chlorination

% RSD		fg/µL
9	Mono-Chlorinated	100
7	Di-Chlorinated	100
9	Tri-Chlorinated	100
11	Tetra-Chlorinated	200
13	Penta-Chlorinated	200
15	Hexa-Chlorinated	200
19	Hepta-Chlorinated	200
18	Octa-Chlorinated	300
16	Nona-Chlorinated	300
13	Deca-Chlorinated	300

TABLE 4. % RSD of nine replicates for the toxic list of PCBs

% RSD		% RSD	
8	2-MoCB	18	2,3,4,4',5-PeCB
8	4-MoCB	15	2,3,3',4,4'-PeCB
6	2,2'-DiCB	14	2,2',3,4,4',5,6'-HpCB
5	2,2',6-TrCB	19	2,2',3,4,4',5',6-HpCB
7	4,4'-DiCB	10	3,3',4,4',5-PeCB
7	2,2',6,6'-TeCB	16	2,3',4,4',5,5'-HxCB
8	2,3,5-TrCB	17	2,3,3',4,4',5-HxCB
6	2',3,5-TrCB	20	2,3,3',4,4',5'-HxCB
6	2,2',4,6,6'-PeCB	19	2,2',3,4,4',5,5'-HpCB
12	3,4,4'-TrCB	26	2,2',3,3',4,4',5-HpCB
12	2,2',4,4',6,6'-HxCB	12	3,3',4,4',5,5'-HxCB
14	3,4,4',5-TeCB	14	2,2',3,3',4,5,5',6,6'-NoCB
16	3,3',4,4'-TeCB	22	2,3,3',4,4',5,5'-HpCB
13	2,2',3,4,4',5,6,6'-HpCB	11	2,3,3',4,4',5,5',6-OcCB
15	2',3,4,4',5-PeCB	16	2,2',3,3',4,4',5,5',6-NoCB
15	2,3',4,4',5-PeCB	13	2,2',3,3',4,4',5,5',6,6'-DeCB

Performance with Complex Matrices[2]

To test the chromatographic and mass acquisition methods with matrix samples, a number of challenging sample types were prepared. The TSQ Quantum XLS Series GC-MS/MS demonstrated excellent sensitivity, selectivity and robustness with these samples, as shown in Figures 5 through 8. These results allow for comparison of the results achieved for the pentachloro-PCBs in matrices covering blood, milk, egg yolk and green cabbage. The system provided clean and background-free mass traces for all types of matrix studied. Even in very complex samples such as blood (Figure 5) and green cabbage (Figure 8), no increase in the level of background can be observed.

Compared to the standard runs, the PCB concentrations in sample range from a mid-femtogram (fg) to the low picogram (pg) level. PCB concentrations were measured at 0.2 and 1.0 pg/µL for native PCBs and at 100 pg/µL for all added ^{13}C-labeled internal standards. The selectivity of the TSQ Quantum XLS Series Triple Quadrupole GC-MS/MS virtually eliminates matrix interference, allowing for low detection limits, enhanced confidence in quantitative results, and accurate identification of these compounds.

FIGURE 5: dl-Pentachloro-PCBs in a blood sample

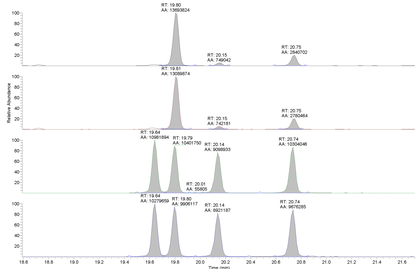


FIGURE 6: dl-Pentachloro-PCBs in milk

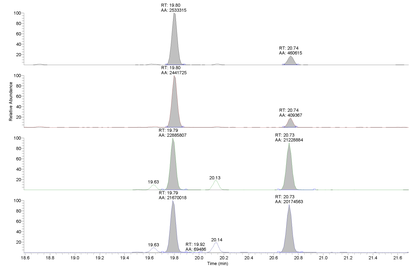


FIGURE 7: dl-Pentachloro-PCBs in egg yolk

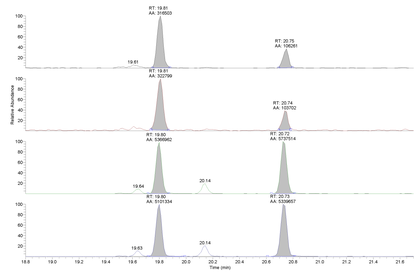
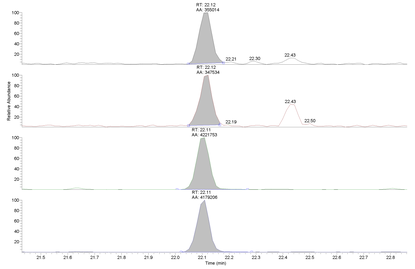


FIGURE 8: dl-Pentachloro-PCBs in green cabbage



Conclusion

The TSQ Quantum XLS Series GC-MS/MS facilitates the screening and quantitation of PCBs at low levels in difficult matrix samples and provides results with high certainty. The analytical setup complies with USEPA Method 1668A, following an isotope dilution quantitation protocol. The added ^{13}C-labeled internal standard components were detected with high reliability as demonstrated in different samples with complex matrix background.

Confirmatory methods provide information on the chemical structure of the analyte. The TSQ Quantum XLS Series GC-MS/MS with its unique hyperbolic quadrupole technology offers superior and uniform selectivity for low level PCB samples in different complex matrices including egg, milk, cabbage and blood. Using the system in H-SRM mode, the PCB pattern that is typical when using high resolution mass spectrometry, such as magnetic sector, can be detected.

The proposed MS/MS measurement scheme using two precursor ions and SRM detection of individual product ions is a valuable solution for screening for PCBs in various complex matrices at the relevant levels. For the fast control of food samples, the TSQ Quantum XLS Series GC-MS/MS exceeds the current EU directives for a minimum of four (4) identification points, in that the method described here offers five (5) identification points.

For contract and governmental control labs, the TSQ Quantum XLS Series Triple Quadrupole GC-MS/MS provides a high productivity solution with increased sample throughput even for complex matrix samples. The system delivers ultimate performance in PCB trace analysis with the added economic advantage of using reduced clean-up methods.

References

1. US EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, United States Environmental Protection Agency, Office of Water, EPA No. EPA-821-R-00-002,December 1999.

2. Thermo Scientific Application Note 10262, "Analysis of PCBs in Food and Biological Samples, Using GC Triple Quadrupole GC-MS/MS", *Dirk Krumwiede, Hans-Joachim Huebschmann.*