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GC Monitoring of Chlorinated Pesticides in Hazardous Waste Sites

SPB-608 capillary columns were evaluated for monitoring organochlorine pesticides in hazardous waste samples under US EPA Contract Laboratory Program, March 1990 Statement of Work requirements. All components in the CLP-specified pesticides test mix were baseline resolved, exceeding CLP performance requirements. The combined decomposition of endrin and 4,4'-DDT was 8.86%, easily meeting the inertness requirement that the combined decomposition of these compounds be less than 30%. Linearity was well within CLP specifications; the mean relative standard deviation of the calibration factors was 9.49% and absolute retention times of all the analytes were within the windows established in accordance with the method.

The Contract Laboratory Program (CLP) March 1990 Statement of Work is the most recent gas chromatography procedure published by the US EPA for the monitoring of chlorinated pesticides in samples from abandoned waste sites. This method specifies stringent inertness, resolution, and linearity requirements for the wide-bore (0.53mm ID) capillary GC column.

SPB™-608 capillary columns, which are manufactured and tested specifically for monitoring organochlorine pesticides and PCBs in wastewater according to US EPA Method 608, are also suitable for the CLP method and for Method 8081 for current waste sites. Although the two methods have similar column performance requirements, the acceptance criteria for the CLP method are more stringent. Using the CLP method requirements as the measure of SPB-608 column performance ensures that the column meets Method 8081 requirements.

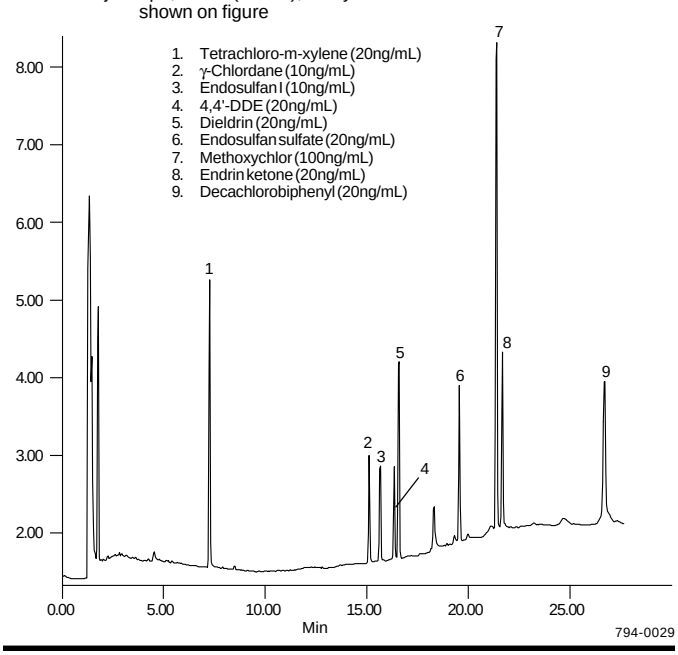
We evaluated the SPB-608 column using the series of test mixtures specified in the CLP method to measure column resolution and inertness, and system linearity. Each mix contains two surrogate compounds, tetrachloro-m-xylene and decachlorobiphenyl.

Column performance, measured using a resolution check mixture containing seven target pesticides at concentrations ranging from 10ng/mL to 100ng/mL, exceeded the CLP method requirement that resolution between consecutive peaks be greater than 60% of the height of the shorter peak. The analytes in the resolution check mix were baseline resolved, including the pairs of analytes cited in the method as having the poorest resolution on the DB-608 column — γ-chlordane/endosulfan I, 4,4'-DDE/dieldrin, and metho-xychlor/endrin ketone (Figure A).

Column inertness is evaluated using a mixture of six target pesticides ranging in concentration from 10ng/mL to 250ng/mL. Decomposition of either endrin or 4,4'-DDT must not exceed 20%,

Figure A. Baseline Resolution of Target Compounds

Column: **SPB-608, 30m x 0.53mm ID, 0.5µm film**
Cat. No.: **25312**
Oven.: 150°C (0.5 min) to 275°C at 6°C/min
Carrier: helium, 5mL/min
Det.: ECD, 300°C
Inj.: 2µL, direct (200°C), analyte concentrations shown on figure

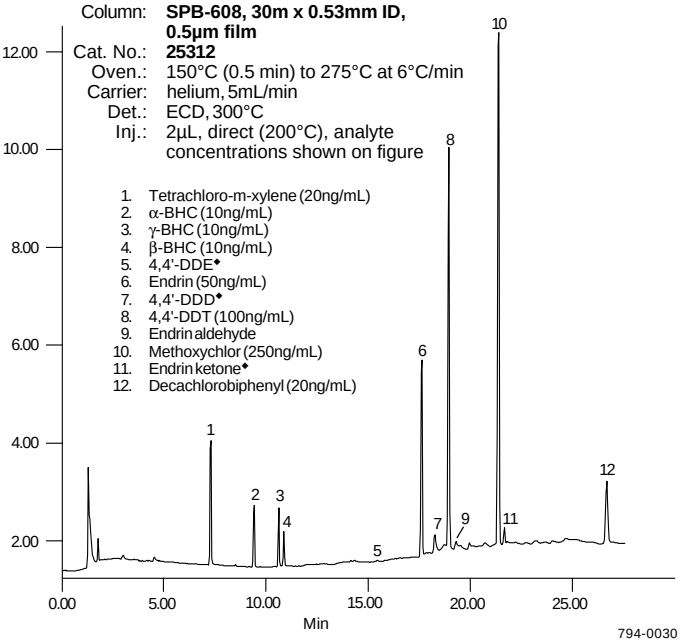


and their combined decomposition must be less than 30%. The recovery of endrin is determined by measuring the two by-products, endrin aldehyde and endrin ketone. The recovery of 4,4'-DDT is determined by measuring the by-products 4,4'-DDD and 4,4'-DDE.

The SPB-608 column easily meets the inertness criteria established in the CLP pesticides method. Endrin decomposition was 8.7%. All decomposition was measured in the form of endrin ketone (Figure B); no measurable amounts of endrin aldehyde were evident. Decomposition of 4,4'-DDT was measured at 0.16%, in the form of 4,4'-DDE. No measurable amounts of 4,4'-DDD were evident. The combined decomposition of 4,4'-DDT and endrin on this column was 8.86%.

The linearity of the system, including the column, is determined by calculating percent relative standard deviation (%RSD) of the calibration factors from a three-point calibration curve for each pesticide and surrogate in individual solutions. Three concentration ranges are used to determine linearity: a low concentration mix

Figure B. Low Levels of Endrin/DDT Decomposition Easily Meet Inertness Requirements



◆Decomposition products.

consisting of the target pesticides in the range of 5 - 10ng/mL, a mid-range concentration mix (4 x the low concentration) and a high concentration mix (16 x the low concentration). The target compounds were analyzed in two different standard mixes, A and B, to avoid coelutions. Absolute retention times were determined by calculating the mean retention time from both mixes.

The method requires that the relative standard deviations (RSD) of the calibration factors for most of the analytes be less than 20%, allowing for up to two of the target analytes to exceed 20%, but be less than 30%. The RSD for the surrogates must also be less than 30%.

Linearity was well within CLP specifications (Table 1). The mean RSD was 9.49%, including all target compounds and surrogates. Absolute retention times of all the target analytes and surrogates in the performance evaluation mixture were within the retention time windows established in the calibration runs for the three concentration ranges (Table 2). The target analytes were baseline resolved (Figure C), well exceeding the CLP requirement that the resolution between adjacent peaks of the individual standard mixes be greater than 90%.

These investigations show that the SPB-608 column easily meets US EPA requirements for stability, inertness, and linearity as specified in the US EPA CLP Pesticide Method, March 1990 Statement of Work.

Table 1. Linearity for Pesticides on an SPB-608 Column

Compound	Calibration Factor %RSD
α-BHC	9.90
β-BHC	3.28
δ-BHC	17.16
γ-BHC (Lindane)	6.32
Heptachlor	2.22
Aldrin	14.61
Heptachlor epoxide	9.80
Endosulfan I	3.33
Dieldrin	7.13
4,4'-DDE	15.66
Endrin	5.00
Endosulfan II	27.86
4,4'-DDD	4.47
Endosulfan sulfate	10.65
4,4'-DDT	6.84
Methoxychlor	6.62
Endrin ketone	13.62
Endrin aldehyde	11.93
α-Chlordane	7.17
γ-Chlordane	5.84
Tetrachloro-m-xylene■	8.78
Decachlorobiphenyl■	10.52

%RSD for up to two target compounds, not including surrogates, may be >20%, but must be ≤30.0%. %RSD for remainder of target compounds must be ≤20.0%. %RSD for surrogates must be ≤30.0%.

■Surrogates

Table 2. Retention Times for Pesticides on an SPB-608 Column

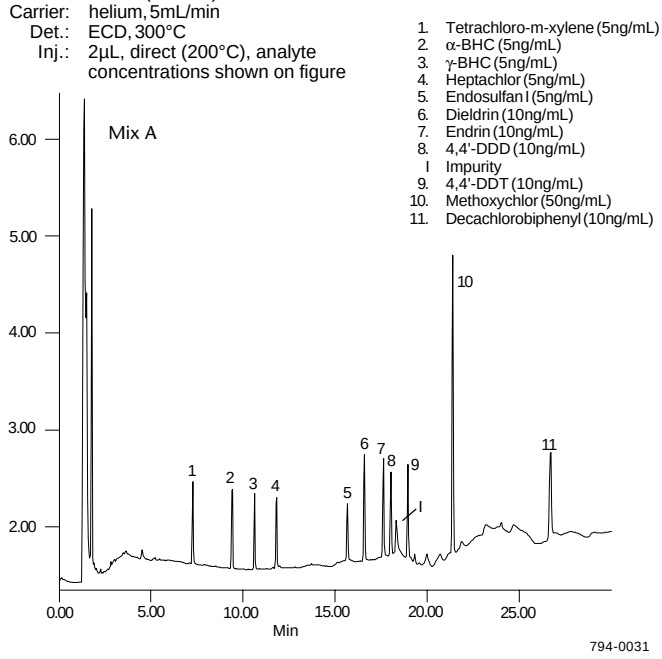
Compound	Mean RT (n=3)	Retention Time Window● From	To
Tetrachloro-m-xylene▲	7.34	7.29	7.39
α-BHC	9.43	9.38	9.48
γ-BHC (Lindane)	10.63	10.58	10.68
β-BHC	10.92	10.87	10.97
Heptachlor	11.84	11.79	11.89
δ-BHC	12.04	11.99	12.09
Aldrin	12.88	12.83	12.93
Heptachlor epoxide	14.06	13.99	14.13
γ-Chlordane	15.17	15.10	15.24
α-Chlordane	15.65	15.58	15.72
Endosulfan I	15.69	15.62	15.76
4,4'-DDE	16.40	16.33	16.47
Dieldrin	16.61	16.54	16.68
Endrin	17.65	17.58	17.72
4,4'-DDD	18.05	17.98	18.12
Endosulfan II	18.22	18.05	18.29
4,4'-DDT	18.98	18.91	19.05
Endrin aldehyde	19.15	19.08	19.22
Endosulfan sulfate	19.62	19.55	19.69
Methoxychlor	21.41	21.34	21.48
Endrin ketone	21.73	21.66	21.80
Decachlorobiphenyl▲	26.76	26.66	26.86

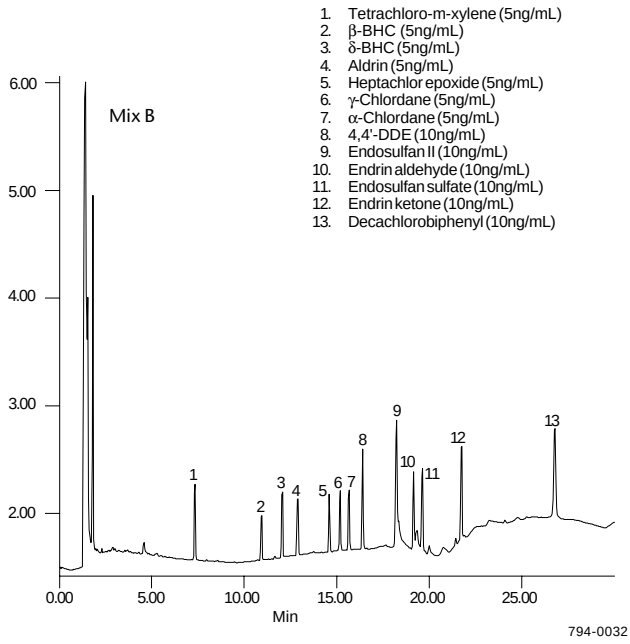
●Retention time windows are ±0.05 minutes for all compounds that elute before heptachlor epoxide; ±0.07 minutes for heptachlor epoxide and other compounds that elute before decachlorobiphenyl; ±0.10 minutes for decachlorobiphenyl.

▲Surrogate retention times are measured from standard mix A analysis.

Figure C. Standard Mixes, Low-Range Concentration

Column: **SPB-608, 30m x 0.53mm ID, 0.5µm film**
Cat. No.: **25312**
Oven.: 150°C (0.5 min) to 275°C at 6°C/min
Carrier: helium, 5mL/min
Det.: ECD, 300°C
Inj.: 2µL, direct (200°C), analyte concentrations shown on figure





Ordering Information:

SPB-608 Fused Silica Capillary Columns

Description	Cat. No.
30m x 0.53mm ID, 0.5µm film	**25312**
15m x 0.53mm ID, 0.5µm film	**25310-U**

Reference

US EPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, Document Number 0LM01.0, Including Revisions 0LM01.1 (December 1990) and 0LM01.1.1 (February 1991).

Reference not available from Supelco.