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Multiple Tools for Demanding Needs: Trace Detection of Organochlorine Pesticides by Agilent 7000E and 7010C GC/MS/MS

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Introduction

Organochlorine pesticides (OCPs) are persistent pollutants that impact the environment.[1] Previous methods for analyzing these compounds have used gas chromatography with an electron capture detector (GC-ECD), but this requires time-consuming separation of all analytes. With a triple quadrupole mass spectrometer (GC/TQ) as a detector, we can employ dynamic multiple reaction monitoring (dMRM) mode which provides more confidence in peak identification than analysis by scan or selected ion monitoring (SIM) mode. Another benefit of dMRM mode is that sensitivity increases by eliminating interference from co-eluting compounds. Using a single quadrupole mass spectrometer, the typical limit of detection (LOD) for a liquid injection is in the ppb or ppm range. This work describes groundbreaking ppt-level sensitivity with GC/TQ by employing method optimization.

Table 1. List of organochlorine pesticides analyzed.

Analyte
4,4'-DDD
4,4'-DDE
4,4'-DDT
Aldrin
α-BHC
β-BHC
γ-BHC
δ-BHC
cis-Chlordane
trans-Chlordane
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
Heptachlor
Heptachlor epoxide
Methoxychlor

Experimental

To analyze the robustness of two different instruments for OCP analysis, an Agilent 8890 GC with either Agilent 7000E (equipped with extractor ion source) or 7010C (equipped with high-efficiency ion source) TQ was used. Standard mixtures containing 20 OCP analytes were prepared in DCM at 0.01-1000 ppb for the 7000E and 0.01-500 ppb for the 7010C. A 30 m x 250 µm x 0.25 mm DB-8270D-UI column was used with a constant flow rate of 1.25 mL/min. Standards were injected into a multimode inlet (MMI) in solvent vent mode with a dimpled liner. Solvent vent mode was used because it led to better peak shape and sensitivity for all OCPs compared to injection in pulsed splitless mode. Injection volume and detector gain were incremented on both systems to study their impact on peak shape, detection level, and dynamic range.

Table 2. Agilent 8890 GC and 7000E or 7010C TQ Parameters

GC and MS Conditions:	
Injection vol.	1-3 µL
Inlet	MMI, solvent vent mode 60°C, hold 0.02 min Ramp 600°C/min → 325°C, hold 5 min 5 psi vent until 0.02 min Purge 60mL/min at 2 min
Column	DB-UI 8270D Column (30m x 250µm, 0.25mm)
Carrier gas	1.25 mL/min constant flow (helium)
Oven (17.9 min run)	40°C hold 0.5 min Ramp 25°C/min → 260°C, no hold Ramp 5°C/min → 280°C, no hold Ramp 25°C/min → 320°C, hold 3 min
MSD Transfer Line	300°C

a)

b)

Figure 1. Agilent 8890 GC with either a) 7000E or b) 7010C TQ was used for this analysis.

Ultra trace analysis of OCPs is possible with both 7000E and 7010C TQ.

All but six OCPs were detected at 10 ppt with a 1 uL injection and gain of 10 on the 7000E. By increasing the injection volume to 3 uL with gain of 10, all but two OCPs were detected at 10 ppt on the 7000E. With a gain of 10 on the 7010C, nineteen OCPs were detected at 10 ppt with both 1 and 3 uL injection volumes.

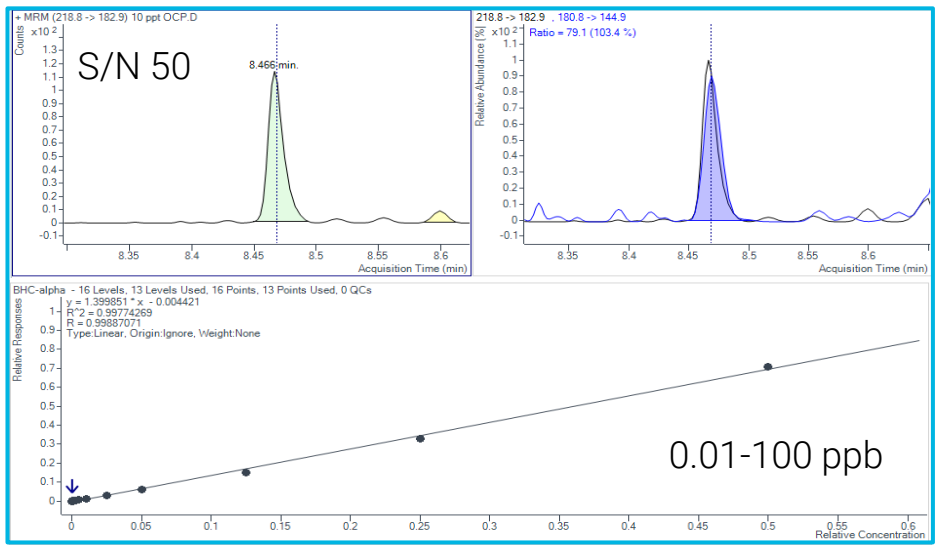

Figure 2. 10 ppt α-BHC, with1 uL injection and gain 10 on 7000E.

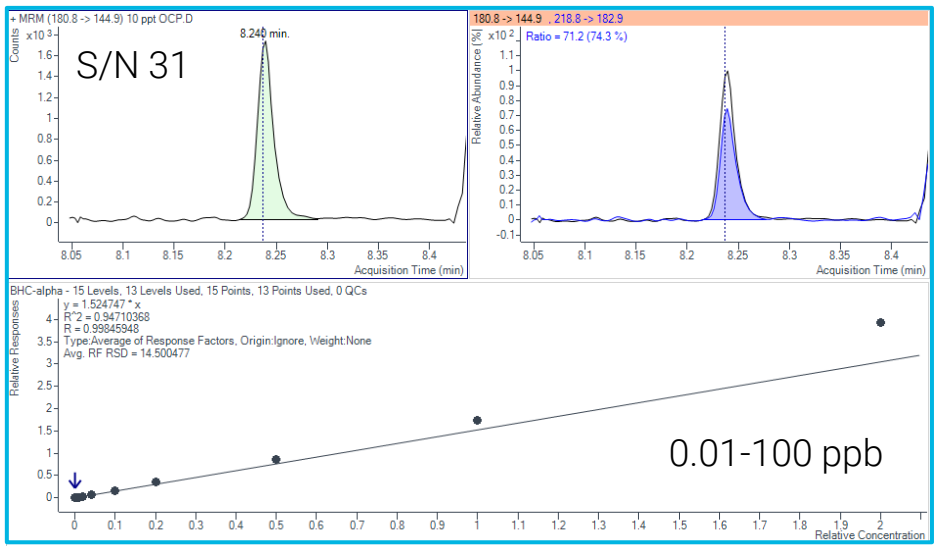

Figure 3. 10 ppt α-BHC, with 1 uL injection and gain 10 on 7010C.

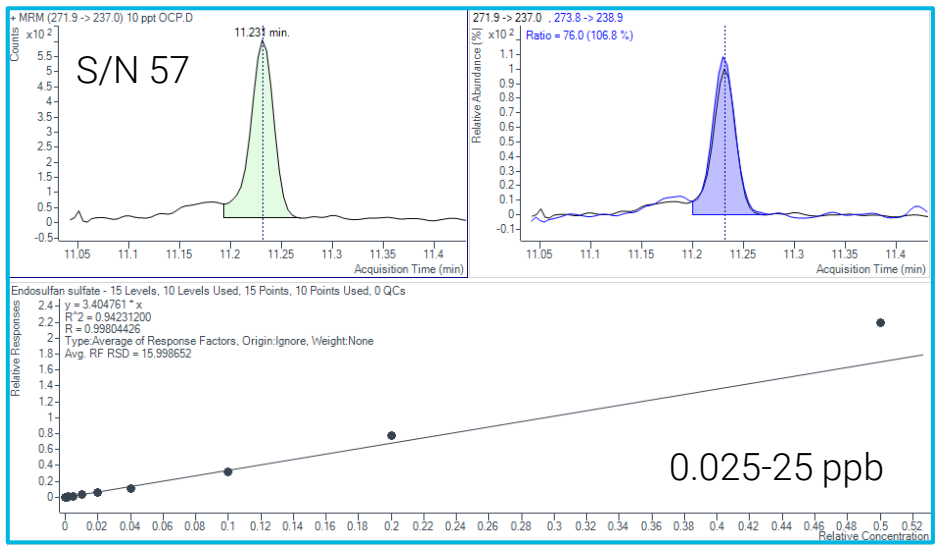

Figure 4. 10 ppt Endosulfan sulfate, with 3 uL injection and gain 10 on 7010C.

Low detection levels were observed for dieldrin and endrin.

Dieldrin, a planar OCP that typically isn't detected at low levels by GC, was detected at 25 ppt with a 1 uL injection on the 7000E. Peak shape was Gaussian with a signal to noise of 286. Endrin, another notoriously difficult planar OCP to analyze by GCMS was detected at 25 ppt from a 1 uL injection on the 7000E with a signal to noise of 31.

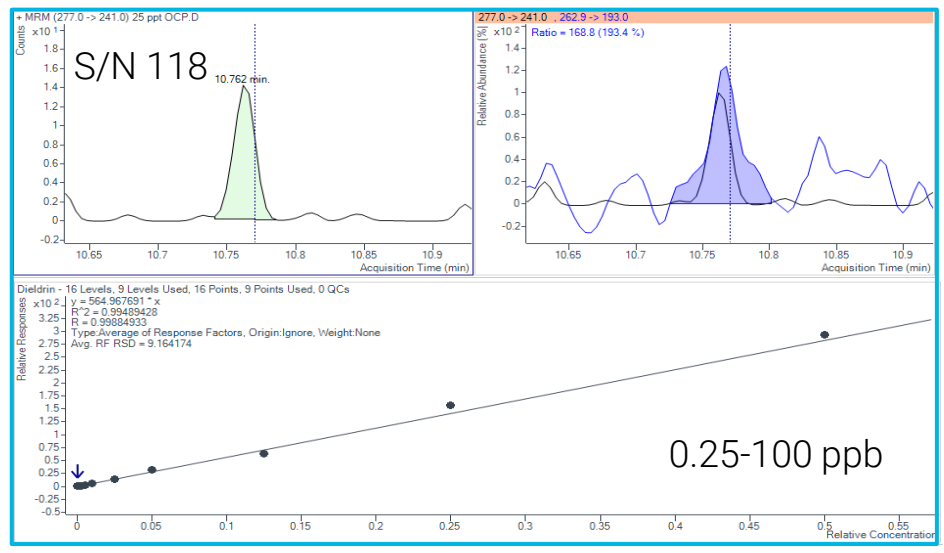

Figure 5. 25 ppt Dieldrin, with 1 uL injection and gain 10 on 7000E.

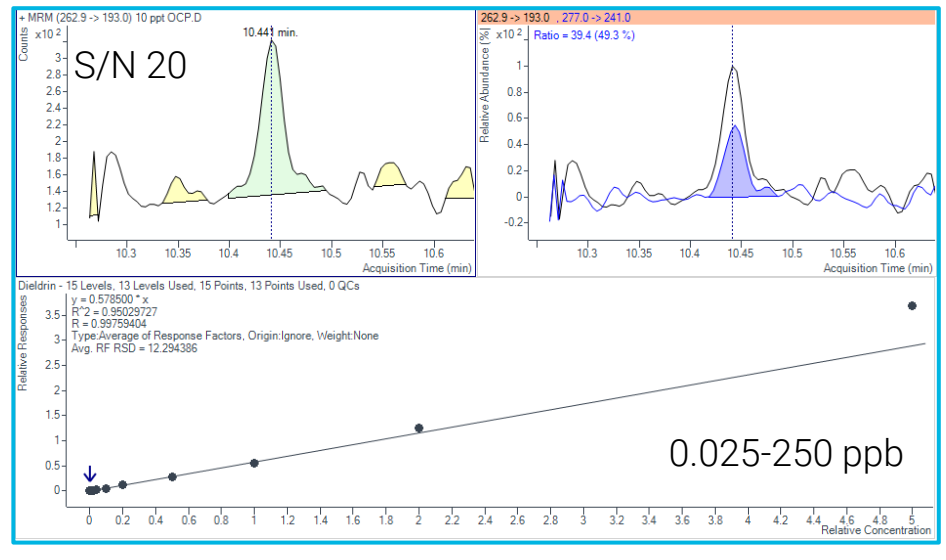

Figure 6. 10 ppt Dieldrin, with1 uL injection and gain 10 on 7010C.

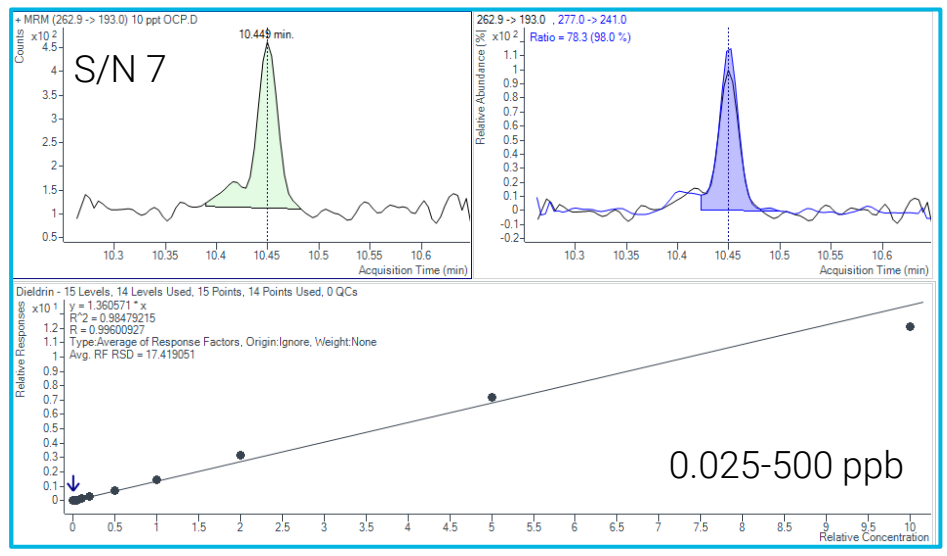

Figure 7. 10 ppt Dieldrin, with 3 uL injection and gain 10 on 7010C.

Results and Discussion

Small volume injection is sufficient for trace analysis.

Comparing 1 uL and 3 uL injection volumes on the 7010C, both with gain of 10, did not show much of a difference. With a 1 uL injection, all compounds were detected at 10 ppt except 4,4'-DDT, which was detected at 25 ppt. With a 3 uL injection, only endrin was detected above 10 ppt. Therefore a 1 uL injection volume is likely sufficient for most analyses.

Table 3. Comparison of detection levels on the 7010C.

7010C	Lowest level detected (ppb) w S/N above 3	
Analyte	1 uL gain 10	3 uL gain 10
4,4'-DDD	0.01	0.01
4,4'-DDE	0.01	0.01
4,4'-DDT	0.025	0.01
Aldrin	0.01	0.01
α-BHC	0.01	0.01
β-BHC	0.01	0.01
γ-BHC	0.01	0.01
δ-BHC	0.01	0.01
cis -Chlordane	0.01	0.01
trans -Chlordane	0.01	0.01
Dieldrin	0.01	0.01
Endosulfan I	0.01	0.01
Endosulfan II	0.01	0.01
Endosulfan sulfate	0.01	0.01
Endrin	0.01	0.25
Endrin aldehyde	0.01	0.01
Endrin ketone	0.01	0.01
Heptachlor	0.01	0.01
Heptachlor epoxide	0.01	0.01
Methoxychlor	0.01	0.01

Table 4. Calibration data on the 7010C with 1 uL injection and gain 10.

Analyte	Cal Range (ppb)	# Levels Used	Avg. RF	Linear R^2	RSE
4,4'-DDD	0.025-50	11	15.4	0.9985	15.4
4,4'-DDE	0.025-25	10	15.8	0.9980	15.8
4,4'-DDT	0.01-2	8	15.2	0.9968	15.2
Aldrin	0.01-100	13	10.9	0.9954	10.9
α-BHC	0.01-100	13	14.5	0.9969	14.5
β-BHC	0.01-50	12	16.8	0.9995	16.8
γ-BHC	0.01-50	12	13.2	0.9996	13.2
δ-BHC	0.01-50	12	18.9	0.9988	18.9
cis -Chlordane	0.01-50	12	18.1	0.9986	18.1
trans -Chlordane	0.01-50	12	16.3	0.9991	16.3
Dieldrin	0.025-250	13	12.3	0.9952	12.3
Endosulfan I	0.025-50	11	15.4	0.9984	15.4
Endosulfan II	0.01-50	12	17.3	0.9980	17.3
Endosulfan sulfate	0.025-50	11	17.3	0.9972	17.3
Endrin	0.025-500	14	10.8	0.9888	10.8
Endrin aldehyde	0.025-100	12	19.6	0.9987	19.6
Endrin ketone	0.025-100	12	12.8	0.9963	12.8
Heptachlor	0.01-100	13	9.2	0.9996	9.2
Heptachlor epoxide	0.025-100	12	8.7	0.9954	8.7
Methoxychlor	0.025-100	12	19.9	0.9965	19.9

Table 5. Calibration data on the 7000E with 1 uL injection and gain 10.

Analyte	Cal Range (ppb)	# Levels Used	Avg. RF	Linear R^2	RSE
4,4'-DDD	0.25-100	9	15.2	0.9960	15.2
4,4'-DDE	0.01-25	11	13.7	0.9990	13.7
4,4'-DDT	0.1-100	10	18.8	0.9974	18.8
Aldrin	0.025-50	11	11.8	0.9887	11.8
α-BHC	0.01-100	13	10.6	0.9977	10.6
β-BHC	0.01-100	13	12	0.9954	12
γ-BHC	0.01-100	13	12.5	0.9963	12.5
δ-BHC	0.01-50	12	13.2	0.9963	13.2
cis -Chlordane	0.01-25	11	13.3	0.9996	13.3
trans -Chlordane	0.01-25	11	17.4	0.9996	17.4
Dieldrin	0.25-100	9	9.2	0.9977	9.2
Endosulfan I	0.05-25	9	18.2	0.9999	18.2
Endosulfan II	0.05-100	11	15.3	0.9980	15.3
Endosulfan sulfate	0.25-25	7	10.9	0.9953	10.9
Endrin	0.25-1000	12	12.1	0.9949	12.1
Endrin aldehyde	0.5-100	8	9.7	0.9980	9.7
Endrin ketone	0.25-100	9	9.2	0.9978	9.2
Heptachlor	0.01-100	13	17.3	0.9965	17.3
Heptachlor epoxide	0.01-50	12	16.5	0.9891	16.5
Methoxychlor	0.05-100	11	15.5	0.9981	15.5

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Increasing gain may be useful for trace analysis.

On the 7000E, gain values of 1, 5, and 10 were compared. With a 3 uL injection, sixteen of the twenty compounds were detected at 10 ppt with both gain 1 and 5. Increasing the gain to 10 enabled eighteen of the twenty compounds to be detected at 10 ppt. Increasing gain may enable lower detection levels for some compounds, but the detection levels at a gain of 1 are likely sufficient for most analyses.

Table 6. Comparison of detection levels on the 7000E.

7000E	Lowest level detected (ppb) w S/N above 3				
Analyte	1 uL gain 10	2 uL gain 10	3 uL gain 10	3 uL gain 5	3 uL gain 1
4,4'-DDD	0.01	0.01	0.01	0.05	0.01
4,4'-DDE	0.01	0.01	0.01	0.01	0.01
4,4'-DDT	0.01	0.01	0.01	0.025	0.05
Aldrin	0.01	0.01	0.01	0.01	0.01
α-BHC	0.01	0.01	0.01	0.01	0.01
β-BHC	0.01	0.01	0.01	0.01	0.01
γ-BHC	0.01	0.01	0.01	0.01	0.01
δ-BHC	0.01	0.01	0.01	0.01	0.01
cis -Chlordane	0.01	0.01	0.01	0.01	0.01
trans -Chlordane	0.01	0.01	0.01	0.01	0.01
Dieldrin	0.025	0.025	0.01	0.01	0.01
Endosulfan I	0.025	0.01	0.01	0.01	0.01
Endosulfan II	0.025	0.01	0.01	0.01	0.01
Endosulfan sulfate	0.01	0.01	0.01	0.01	0.01
Endrin	0.025	0.1	0.05	0.5	0.1
Endrin aldehyde	0.025	0.01	0.01	0.01	0.1
Endrin ketone	0.05	0.05	0.05	0.025	0.025
Heptachlor	0.01	0.01	0.01	0.01	0.01
Heptachlor epoxide	0.01	0.01	0.01	0.01	0.01
Methoxychlor	0.01	0.01	0.01	0.01	0.01

Conclusions

Both the 7000E and 7010C TQ systems are viable options for trace-level OCP analysis.

- Most OCPs could be detected at levels as low as 0.01 ppb with both systems.
- The 7010C is well-suited for ultra-low detection limits for analytes.
- The 7000E is well-suited for larger dynamic ranges of analytes.
- A large injection volume and high gain are not necessary for trace-level detection.
- The large dynamic ranges achieved with the evaluated GC/TQ instruments accommodate the most demanding analytical needs.

References

[1]Mrema, E., et al. "Persistent organochlorinated pesticides and mechanisms of their toxicity." *Toxicology* 307 (2013): 74-88.

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