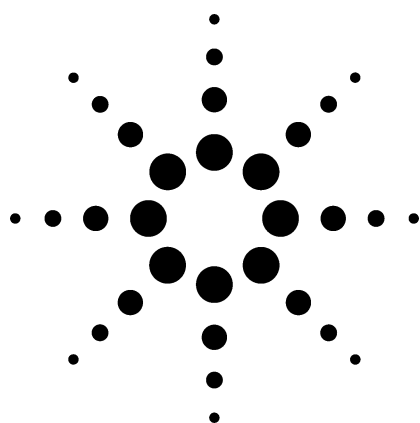


Analysis of Organochlorine Pesticides and PCB Congeners with the Agilent 6890 Micro-ECD



Application

Gas Chromatography

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Abstract

A new electron capture detector (ECD) for the Agilent 6890 Series gas chromatograph (GC) was used to analyze polychlorinated biphenyl congeners and organochlorine pesticides. The linearity of the 6890 Micro-ECD in the calibration range of 2 to 400 ppb was evaluated. The micro-ECD easily meets the linearity requirements of U.S. EPA contract laboratory programs for pesticides. Its limit of detection for these compounds goes down to less than 50 ppt. The micro-ECD also exhibits good reproducibility.

Key Words

Organochlorine pesticides, PCB congeners, 6890 GC, micro-ECD; pesticide analysis, ECD.

Introduction

The electron capture detector (ECD) is the detector of choice in many Contract Laboratory Programs (CLP)¹ and EPA methods for pesticide analysis because of its sensitivity and selectivity for halogenated compounds. However, there are drawbacks to the ECD design. The ECD is inherently nonlinear², with a limited linear range. The limited linear range means that dilution and reanalysis are frequently required for samples that are outside the calibration range.

Also, the typical ECD is designed to be compatible with both packed and capillary columns. This results in a flow cell that is larger than that required for capillary columns alone, which reduces detector sensitivity.

To address these problems, a new ECD was developed for the 6890 Series gas chromatograph (GC). The 6890 Micro-ECD has a smaller flow cell optimized for capillary columns and was redesigned to improve the linear operating range.

This application note examines the linearity, reproducibility, and limit of detection of the new ECD with mixtures of polychlorobiphenyl (PCB) congeners and organochlorine pesticides (OCPs).

Experimental

All experiments were performed on an 6890 Series GC with electronic pneumatics control (EPC) and the 6890 Micro-ECD. Table 1 shows the experimental conditions for PCB congeners and OCPs.

Table 1. Experimental Conditions for PCB Congener and OCP Analysis.

System Conditions	PCB Congener Analysis	OCP Analysis
Oven	80 °C (2 min); 30 °C/min to 200 °C; 10 °C/min to 320 °C (5 min).	80 °C (2 min); 25 °C/min to 190 °C; 5 °C/min to 280 °C; 25 °C/min to 300 °C (2 min).
Inlet	Split/splitless; 300 °C	Split/splitless; 250 °C
Carrier	Helium, 16.8 psi (80 °C); 1.3-mL/min constant flow	Helium, 23.9 psi (80 °C); 2.2-mL/min constant flow
Sampler	Agilent 7673, 10- μ L syringe, 1- μ L splitless injection	7673, 10- μ L syringe, 1- μ L splitless injection
Column	30-m, 250- μ m id, 0.25- μ m film HP-5MS (part no. 19091S-433)	30-m, 250- μ m id, 0.25- μ m film HP-5MS (part no. 19091S-433)
Detector	330 °C; makeup gas: nitrogen, constant column and makeup flow	330 °C; makeup gas: nitrogen, constant column and makeup flow



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The solutions were prepared by making appropriate dilutions of a stock solution with isooctane. For PCB congeners, the stock solution was an EPA PCB congener calibration check solution (from Ultra Scientific Company, part number RPC-EPA-1). For OCPs, the solution was an OCP calibration check solution (part number 8500-5876).

Results and Discussion

Linearity and Response Factors

A series of dilutions of the PCB mixture from 2 ppb to 200 ppb and of the OCP mixture from 2 ppb to 400 ppb was injected into the 6890 Micro-ECD system. The linearity was determined by calculating the correlation coefficient from the resulting calibration curve.

Figures 1 and 2 present typical chromatograms of OCPs and PCBs at 20 or 40 ppb and 50 ppb, respectively. Figure 3 is a calibration curve of decachlorobiphenyl, typical of other PCB congeners. Figure 4 shows the calibration curve of 4, 4' DDE, typical of OCPs. The correlation coefficient,

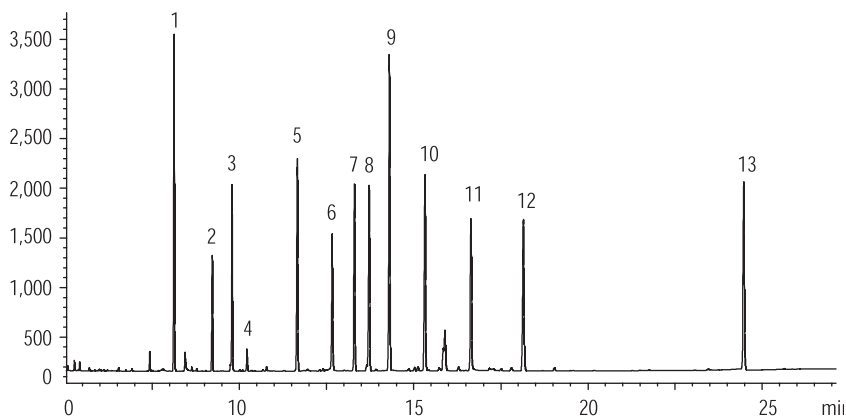


Figure 1. Typical chromatogram of OCPs at 20 or 40 ppb.
See table 1 for conditions. See table 5 for peak identification.

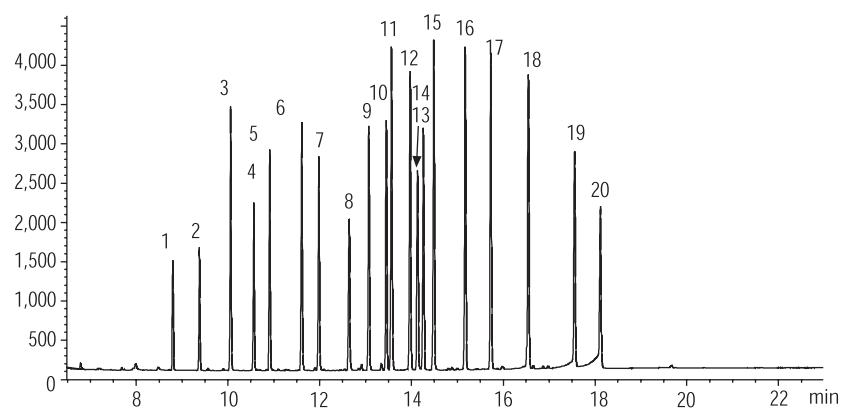


Figure 2. Typical chromatogram of PCB congeners at 50 ppb.
See table 1 for conditions. See table 4 for peak identification.

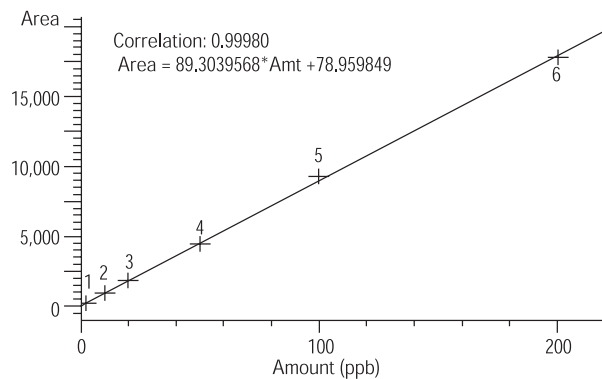


Figure 3. Typical linearity of PCB congener analysis: decachlorobiphenyl from 2-200 ppb.

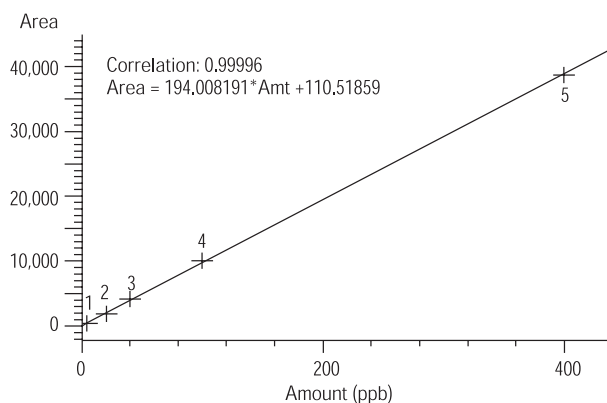


Figure 4. Typical linearity of OCP analysis: 4,4' DDE from 4 to 400 ppb.

average response factors, and percent relative standard deviation (%RSD) for the response factors for each analyte are shown in tables 2 and 3.

All correlation coefficients were at least 0.9996. In these experiments, the 6890 Micro-ECD is linear over this range. The typical range required by CLP methods is 5-80 ppb¹, so the 6890 Micro-ECD exceeds the range by almost twofold.

In addition, the CLP method requires the percent RSD of the response factors for most components to be less than 20 percent for a three-point calibration curve (5 to 80 ppb). As shown in tables 2 and 3, the percent RSD of the response factors ranged from 0.55 percent to 12.5 percent for the PCB congeners and from 2.8 percent to 10 percent for the OCPs over a concentration range of two orders of magnitude (2 to 400 ppb). Furthermore, the average response factor of each analyte was so consistent and reproducible that the internal standard technique can be used to quantitate all OCPs and PCB congeners.

Table 2. PCB Congener Analysis: Linearity of the 6890 Micro-ECD 2 ppb to 200 ppb.
See table 1 for conditions.

Peak	Name	Average Response Factor	%RSD of Response Factor	Correlation (%)
1	2,4-Dichlorobiphenyl	2e-2	12.5	99.97
2	2,2',5-Trichlorobiphenyl	2e-2	11.1	99.97
3	2,4,4'-Trichlorobiphenyl	8.5e-3	7.5	99.99
4	2,2',5,5'-Tetrachlorobiphenyl	1.3e-2	10.2	99.97
5	2,2',3,5-Tetrachlorobiphenyl	1e-2	9.4	99.98
6	2,3,4,4'-Tetrachlorobiphenyl	8e-3	6.7	99.99
7	2,2',4,5,5'-Pentachlorobiphenyl	9e-3	8.8	99.98
8	3,3',4,4'-Tetrachlorobiphenyl	1.2e-2	12.6	99.97
9	2,3,4,4',5-Pentachlorobiphenyl	8e-3	5.5	99.99
10	2,2',4,4',5,5'-Hexachlorobiphenyl	8e-3	8.1	99.98
11	2,3,3',4,4'-Pentachlorobiphenyl	6e-3	1.9	99.99
12	2,2',3,4,4',5-Hexachlorobiphenyl	6.5e-3	3.8	99.99
13	3,3',4,4',5-Pentachlorobiphenyl	9e-3	6.5	99.99
14	2,2',3,4,5,5',6-Heptachlorobiphenyl	8e-3	5.7	99.99
15	2,2',3,3',4,4'-Hexachlorobiphenyl	5.6e-3	1.8	99.99
16	2,2',3,4,4',5,5'-Heptachlorobiphenyl	5.8e-3	1.0	99.99
17	2,2',3,3',4,4',5-Heptachlorobiphenyl	5.8e-3	0.57	99.99
18	2,2',3,3',4,4',5,6-Octachlorobiphenyl	6e-3	0.78	99.99
19	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	8e-3	3.1	99.96
20	Decachlorobiphenyl	1e-2	9.5	99.98

Table 3. OCP Analysis: Linearity of the 6890 Micro-ECD 2 or 4 ppb to 200 or 400 ppb.
See table 1 for conditions.

Peak	Name	Average Response Factor	% RSD of Response Factor	Correlation (%)
1	2,4,5,6-Tetra-m-xylene	4.2e-3	5.3	99.97
2	beta-BHC	1.1e-2	7.1	99.99
3	delta-BHC	6.4e-3	4.7	99.99
4	Aldrin	4.7e-3	9.5	99.97
5	Heptachlor epoxide	4.7e-3	5.4	99.99
6	gamma-Chlordane	6.6e-3	6.6	99.99
7	alpha-Chlordane	5e-3	4.3	99.98
8	4,4' DDE	5e-3	2.8	99.99
9	Endosulfan II	2.9e-3	4.4	99.98
10	Endrin aldehyde	4.5e-3	5.9	99.94
11	Endosulfan sulfate	5.1e-3	5.3	99.97
12	Endrin ketone	4.7e-3	9.0	99.89
13	Decachlorobiphenyl	3.7e-3	9.9	99.96

Reproducibility

The reproducibility of the 6890 Micro-ECD was established by analyzing each mixture using identical conditions five times. Each analyte in the PCB congener mixture was injected at a concentration of 50 ppb, and the analytes in the OCP mixture were 20 or 40 ppb. The results are shown in tables 4 and 5. The highest %RSD for any analyte is 3.69 percent for aldrin, which is well below the CLP maximum allowable RSD of 15 percent.¹

Table 4. PCB Congener Analysis: Reproducibility of the 6890 Micro-ECD 50 ppb; N=5.
See table 1 for conditions.

Peak	Name	Average Area	RSD (%)
1	2,4-Dichlorobiphenyl	2229	1.26
2	2,2',5-Trichlorobiphenyl	2547	1.29
3	2,4,4'-Trichlorobiphenyl	5687	1.41
4	2,2',5,5'-Tetrachlorobiphenyl	3721	1.43
5	2,2',3,5-Tetrachlorobiphenyl	4941	1.46
6	2,3,4,4'-Tetrachlorobiphenyl	5943	1.40
7	2,2',4,5,5'-Pentachlorobiphenyl	5089	1.47
8	3,3',4,4'-Tetrachlorobiphenyl	3822	1.72
9	2,3,4,4',5-Pentachlorobiphenyl	6203	1.62
10	2,2',4,4',5,5'-Hexachlorobiphenyl	6189	1.44
11	2,3,3',4,4'-Pentachlorobiphenyl	8375	1.68
12	2,2',3,4,4',5-Hexachlorobiphenyl	7538	1.56
13	3,3',4,4',5-Pentachlorobiphenyl	5092	2.02
14	2,2',3,4,5,5',6-Heptachlorobiphenyl	6224	1.69
15	2,2',3,3',4,4'-Hexachlorobiphenyl	8921	1.67
16	2,2',3,4,4',5,5'-Heptachlorobiphenyl	8527	1.82
17	2,2',3,3',4,4',5-Heptachlorobiphenyl	8625	1.91
18	2,2',3,3',4,4',5,6-Octachlorobiphenyl	8338	2.13
19	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	6097	2.55
20	Decachlorobiphenyl	4622	2.85

Table 5. OCP Analysis: Reproducibility of the 6890 Micro-ECD; N=5.
See table 1 for conditions.

Peak	Name	Concentration (ppb)	Average Area	RSD (%)
1	2,4,5,6-Tetra-m-xylene	20	4785	0.7
2	beta-BHC	20	1802	0.81
3	delta-BHC	20	3251	1.50
4	Aldrin	20	402	3.69
5	Heptachlor epoxide	20	4316	1.58
6	gamma-Chlordane	20	2958	1.23
7	alpha-Chlordane	20	4219	1.06
8	4,4' DDE	40	4103	1.76
9	Endosulfan II	40	7176	1.27
10	Endrin aldehyde	40	4719	0.85
11	Endosulfan sulfate	40	4040	3.04
12	Endrin ketone	40	4386	2.52
13	Decachlorobiphenyl	40	5369	0.85

Detection Limit

To establish the lower limit of detection for the 6890 Micro-ECD with PCBs and OCPs, 1- μ L injections were made at gradually decreasing concentrations. Figures 5 and 6 show chromatograms with analyte concentrations of 50 to 100 ppt.

All the analyte peaks for both the PCB congener and OCP mixtures are still easy to quantitate, and in fact smaller concentrations can be reliably analyzed. Aldrin, which has the lowest response of the OCPs, still exhibits an adequate signal-to-noise ratio at the 50 ppt level under these analysis conditions.

Conclusion

The Agilent 6890 Micro-ECD response was linear over the concentration range of 2 to 200 ppb, produced reproducible results, and exhibited excellent sensitivity for mixtures of PCB congeners and OCPs.

References

1. U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis," OLM03.1, August 1994.
2. R. Buffington and M.K. Wilson, eds., *Detectors for Gas Chromatography*, Agilent Technologies, Inc., Part Number 5958-9433, 1987.

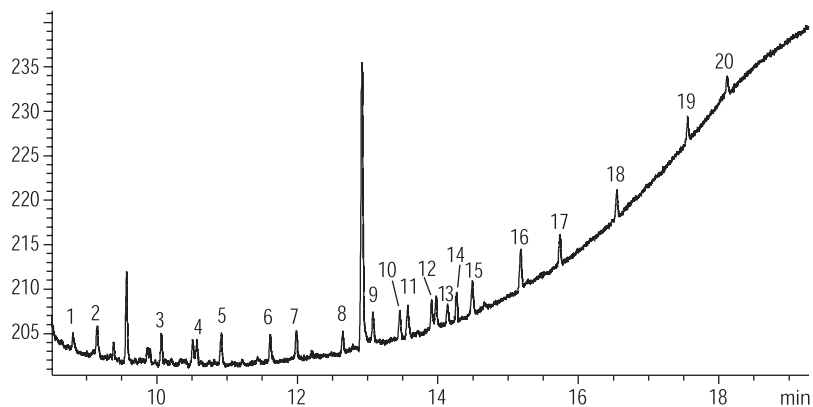


Figure 5. PCB congener mixture at 50 ppt each.

See table 1 for conditions. See table 4 for peak identification.

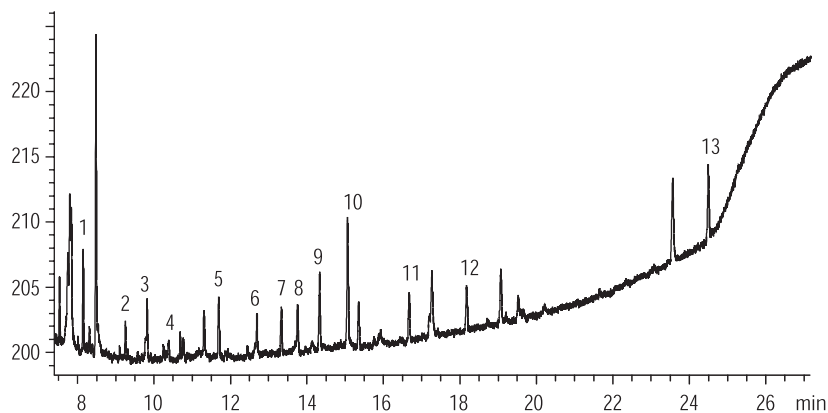


Figure 6. OCP Mixture at 50 to 100 ppt.

See table 1 for conditions. See table 5 for peak identification.

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