

Sensitive and Reproducible Determination of Organochlorine Pesticides in Water

Large volume injection and dual-column confirmation
with the Agilent GC/ECD system

Authors

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Abstract

USEPA Method 8081B requires sensitive and reliable determination of organochlorine pesticides together with confirmatory analysis on a second GC column. A large volume injection (LVI) gas chromatography-electron capture detector (GC/ECD) method was developed for the quantitative analysis of 31 organochlorine pesticides. The Agilent GC system equipped with a Multimode Inlet (MMI) operated in solvent vent mode enabled a 5 μ L injection volume while maintaining good chromatographic performance and sensitivity. Calibration linearity, instrument detection limits (IDLs), and multiday system stability were evaluated using DB-5ms and DB-1701 analytical columns. Excellent linearity with regression coefficients (R^2) greater than 0.992, IDLs of 2.39 ppb or lower, and excellent retention time repeatability with %RSD values of 0.07% or lower were achieved.

Introduction

Organochlorine pesticides (OCPs) remain important environmental contaminants due to their persistence, bioaccumulation potential, and toxicity. Regulatory laboratories often require sensitive and robust analytical methods capable of detecting these compounds at trace levels in environmental samples. USEPA Method 8081B is commonly used for the analysis of organochlorine pesticides using GC/ECD due to the strong electron-capturing properties of halogenated compounds.¹

Large volume injection (LVI) techniques can significantly improve detection sensitivity by introducing more analyte mass into the GC system. However, successful LVI implementation requires careful optimization to minimize solvent flooding, peak distortion, and poor chromatographic performance. The Agilent Multimode Inlet (MMI) provides a flexible solvent vent mode that simplifies LVI method development while maintaining analytical robustness.

In this work, an Agilent GC/ECD system equipped with MMI was evaluated for the quantitative analysis of 31 organochlorine pesticides using two analytical columns DB-5ms and DB-1701. The use of two columns follows the recommendations of USEPA Method 8081, which requires compound identification based on a primary column to be confirmed on a second column with a different stationary phase to improve analyte identification confidence. Calibration performance, unknown sample quantification, IDL determination, and multiday stability performance were assessed.

Table 1. Thirty-one organochlorine pesticides included in EPA Method 8081B.

No.	Compound Name	CAS No.
1	2,4'-DDT	789-02-6
2	4,4'-DDD	72-54-8
3	4,4'-DDE	72-55-9
4	4,4'-DDT	50-29-3
5	Aldrin	309-00-2
6	alpha-BHC	319-84-6
7	alpha-Chlordane	5103-71-9
8	beta-BHC	319-85-7
9	cis-Permethrin	54774-45-7
10	Decachlorobiphenyl	2051-24-3
11	delta-BHC	319-86-8
12	Dicofol	115-32-2
13	Dieldrin	60-57-1
14	Endosulfan I	959-98-8
15	Endosulfan II	33213-65-9
16	Endosulfan Sulfate	1031-07-8

Experimental

Reagents, standards and samples

Calibration working solutions (5, 10, 20, 50, 100, and 200 ppb) were prepared in hexane.

Instrument parameters

The Agilent GC/ECD instrument conditions and analysis parameters are shown in Tables 2 and 3.

Table 2. GC/ECD parameters for OCPs analysis with an Agilent DB-5ms column.

Gas Chromatography Conditions	
GC Column	DB-5ms, 30 m × 0.25 mm, 0.25 µm column (p/n 122-5532)
Column Pneumatics	Constant flow
Carrier Gas	Helium
Injection Volume	5.0 µL
Injector Mode	Solvent vent
Inlet Temperature	60 °C for 0.03 min, then to 325 °C at 600 °C/min
Injector Liner	Agilent Ultra Inert dimpled splitless liner (p/n 5190-2297)
Flow Rate	1.1 mL/min
ECD Temperature	320 °C
ECD Make Up Gas Flow Rate	15 mL/min
Oven Temperature Program	60 °C for 2 min 10 °C/min to 100 °C 10 °C/min to 180 °C, hold 3 min 5 °C/min to 220 °C, hold 10 min 10 °C/min to 250 °C, hold 6 min 10 °C/min to 280 °C, hold 7 min

Table 3. GC/ECD parameters for OCPs analysis with an Agilent DB-1701 column.

Gas Chromatography Conditions	
GC Column	DB-1701, 30 m × 0.25 mm, 0.25 µm column (p/n 122-0732)
Column Pneumatics	Constant flow
Carrier Gas	Helium
Injection Volume	5.0 µL
Injector Mode	Solvent vent
Inlet Temperature	36 °C for 0.08 min, then to 325 °C at 600 °C/min
Injector Liner	Agilent Ultra Inert dimpled splitless liner (p/n 5190-2297)
Flow Rate	0.75 mL/min
ECD Temperature	320 °C
ECD Make Up Gas Flow Rate	15 mL/min
Oven Temperature Program	36 °C for 0 min 50 °C/min to 150 °C, hold 2 min 4 °C/min to 200 °C, hold 12 min 2 °C/min to 240 °C, hold 3 min 4 °C/min to 275 °C, hold 10 min

Large volume injection method development and optimization

Large volume injection (LVI) techniques have gained wide attention for lowering system detection limits to meet newer and more stringent regulations. By introducing more sample into the system, the mass of analyte reaching the detector will be proportionately increased, resulting in larger peak area and peak height. If the baseline noise stays constant, larger peak height means greater signal-to-noise ratios and lower system detection limits. With properly optimized injection conditions, chromatography issues caused by larger sample volume, such as distorted analyte peaks and long solvent tailing, can be minimized.

The Agilent Multimode Inlet incorporates different injection modes into one inlet by using the same consumables and inlet liner. Its operational modes include hot split/splitless (also in pulsed mode), cold split/splitless (also in pulsed mode), and solvent vent. The LVI refers to the solvent vent mode.

As a solvent elimination technique, LVI is a function of the solvent type, inlet temperature, vent flow of evaporation gas, and analyte boiling point. Furthermore, inlet pressure during evaporation, vent time and inlet liner also have an impact on the rate of solvent removal and entire system performance.

The solvent vent mode is how the MMI perform LVI. In solvent vent mode, the inlet is kept at a low initial temperature during sample application. Pneumatically, the inlet is in split mode with a low inlet pressure. The flow of gas through the inlet liner and out to vent removes the evaporating solvent. The sample is injected so that the incoming liquid is deposited on the liner wall and the solvent evaporates at a similar rate. Once the entire sample has been injected, the inlet switches to a splitless mode for analyte transfer. The inlet is then heated to vaporize the concentrated sample and any remaining solvent and they are transferred to the column. After a sufficient period to ensure the sample transfer, the inlet is then switched to a purge mode to allow any remaining material in the inlet liner to be removed to waste. During the sample injection and solvent venting period, the GC oven has been held at an appropriate temperature to allow the solvent to refocus the analytes on the column. When this refocusing is complete, the oven is then programmed to perform the separation.

LVI method development and optimization on MMI were initially based on the solvent elimination calculator integrated in the instrument control software. This calculator was designed to determine reasonable starting conditions for a LVI method.

Following the starting conditions recommended by the solvent elimination calculator, the acquisition method is optimized for an injection volume of 5 μL of sample in hexane. This method is used for the analysis of all the calibration standards, unknown samples, IDL samples and stability samples provided. Figures 1A and 1B show representative chromatograms of the 31 OCPs obtained on DB-5ms and DB-1701.

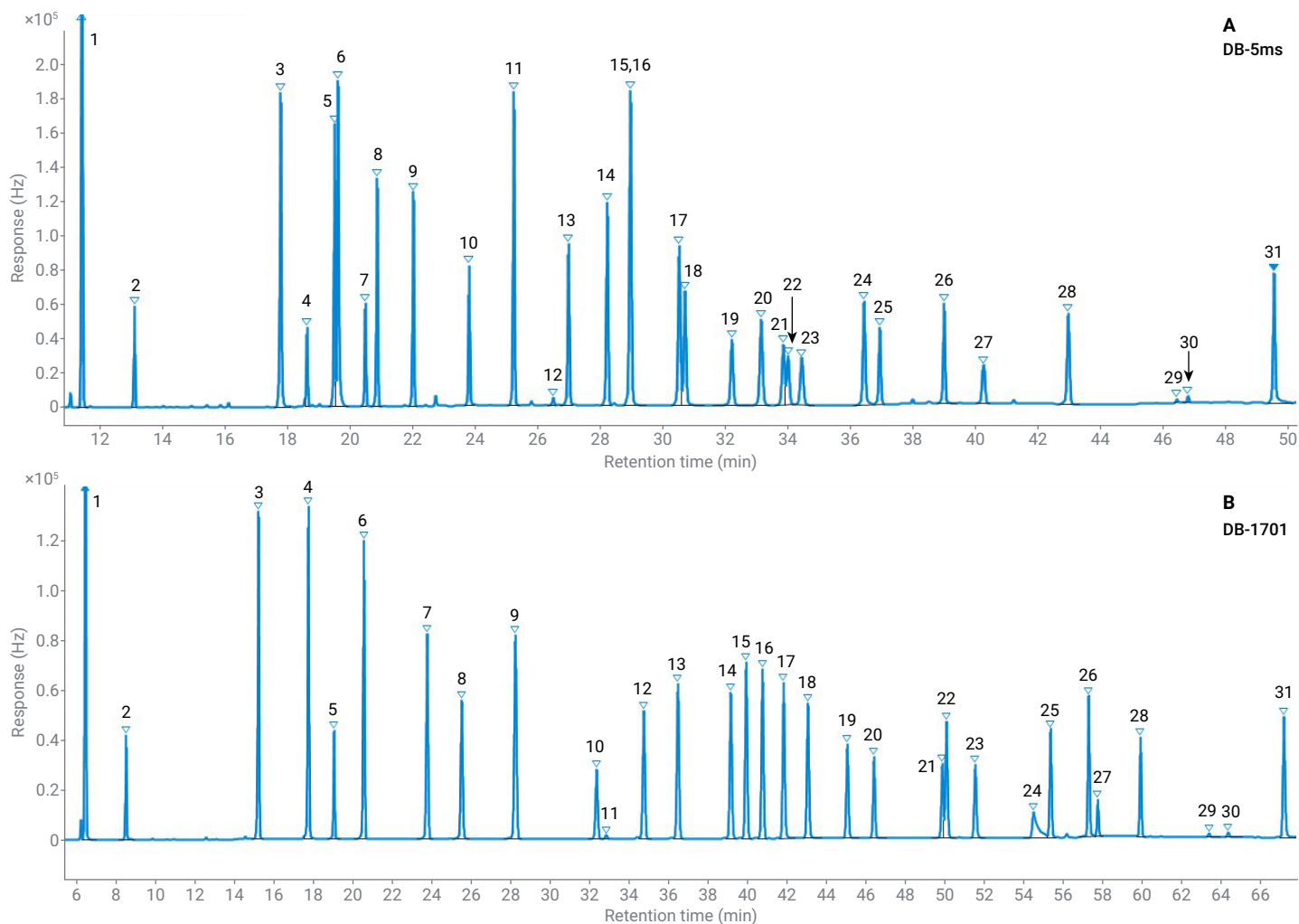


Figure 1. Organochlorine pesticides analysis on Agilent DB-5ms (A) and DB-1701 (B).

Results and discussion

Calibration curves

Six-point calibration curves (5, 10, 20, 50, 100 and 200 ppb) were generated for all 31 target pesticides on both DB-5ms and DB-1701 columns. Excellent linearity was obtained across the calibration range, with all analytes achieving regression coefficients (R^2) greater than 0.992. Most compounds demonstrated R^2 values above 0.997, indicating highly reliable quantitative performance.

Table 4. Calibration results of organochlorine pesticides with an Agilent DB-5ms column.

No.	Compound Name	RT (min)	R^2
1	Hexachlorobutadiene	11.445	0.995
2	Hexachlorocyclopentadiene	13.120	0.994
3	Tetrachloro-m-xylene	17.786	0.997
4	Trifluralin	18.641	0.998
5	alpha-BHC	19.512	0.998
6	Hexachlorobenzene	19.615	0.998
7	beta-BHC	20.495	0.998
8	Lindane (gamma-BHC)	20.870	0.996
9	delta-BHC	22.026	0.999
10	Heptachlor	23.809	0.997
11	Aldrin	25.236	0.998
12	Dicofol	26.498	0.998
13	Heptachlor Epoxide	26.985	0.998
14	gamma-Chlordane	28.220	0.998
15,16	alpha-Chlordane, Endosulfan I	28.954	0.998
17	4,4'-DDE	30.517	0.998
18	Dieldrin	30.669	0.997
19	Endrin	32.196	0.999
20	Endosulfan II	33.131	0.998
21	4,4'-DDD	33.838	0.998
22	2,4'-DDT	33.991	0.997
23	Endrin Aldehyde	34.424	1.000
24	Endosulfan Sulfate	36.425	1.000
25	4,4'-DDT	36.926	1.000
26	Methoxychlor	38.983	1.000
27	Endrin Ketone	40.222	0.998
28	Mirex	42.947	0.997
29	cis-Permethrin	46.427	1.000
30	trans-Permethrin	46.789	0.999
31	Decachlorobiphenyl	49.527	0.997

Table 5. Calibration results of organochlorine pesticides with an Agilent DB-1701 column.

No.	Compound Name	RT (min)	R^2
1	Hexachlorobutadiene	6.453	1.000
2	Hexachlorocyclopentadiene	8.508	0.997
3	Tetrachloro-m-xylene	15.203	0.998
4	Hexachlorobenzene	17.730	0.998
5	Trifluralin	19.030	0.999
6	alpha-BHC	20.536	0.997
7	Lindane (gamma-BHC)	23.740	0.997
8	Heptachlor	25.482	0.998
9	Aldrin	28.201	0.999
10	beta-BHC	32.309	0.998
11	Dicofol	34.353	0.999
12	delta-BHC	34.700	0.997
13	Heptachlor Epoxide	36.428	0.999
14	Endosulfan I	39.101	0.999
15	gamma-Chlordane	39.878	0.999
16	alpha-Chlordane	40.704	1.000
17	4,4'-DDE	41.775	0.999
18	Dieldrin	42.997	0.999
19	Endrin	44.993	1.000
20	2,4'-DDT	46.343	0.998
21	4,4'-DDD	49.804	1.000
22	Endosulfan II	50.007	0.999
23	4,4'-DDT	51.467	0.996
24	Endrin Aldehyde	54.416	0.998
25	Mirex	55.277	0.999
26	Endosulfan Sulfate	57.203	0.999
27	Methoxychlor	57.667	0.992
28	Endrin Ketone	59.832	0.998
29	cis-Permethrin	63.288	0.998
30	trans-Permethrin	64.263	0.997
31	Decachlorobiphenyl	67.082	0.999

Instrument detection limits (IDLs)

Instrument detection limits (IDLs) were calculated with 99% statistical confidence that the measured analyte signal represents a true concentration greater than zero. For this study, the IDLs were derived from the analysis of seven replicate injections of the 10 ppb standard.

The IDL was calculated using Equation 1:

Equation 1.

$$IDL = (t_{\alpha, n-1}) \times (\%RSD) \times (\text{amount of standard})/100$$

Where:

$t_{\alpha, n-1}$ is the Student's t-value corresponding to the selected confidence level and degrees of freedom ($n = 7$, therefore $n - 1 = 6$),

%RSD is the relative standard deviation of the seven replicate injections, and amount of standard is the concentration of the lowest calibration standard used for IDL determination.

At the 99% confidence level and with six degrees of freedom, the corresponding $t_{\alpha, 6}$ value is 3.14.

Applying this calculation, the IDLs for the target pesticides are summarized in the tables below. With both columns, the IDLs were calculated to be 2.39 ppb or better.

Table 6. GC/ECD IDLs for organochlorine pesticides with an Agilent DB-5ms column.

No.	Compound Name	Standard Deviation (ppb)	IDL (ppb)
1	Hexachlorobutadiene	0.712	2.24
2	Hexachlorocyclopentadiene	0.643	2.02
3	Tetrachloro-m-xylene	0.681	2.14
4	Trifluralin	0.708	2.22
5	alpha-BHC	0.441	1.38
6	Hexachlorobenzene	0.761	2.39
7	beta-BHC	0.479	1.50
8	Lindane (gamma-BHC)	0.571	1.79
9	delta-BHC	0.611	1.92
10	Heptachlor	0.602	1.89
11	Aldrin	0.652	2.05
12	Dicofol	0.489	1.54
13	Heptachlor Epoxide	0.395	1.24
14	gamma-Chlordane	0.622	1.95
15,16	alpha-Chlordane, Endosulfan I	0.608	1.91

No.	Compound Name	Standard Deviation (ppb)	IDL (ppb)
17	4,4'-DDE	0.620	1.95
18	Dieldrin	0.469	1.47
19	Endrin	0.455	1.43
20	Endosulfan II	0.523	1.64
21	4,4'-DDD	0.393	1.23
22	2,4'-DDT	0.560	1.76
23	Endrin Aldehyde	0.601	1.89
24	Endosulfan Sulfate	0.572	1.80
25	4,4'-DDT	0.431	1.35
26	Methoxychlor	0.587	1.84
27	Endrin Ketone	0.277	0.87
28	Mirex	0.377	1.18
29	cis-Permethrin	0.482	1.51
30	trans-Permethrin	0.484	1.52
31	Decachlorobiphenyl	0.474	1.49

Table 7. GC/ECD IDLs for organochlorine pesticides with an Agilent DB-1701 column.

No.	Compound Name	Standard Deviation (ppb)	IDL (ppb)
1	Hexachlorobutadiene	0.366	1.15
2	Hexachlorocyclopentadiene	0.227	0.71
3	Tetrachloro-m-xylene	0.371	1.17
4	Hexachlorobenzene	0.457	1.44
5	Trifluralin	0.370	1.16
6	alpha-BHC	0.390	1.22
7	Lindane (gamma-BHC)	0.443	1.39
8	Heptachlor	0.445	1.40
9	Aldrin	0.487	1.53
10	beta-BHC	0.428	1.34
11	Dicofol	0.340	1.07
12	delta-BHC	0.451	1.41
13	Heptachlor Epoxide	0.474	1.49
14	Endosulfan I	0.485	1.52
15	gamma-Chlordane	0.364	1.14
16	alpha-Chlordane	0.492	1.55

No.	Compound Name	Standard Deviation (ppb)	IDL (ppb)
17	4,4'-DDE	0.491	1.54
18	Dieldrin	0.481	1.51
19	Endrin	0.482	1.51
20	2,4'-DDT	0.377	1.18
21	4,4'-DDD	0.319	1.00
22	Endosulfan II	0.371	1.16
23	4,4'-DDT	0.467	1.47
24	Endrin Aldehyde	0.298	0.94
25	Mirex	0.420	1.32
26	Endosulfan Sulfate	0.380	1.19
27	Methoxychlor	0.367	1.15
28	Endrin Ketone	0.420	1.32
29	cis-Permethrin	0.487	1.53
30	trans-Permethrin	0.500	1.57
31	Decachlorobiphenyl	0.469	1.47

System stability test

System stability was evaluated using 15 replicate injections acquired over five days (three injections per day). Excellent retention time repeatability was achieved, with all compounds demonstrating retention time %RSD values of 0.07% or

lower. Peak area stability was also excellent, with area %RSD values of 7.83% or lower for all pesticides. These results demonstrate the robustness and long-term reproducibility of the Agilent GC/ECD system for routine environmental pesticide analysis.

Table 8. GC/ECD stability test for organochlorine pesticides with an Agilent DB-5ms column.

No.	Compound Name	%RSD for RT (n = 15)	%RSD for Area (n = 15)
1	Hexachlorobutadiene	0.040	6.76
2	Hexachlorocyclopentadiene	0.030	4.17
3	Tetrachloro-m-xylene	0.040	5.77
4	Trifluralin	0.050	6.18
5	alpha-BHC	0.050	5.54
6	Hexachlorobenzene	0.040	7.83
7	beta-BHC	0.040	5.96
8	Lindane (gamma-BHC)	0.040	5.60
9	delta-BHC	0.040	4.59
10	Heptachlor	0.040	2.67
11	Aldrin	0.040	4.77
12	Dicofol	0.040	4.66
13	Heptachlor Epoxide	0.050	5.30
14	gamma-Chlordane	0.050	5.30
15,16	alpha-Chlordane, Endosulfan I	0.050	4.23

No.	Compound Name	%RSD for RT (n = 15)	%RSD for Area (n = 15)
17	4,4'-DDE	0.050	7.16
18	Dieldrin	0.060	6.46
19	Endrin	0.060	7.01
20	Endosulfan II	0.070	3.31
21	4,4'-DDD	0.070	7.18
22	2,4'-DDT	0.070	6.44
23	Endrin Aldehyde	0.070	5.61
24	Endosulfan Sulfate	0.050	4.19
25	4,4'-DDT	0.040	4.41
26	Methoxychlor	0.040	6.07
27	Endrin Ketone	0.040	4.38
28	Mirex	0.050	3.70
29	cis-Permethrin	0.030	5.69
30	trans-Permethrin	0.030	5.84
31	Decachlorobiphenyl	0.030	5.94

Table 9. GC/ECD stability test for organochlorine pesticides with an Agilent DB-1701 column.

No.	Compound Name	%RSD for RT (n = 15)	%RSD for Area (n = 15)
1	Hexachlorobutadiene	0.040	6.81
2	Hexachlorocyclopentadiene	0.030	7.49
3	Tetrachloro-m-xylene	0.030	5.45
4	Hexachlorobenzene	0.020	4.94
5	Trifluralin	0.040	4.55
6	alpha-BHC	0.030	6.64
7	Lindane (gamma-BHC)	0.040	6.58
8	Heptachlor	0.040	6.09
9	Aldrin	0.050	4.39
10	beta-BHC	0.040	5.91
11	Dicofol	0.040	5.14
12	delta-BHC	0.030	4.74
13	Heptachlor Epoxide	0.040	4.97
14	Endosulfan I	0.030	4.94
15	gamma-Chlordane	0.040	4.62
16	alpha-Chlordane	0.030	4.41

No.	Compound Name	%RSD for RT (n = 15)	%RSD for Area (n = 15)
17	4,4'-DDE	0.030	4.02
18	Dieldrin	0.030	5.10
19	Endrin	0.030	5.84
20	2,4'-DDT	0.030	6.45
21	4,4'-DDD	0.030	5.32
22	Endosulfan II	0.030	5.49
23	4,4'-DDT	0.030	5.04
24	Endrin Aldehyde	0.030	7.33
25	Mirex	0.020	3.80
26	Endosulfan Sulfate	0.020	5.58
27	Methoxychlor	0.020	6.45
28	Endrin Ketone	0.020	5.56
29	cis-Permethrin	0.030	4.35
30	trans-Permethrin	0.030	5.26
31	Decachlorobiphenyl	0.030	6.63

Conclusion

The Agilent GC/ECD system equipped with a Multimode Inlet successfully demonstrated robust quantitative analysis of 31 organochlorine pesticides using large volume injection technology. The solvent vent LVI approach enabled high sensitivity while maintaining good chromatographic performance and excellent reproducibility.

Key performance highlights included:

- Successful dual-column setup meeting EPA 8081 confirmatory identification requirements
- Excellent calibration linearity with R^2 values greater than 0.992
- IDLs of 2.39 ppb or lower for all analytes
- Excellent retention time repeatability with %RSD $\leq$ 0.07%
- Stable multiday peak area reproducibility with %RSD $\leq$ 7.83%

The combination of Agilent GC/ECD instrumentation, MMI solvent vent technology, and optimized large volume injection workflow provides an effective solution for routine environmental monitoring of organochlorine pesticides.

Reference

1. **Method 8081B: Organochlorine Pesticides by Gas Chromatography, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods**

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DE-017040

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Printed in the USA, September 17, 2026
5994-9441EN