Analysis of Complex Samples by GC/MS/MS – Pesticides in Marine Biota

Application Brief

Author

Chris Sandy

Agilent Technologies, Inc.

UK and Ireland Sales Headquarters

710 Wharfedale Road

Winnersh Triangle

Wokingham, Berkshire, RG41 5TP

UK

Introduction

The analysis of organochlorine pesticide residues in marine biota samples (mussels) by GC/MS is extremely challenging. Despite accelerated solvent extraction (ASE), followed by size exclusion chromatography and alumina clean-up, the extracted samples still contain large amounts of matrix materials. On a single quadrupole GC/MS system, these materials not only interfere with the quantitative analysis in selected ion monitoring (SIM) mode, but also cause problems with both the liner and GC column. This results in the shifting of GC retention times and decreasing signal intensities. In addition the MS ion source is quickly contaminated.

Avoiding retention time shifts is especially important when acquiring data in multiple reaction monitoring (MRM) mode with a GC/QQQ since complex multiresidue analysis requires careful placement of MRM segment times.

This application brief describes the analysis of a marine biota sample using the Agilent 7000A Triple Quad GC/MS system in MRM mode in combination with Agilent Capillary Flow Technology to provide backflushing of high-boiling materials. System up-time is maximized and the need for maintenance is reduced by keeping the chromatographic system and MS ion source cleaner of high-boiling matrix materials between each injection.

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The Analytical Challenge

The full-scan total ion chromatogram (TIC) (Figure 1) shows the chromatogram of a marine biota extract from 50 to 550 amu. After all the analytes have eluted from the column, large amounts of matrix material still remain in the chromatographic system.

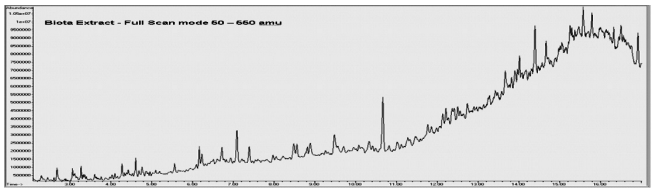

Figure 1. Full-scan TIC of a marine biota extract from 50 to 550 amu.

The SIM TICs of clean solvent injections on either side of two extract injections (Figure 2) shows the extent of the chemical background that builds up in the gas chromatograph.

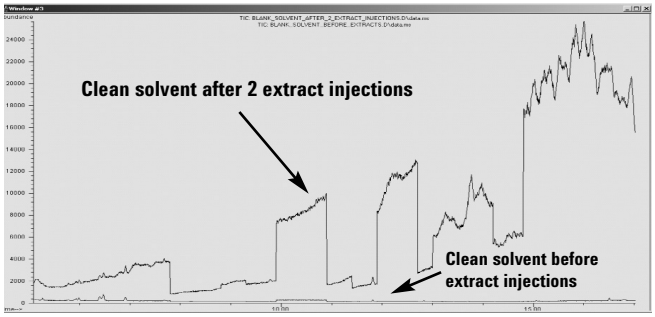

Figure 2. SIM TICs of clean and extract injections illustrating the buildup of the chemical background in the GC.

Experimental

Agilent Method Translation software (Figure 3) was used to create a 2x speed method from the normal 42-minute analysis provided by the Agilent RTL Pesticide method. The column used was a 15 m × 0.25 mm id × 0.25 µm HP-5MS Ultra Inert column (19091S-431 UI).

The column head-pressure was converted to allow for the 4.0 psig AUX pressure applied at the end of the column at the capillary flow device and the system run in constant pressure mode (Figure 4). Injection volume was 2 µL splitless.

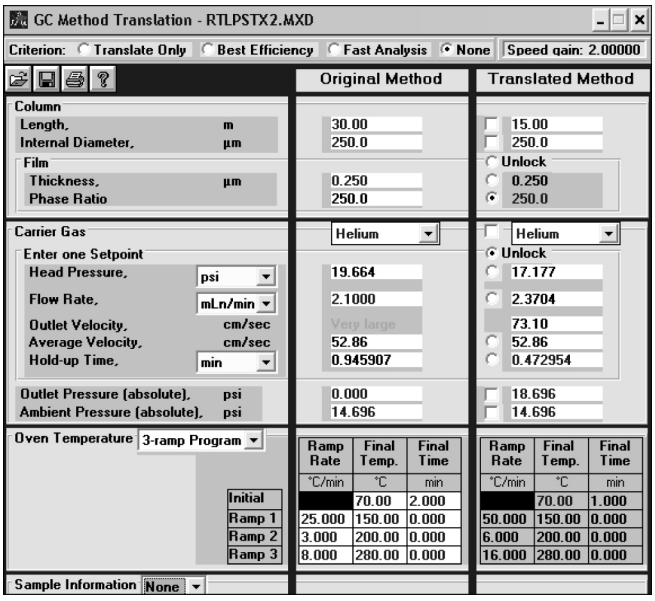

Figure 3. Agilent GC Method Translation software.

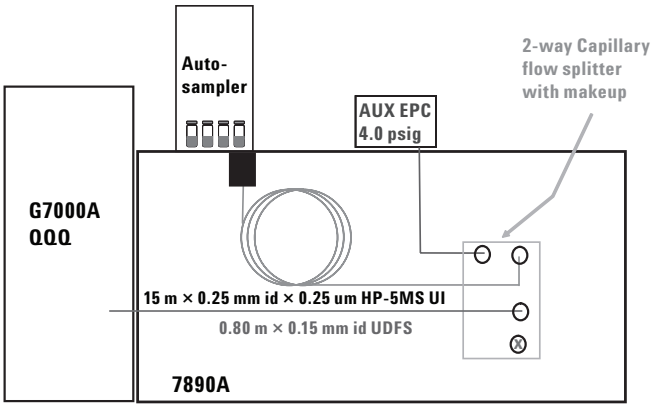

Figure 4. Agilent 7000A Triple Quad GC/MS system in MRM mode.

The 7000A mass spectrometer was operated in MRM mode. Table 1 gives the retention times, mass transitions, and collision voltages used for each analyte.

Table 1. Analyte Retention Times, Mass Transitions, and Collision Voltages

TS	Target	Ret Time	Parent Ion m/z	Quant m/z	Qual m/z	CV
1	a-HCH	6.19	219	147	183	20
	b-HCH	6.76	219	147	183	20
	Lindane	6.89	219	147	183	20
	d-HCH	7.45	219	147	183	20
2	PCB 28	8.25	256	186	151	20
3	PCB 52	9.15	292	220	257	20
4	Aldrin	9.47	263	193	228	30
5	Isodrin	10.24	193	123	157	30
6	PCB 155 (ISTD)	11.28	360	290		20
7	PCB 101	11.51	326	256	291	20
8	Dieldrin	12.18	263	193	228	30
	Endrin	12.56	263	193	228	30
9	PCB 118	12.84	326	256		20
10	PCB 153	13.25	360	290	325	20
	PCB 138	13.72	360	290	325	20
11	PCB 180	14.75	394	324	359	20
12	Mirex (ISTD)	15.09	272	237		20

The collision cell was operated with nitrogen at 2.60 psi and helium quench gas at 6.25 psi. The TIC MRM is shown in Figure 5; each MRM segment is indicated by a grey marker line.

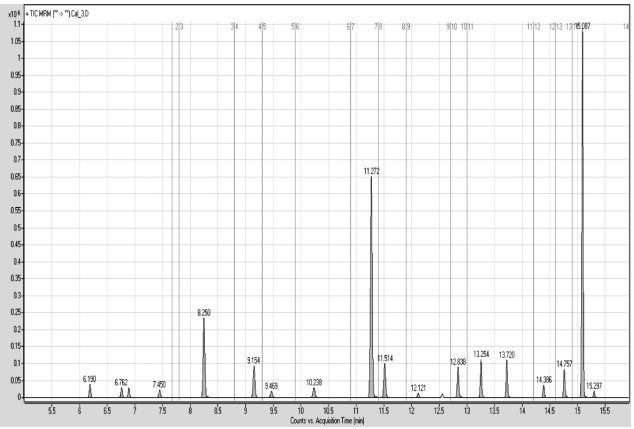

Figure 5. TIC of the Agilent 7000A Triple Quad GC/MS system in MRM mode.

Calibration

Internal standard calibration curves were created over the range of 0.8 to 200 ppb. Example MRM quant transitions for low-concentration standards of dieldrin and endrin are shown in Figure 6.

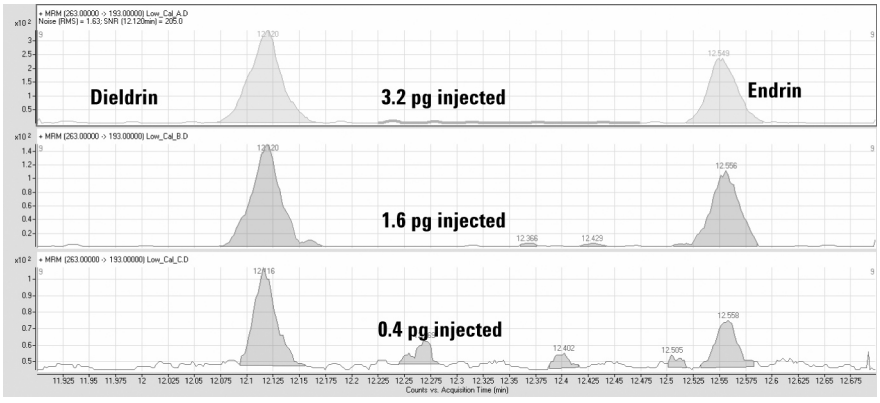

Figure 6. Example MRM quantitative transitions for low-concentration standards of dieldrin and endrin.

Quantitative Results

Table 2 shows quantitative results (ppb) from three replicate injections of the marine biota extract. Two of the chlorinated pesticides (dieldrin and beta hexachlorocyclohexane [HCH]) were identified and quantitated.

Table 2. Quantitative Results from Three Replicate Injections of Marine Biota Extract

Sample	a-HCH	b-HCH	g-HCH	d-HCH	Aldrin	Isodrin	Dieldrin	Endrin
Extract Biota Blank	ND	ND	ND	ND	ND	ND	ND	ND
Extract	ND	0.69	ND	ND	ND	ND	0.56	ND
Extract	ND	0.90	ND	ND	ND	ND	0.55	ND
Extract	ND	0.82	ND	ND	ND	ND	0.47	ND
Mean (ppb)		0.80					0.53	

Conclusion

The combination of Agilent Capillary Flow Technology and backflush mode with the high selectivity and sensitivity of the Agilent 7000A Triple Quad GC/MS system operated in MRM mode provides a robust solution for the analysis of organochlorine pesticides at trace levels in marine biota extracts.

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