



AN 9163 Femtogram Sensitivity for PCBs in a Single Injection by GC-MS/MS

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Introduction

Contamination of the environment with polychlorinated biphenyls (PCBs) is a serious global concern due to their persistence and long term health effects to both humans and animals. Initially, analytical tests looked for chromatographic patterns that signified different manufacturers' PCB blends. These tests were traditionally run either with GC/ECD or GC/MS. Later, as it became more important to classify the PCBs based on their toxicity rather than their origin, the ability to detect and identify individual PCB congeners became necessary. The individual PCB congeners were evaluated for their adverse health effects, and as a result, twelve were named by the World Health Organization as most 'dioxin-like' in their toxicity. Concurrently, the need arose to detect the lower levels of PCBs that are found in our food supply. For this type of analysis, one requiring low detection limits and high specificity, an extensive sample cleanup followed by high resolution mass spectrometry (HRMS) had traditionally been required. Alternatively, the use of tandem mass spectrometry (MS/MS) can produce similar results with reduced sample cleanup.

With HRMS, specificity is enabled through the instruments ability to discern exact mass. With MS/MS, specificity is obtained through the product ion spectrum and its relationship to the parent ion. MS/MS first isolates the target ion(s), then applies a selected RF voltage to generate an interpretable product ion spectrum. A coeluting contaminant peak will not produce the

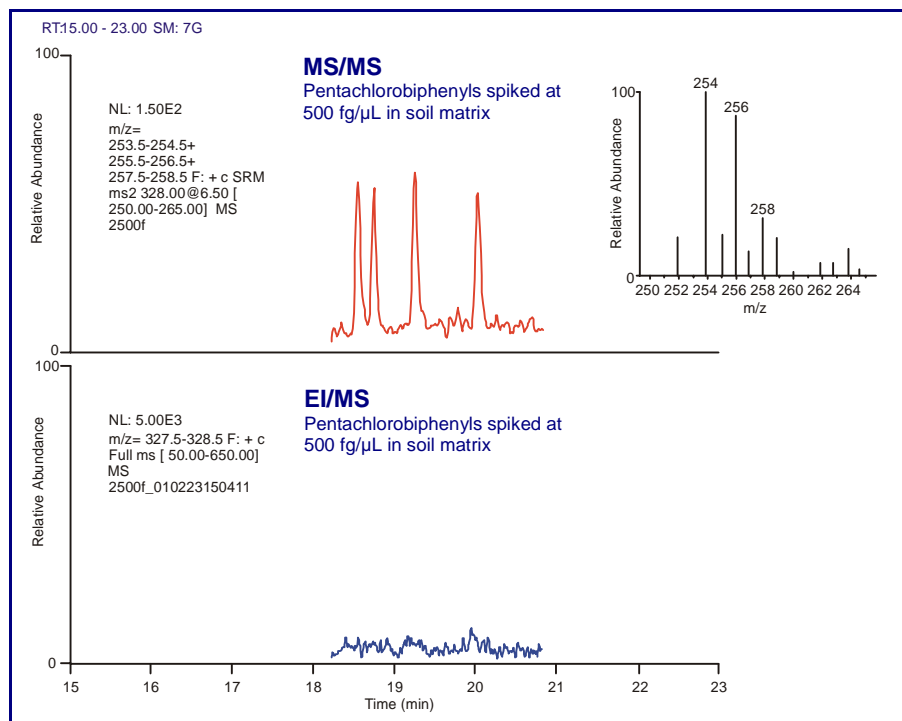


Figure 1. MS and MS/MS sensitivity comparison for trace analysis of PCBs in a soil extract

correct product ion spectrum, and so will not be quantitated as the target analyte. Since the large majority of matrix ions are removed from detection by MS/MS, the extracted ion chromatogram is virtually free of interference (Figure 2). Further enhancement of the ion trap, allows for greater sensitivity, lowering the detection limit approximately five-fold for the polychlorinated biphenyl class, and giving the user detection limits in the femtogram range.

This study will show how optimized MS/MS can give femtogram level detection of PCBs in soil, without the necessity of lengthy sample cleanup.

Instrument Parameters

PolarisQ Ion Trap
 Source temperature: 250°C
 Ionization mode: Electron Ionization
 AGC: 15
 Injection waveforms: On
 Waveform amplitude: 9.7 volts
 Trap pressure: 17 mtorr
 MS/MS parameters: See Table 1

TRACE GC
 Column: BPX5, 0.15mm x 25m, 25µm
 Oven: 100°C, 1 min
 Ramp One: 20°C/min to 200°C, hold 1.5 min
 Ramp Two: 3°C/min to 270°C, hold 1.67 min
 Purged/Packed injector
 Injector temperature: 250°C
 Wide Bore injection: Split
 Split ratio: 15:1
 Constant flow: 0.9 mL/min He

AS2000
 Injection volume: 2 µL

Method

Soil samples of five grams each were sonicated for fifteen minutes in 5 mL of either dichloromethane or acetone. The solvent was then removed from the matrix, and evaporated to dryness with nitrogen. The residue was redissolved in 2.0 mL of isooctane. The liquid was portioned to make blanks, and spiked levels of 500 fg/ μ L, 2.5 pg/ μ L, and 50 pg/ μ L concentrations for each of the soil samples. Samples were then analyzed by the instrument parameters listed on page 1.

Results and Discussion

The selectivity provided by MS/MS is illustrated in *Figure 1* which shows both the extracted ion chromatogram of four of the five pentachlorobiphenyl congeners studied and a representative spectrum. *Figure 1* also shows the same sample run in EI/MS full scan mode. The MS/MS product ion spectrum confirms their presence, giving the user both quantitative and confirmatory information in a single injection. No peaks are visible in full scan, their signal having been depressed by the abundant matrix signal.

Figures 3-6 on page 3 show the product ion spectra, typical sensitivities, and linear dynamic range for the selected chlorinated biphenyl compounds.

A substantial increase in sensitivity, approximately five-fold, was observed in the full scan data for all of the polychlorinated biphenyls studied, correlating with an increase in trap pressure (adjustable trap pressure controller - P/N 120053-001)¹. With MS/MS, it appears that it is the increase in parent ion sensitivity that leads to the increase in sensitivity for the product ions.

All twelve PCBs demonstrated linearity over the three orders of magnitude studied. The results from this study imply that these components may actually have a greater dynamic range using MS/MS than stated here. The lowest concentration injected was 200 fg/ μ L in split mode, and was found to be within the linear range. The lower limit of detection was not found during this study.

Low level (500 fg/ μ L) and mid-level (50 pg/ μ L) concentrations were examined for adherence to the ion ratio criteria found in Table 8 of Method 1668². *Table 2* below shows the results of these comparisons. Both the low and mid-levels met these criteria.

Conclusion

The GC-MS/MS technique is ideal for samples with matrix, giving both high selectivity and linearity with a large dynamic range. MS/MS was proven to minimize the effect of matrix left after sample cleanup. Finally, sensitivity for PCB detection is greatly increased with the use of increased trap pressure.

Table 1. MS/MS parameters

Compound	Precursor Ion	Width (amu)	Product Ions Scan Range	Isolation Time (ms)	Collision Energy (V)	Collision Time (ms)	q	Microscans/Scan	Maximum Ion Time (ms)
TeCBs	293	10	217-227	16	6.6	30	0.45	3	100
PeCBs	328	10	250-265	16	6.5	30	0.45	3	100
HxCBs	362	10	285-300	16	6.8	30	0.45	3	100
HpCB	394	10	314-335	16	6.8	30	0.45	3	100

Table 2. Ion Ratio criteria from Method 1668 Rev A and comparison of results in actual Standards²

Fragment Ion Formula	m/z's Forming Ratio	Theoretical Ratio	Lower QC Limit	Upper QC Limit	Actual ratio @ 50pg/ μ l	Actual ratio @ 500fg/ μ l
C ₁₂ H ₆ Cl ₂	m/(m+2)	1.56	1.33	1.79	1.75	1.67
C ₁₂ H ₅ Cl ₃	m/(m+2)	1.04	0.88	1.20	1.13	1.08
C ₁₂ H ₄ Cl ₄	m/(m+2)	0.77	0.65	0.89	0.85	0.70
C ₁₂ H ₃ Cl ₅	(m+2)/(m+4)	1.55	1.32	1.78	1.78	1.78

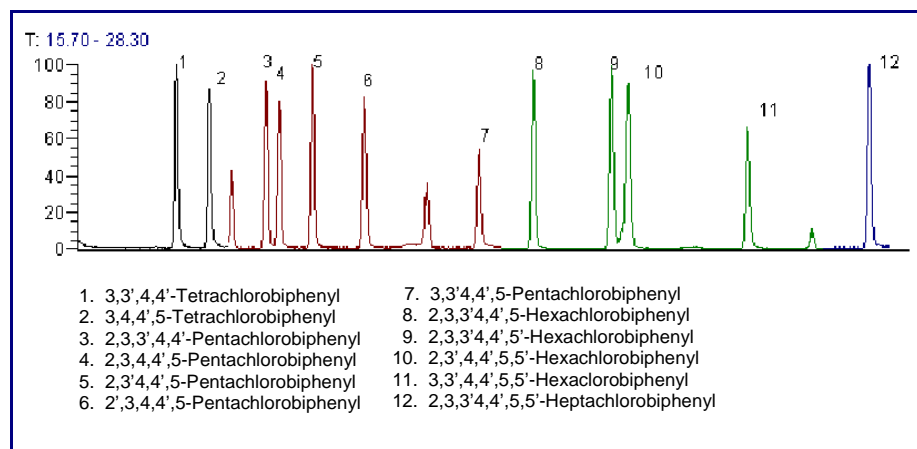


Figure 2. Composite Extracted Ion Chromatogram of twelve target PCBs designated by the World Health Organization

References

1. Grabic R., Novak J., Pacakova V.; "Optimization of a GC-MS/MS Method for the Analysis of PCDDs and PCDFs in Human and Fish Tissue"; *J. High Resol. Chromatogr.* 23, 595-599 No. 10, 2000)
2. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, US EPA, December 1999.

Copies of this and other applications as well as technical information can be obtained from:

www.thermofinnigan.com

World Health Organization Target PCBs

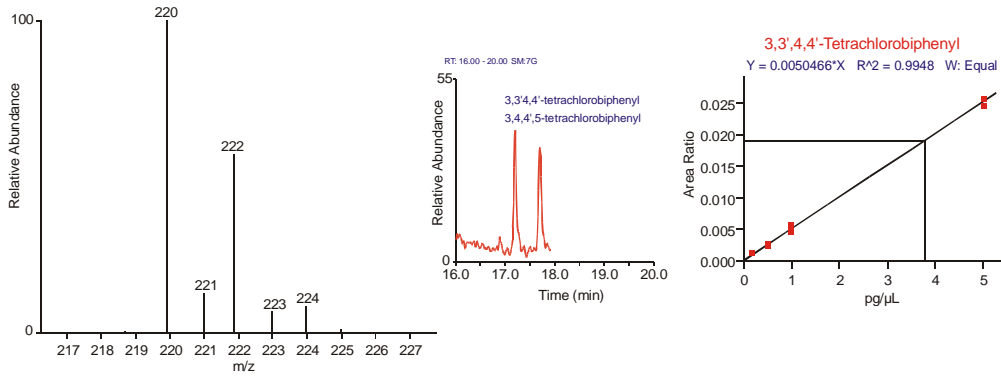


Figure 3. 3,3',4,4'-Tetrachlorobiphenyl MS/MS spectrum, quantitation ions and linearity

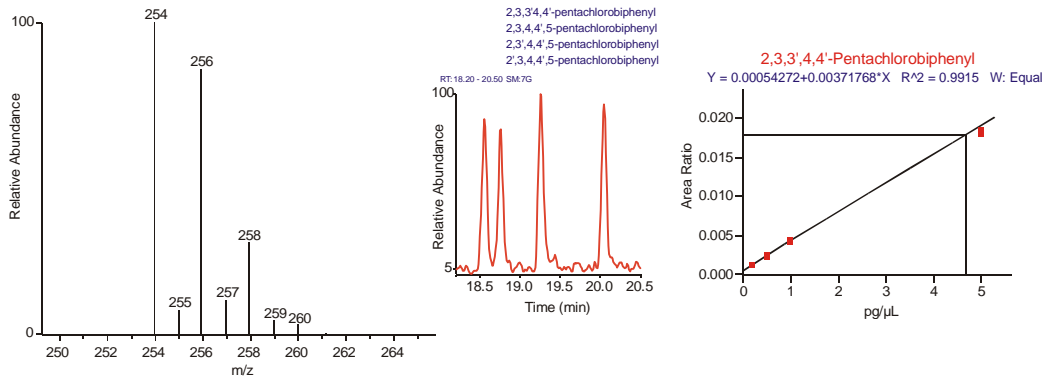


Figure 4. 2,3,3',4,4'-Pentachlorobiphenyl MS/MS spectrum, quantitation ions and linearity

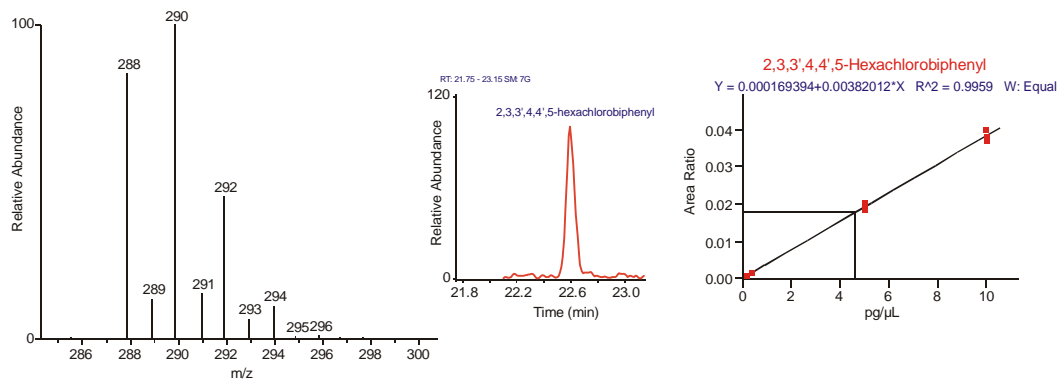


Figure 5. 2,3,3',4,4',5-Hexachlorobiphenyl MS/MS spectrum, quantitation ions and linearity

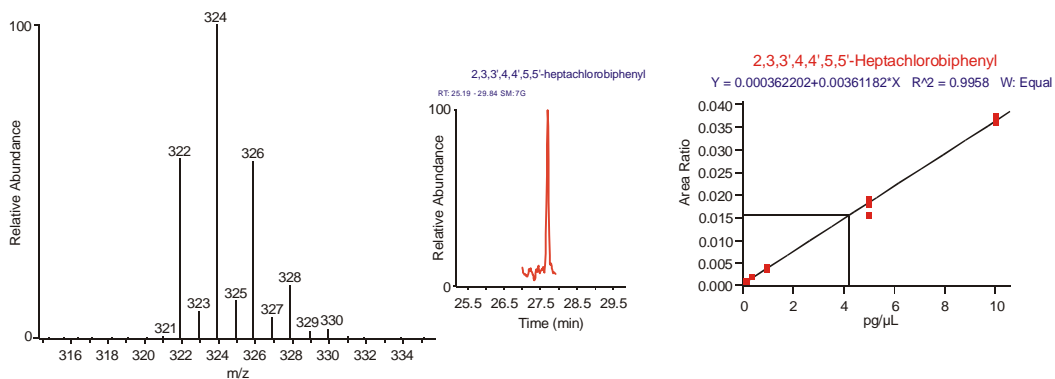


Figure 6. 2,3,3',4,4',5,5'-Heptachlorobiphenyl MS/MS spectrum, quantitation ions and linearity