Detection of Organochlorine Pesticides by GC-ECD Following U.S. EPA Method 8081

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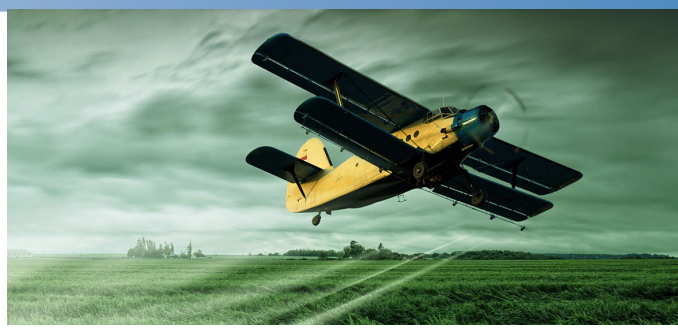
Keywords
Chromeleon chromatography data system, electron capture detector, environmental, gas chromatography, organochlorine pesticides, U.S. EPA 8081

Goal
To accurately detect and quantitate organochlorinated pesticides in extracts from solid and liquid matrices using gas chromatography (GC) with an electron capture detector (ECD).



Introduction
Organochlorine insecticides are among the oldest and most toxic synthetic pesticides. First introduced in the 1940s, these chemicals were used extensively until most of them were banned in the 1970s and 1980s due to their health risks. Organochlorines are neurotoxic and some organochlorine compounds are suspected carcinogens. Organochlorines, such as DDT and lindane, also break down slowly once released. This persistence in the environment leads these organochlorines to be incorporated into ecosystems and food chains where they remain for years. For these reasons, the presence of these analytes in water, soils, and other solids must be strictly controlled and various analytical methods have been developed to extract and purify them from various matrixes. The presence of chlorine atoms in their structure makes organochlorines an excellent target for an electron capture detector (ECD)—a sensitive, cheaper, and easier-to-operate alternative to mass spectrometry. This application note describes a convenient method for analyzing and quantifying organochlorinated pesticides via GC and ECD.

Experimental Conditions
Sample Preparation
Matrix extraction and purification are performed following U.S. Enivronmental Protection Agency Method 8081 guidelines.

Instrument Setup
A method was developed for the Thermo Scientific™ TRACE™ 1310 Gas Chromatograph used with a Thermo Scientific™ TriPlus RSH™ Autosampler, an Instant Connect Split/Splitless (SSL) Injector and an Instant Connect Electron Capture Detector (ECD) for TRACE 1300 Series GC.

Recommended Conditions	
TRACE 1310 GC	
Injection Volume:	1 µL
Liner:	Splitless with glass wool (P/N 453A1925)
Carrier Gas:	Helium, constant flow, 1 mL/min
Column Type:	30 m, 0.25 mm, 0.25 µm, TG-5MS (P/N 26098-420)
Column Oven:	Initial 100 °C, hold 1.0 min. Ramp at 20.0 °C/min up to 180°C. Ramp at 5.0 °C/min to 270 °C. Ramp at 20.0 °C/min to 320 °C. Hold 2.0 min.
Instant Connect SSL Injector	
Inlet Temperature:	250 °C
Mode:	Splitless, 2 min; split flow 50 mL/min
Instant Connect ECD	
Temperature:	320 °C
Makeup Gas:	Nitrogen, 15 mL/min makeup flow

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Method

The experimental method follows the guidelines for U.S. EPA method 8081, with slight modifications to the GC ramp and use of a column with 0.25 µm film thickness to guarantee better separation. The TriPlus RSH Autosampler is operated in liquid injection mode. All other parameters are those indicated by U.S. EPA Method 8081. Ethyl acetate is used as the solvent for washing the syringe. The standards used for calibration are ordered from Restek. All samples are acquired and processed using the Thermo Scientific™ Dionex™ Chromeleon™ 7.2 chromatography data system (CDS) software.

Figure 1. TRACE 1310 GC and TriPlus RSH Autosampler.

Results and Discussion

Separation, linearity, repeatability, and limit of detection were assessed for each compound.

The chromatogram of a 5 ppb calibration point is shown in Figure 2.

Good peak shape and separation were observed.

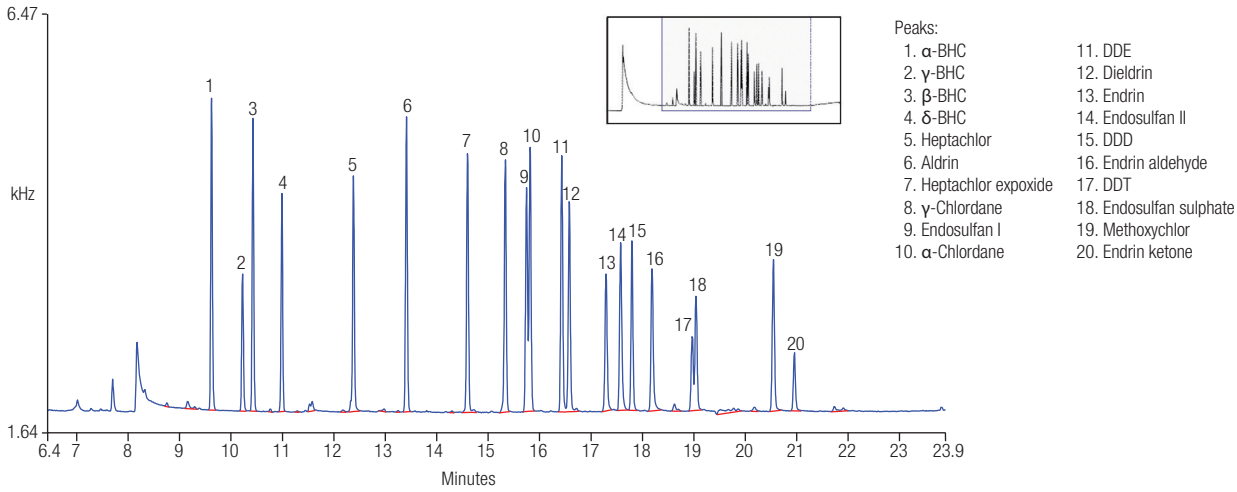

Figure 2. Chromatogram for 5 ppb calibration point.

Table 1. Calibration results for the analyzed components.

Peak Name	Retention Time (min.)	Coefficient of Determination	C1 (Slope)
α-BHC	9.623	0.99978	0.0231
γ-BHC	10.227	0.99996	0.0122
β-BHC	10.430	0.99983	0.0215
δ-BHC	10.992	0.99992	0.0193
Heptachlor	12.383	0.99984	0.0200
Aldrin	13.413	0.99957	0.0227
Heptachlor epoxide	14.602	0.99964	0.0208
γ-Chlordane	15.337	0.99987	0.0226
Endosulfan I	15.748	0.99923	0.0181
α-Chlordane	15.818	0.99968	0.0222
DDE	16.433	0.99973	0.0225
Dieldrin	16.578	0.99983	0.0207
Endrin	17.295	0.99997	0.0159
Endosulfan II	17.577	0.99986	0.0201
DDD	17.797	0.99919	0.0172
Endrin aldehyde	18.187	0.99985	0.0184
DDT	18.967	0.99883	0.0113
Endosulfan sulphate	19.040	0.99856	0.0187
Methoxychlor	20.550	0.99998	0.0174
Endrin ketone	20.958	0.99889	0.0079

As outlined in the U.S. EPA 8081 method, endosulfan I and α-chlordane and DDT and endosulfan sulfate tend to coelute on the 5% phenyl 95% dimethylpolysiloxane stationary phase used for this application. As shown in Figure 3, good resolution was achieved with a score of 1.0 for the α-chlordane-endosulfan I pair and 0.9 for DDT-endosulfan sulphate.

Compounds were quantitated using an external calibration method and a seven-point curve. The seven-point calibration curve ranged from 0.1 to 100 ppb with concentrations of 0.1, 0.5, 1, 2, 5, 10, 100 ppb for each of the analytes. The results are reported in Table 1 and Figure 4.

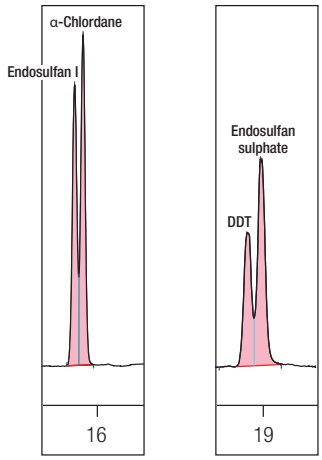

Figure 3. Resolution of "critical couples".

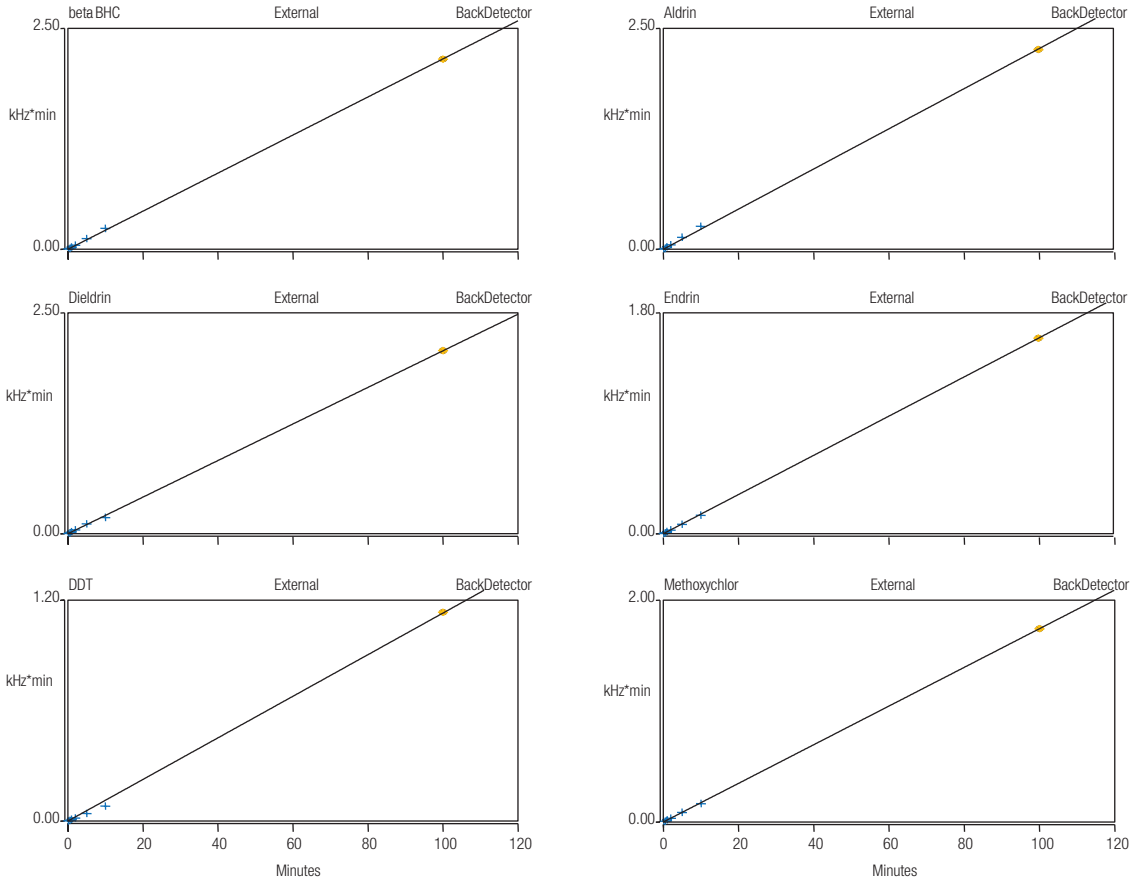

Figure 4. Calibration curves for six of the analyzed pesticides.

The limit of detection was assessed by applying the U.S. EPA guidelines, performing 14 replicate injections, calculating the standard deviation of the response, and then multiplying that value for the "t" value at 99% confidence level, related to the number of replicate injections. The results are reported in Table 2.

Table 2. Limit of detection.

	Std. Dev	No. of Repeats	t(14-1)	Calculated LOD (ppb)
α-BHC	0.009	14	2.650	0.023
γ-BHC	0.009	14	2.650	0.025
β-BHC	0.007	14	2.650	0.018
δ-BHC	0.007	14	2.650	0.019
Heptachlor	0.011	14	2.650	0.029
Aldrin	0.005	14	2.650	0.013
Heptachlor epoxide	0.008	14	2.650	0.021
γ-Chlordane	0.073	14	2.650	0.194
Endosulfan I	0.013	14	2.650	0.034
α-Chlordane	0.019	14	2.650	0.050
DDE	0.008	14	2.650	0.020
Dieldrin	0.011	14	2.650	0.030
Endrin	0.018	14	2.650	0.049
Endosulfan II	0.023	14	2.650	0.062
DDD	0.009	14	2.650	0.025
Endrin aldehyde	0.01	14	2.650	0.026
DDT	0.008	14	2.650	0.020
Endosulfan sulphate	0.01	14	2.650	0.028
Methoxychlor	0.013	14	2.650	0.035
Endrin ketone	0.039	14	2.650	0.103

The repeatability of both retention times and areas has been tested as well on 10 ppb injections (number of injections = 10).The results are reported in Table 3.

Table 3. Retention time and area repeatability (n = 10).

	Ret. Time RSD%	Peak Area RSD%
α-BHC	0.03	2.41
γ-BHC	0.04	2.69
β-BHC	0.03	2.02
δ-BHC	0.03	1.59
Heptachlor	0.03	2.40
Aldrin	0.02	2.16
Heptachlor epoxide	0.02	1.97
γ-Chlordane	0.02	2.47
Endosulfan I	0.02	2.04
α-Chlordane	0.02	1.75
DDE	0.02	2.09
Dieldrin	0.02	2.18
Endrin	0.02	2.00
Endosulfan II	0.02	2.82
DDD	0.02	2.18
Endrin aldehyde	0.02	2.66
DDT	0.02	4.76
Endosulfan sulphate	0.02	1.71
Methoxychlor	0.02	2.25
Endrin ketone	0.02	4.14

Conclusion

This application demonstrated the performance of the TRACE 1300 Series GC, equipped with an Instant Connect SSL Injector and Instant Connect ECD for the analysis of organochlorine pesticides. The system shows excellent results in terms of linearity, sensitivity, and reproducibility. These results indicate that this system is a sensitive, cheaper and simpler alternative to mass spectrometry for assessing the presence of organochlorine residues, as a result of the excellent selectivity of the ECD for chlorinated compounds.

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