



Project Summary

Application of Open-Tubular Columns to SW-846 GC Methods

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The document "Test Methods for Evaluating Solid Waste," Office of Solid Waste, Manual SW-846, provides a compilation of methods for evaluating RCRA solid wastes for environmental and human hazards. One of the methods in this document, Method 8000, provides guidance on gas chromatographic analysis with specific details on instrument calibration, maintenance, and quality control. Since most of the GC methods in the SW-846 manual specify the use of packed columns, and since for the past 10 years the scientific community has had access to the fused-silica capillary column technology, we were asked by the U.S. Environmental Protection Agency to develop gas chromatographic procedures that employ fused-silica open-tubular columns. When compared to packed columns, the open-tubular columns offer improved resolution, and thus better selectivity, increased sensitivity, and shorter analysis times. Furthermore, when injection is performed using an injection tee and two dissimilar columns connected to two identical detectors, then sample throughput is increased by a factor of two because the primary and confirmatory analyses are being conducted simultaneously. We have used the dual-column/dual-detector approach in this study to establish gas chromatographic conditions for six groups of target analytes: Method 8040 phenols, Methods 8080/8081 organochlorine pesticides, Method 8090 nitroaromatic compounds, Method 8110 haloethers, Method 8120 chlorinated

hydrocarbons, and Methods 8140/8141 organophosphorus pesticides. In each case, the list of target analytes was expanded to cover more target analytes than those currently listed in the methods mentioned above. The approach taken was as follows: select columns for the dual-column/dual-detector approach, establish conditions that give the best chromatography for the target analytes in terms of resolution and peak shape, establish method reproducibility and linearity, select at least one internal standard and surrogate compound per method, and finally test the procedure with blind performance evaluation samples of known composition as well as with extracts of real matrices.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Regulation of hazardous wastes under the Resource Conservation and Recovery Act (RCRA) of 1976 and its elements requires use of analytical methodologies that provide reliable data. The document "Test Methods for Evaluating Solid Waste," Office of Solid Waste Manual SW-846, revised recently (1), provides a compilation of methods for evaluating RCRA solid wastes for environmental and human health hazards. One of the methods in this document, Method 8000, provides guidance on gas chromato-

graphic analysis with specific details on sample extraction, extract cleanup, and, occasionally, derivatization of analytes being given in the various methods included in this manual. Since most of the methods in the SW-846 manual specify the use of packed columns, and since for the past ten years the scientific community had access to the fused-silica capillary column technology, we were asked to develop gas chromatographic procedures that employ fused-silica open-tubular columns. When compared to packed columns, the open-tubular columns offer improved resolution, and thus better selectivity, increased sensitivity, and faster analyses. Furthermore, when analysis is performed using an injection tee and two dissimilar columns connected to two identical detectors, then sample throughput is increased by a factor of two because the primary and confirmatory analyses are being conducted simultaneously. We have used the dual-column/dual-detector approach in this study to select gas chromatographic conditions for six groups of target analytes: Method 8040 phenols, Methods 8080/8081 organochlorine pesticides, Method 8090 nitroaromatic compounds, Method 8110 haloethers, Method 8120 chlorinated hydrocarbons, and Methods 8140/8141 organophosphorus pesticides.

The results of the study presented in this report indicate that the dual-column/dual-detector approach using two 30-m x 0.53-mm ID fused-silica open-tubular columns coated with dissimilar stationary phases and connected to either an 8-in injection tee or a press-fit Y-shaped splitter is reliable for the gas chromatographic determination of the target compounds mentioned above. Also included in this report as an appendix is a literature review covering the state-of-the-art technology on the 0.53-mm ID fused-silica open-tubular columns and a protocol for the gas chromatographic determinations using the dual-column/dual-detector approach.

Experimental

Apparatus

a. Gas chromatographs – Varian 6000 with constant-current/pulsed-frequency dual electron capture detector (ECD) interfaced to a Varian Vista 402 data system; Varian 6500 with constant-current/pulsed-frequency dual ECD interfaced to a Varian Vista 604 data system; Varian 3700 with constant-current/pulsed-frequency dual ECD interfaced to two Spectra-Physics SP4290 integrators.

- b. Autosampler – Varian, Model 8000
 c. GC Columns – DB-5 and DB-1701, 30-m x 0.53-mm ID fused-silica open-tubular columns for the analysis of phenols, organochlorine pesticides, nitroaromatics, haloethers, and chlorinated hydrocarbons; DB-5 and DB-210, 30-m x 0.53-mm ID fused-silica open-tubular columns for the analysis of organophosphorus pesticides. The GC operating conditions are given with the individual methods.
 d. Splitters – J&W Scientific press-fit Y-shaped 3-way union glass splitter or Supelco 8-in glass injection tee.

Materials

Standards – Analytical reference standards of the test compounds were obtained from the U.S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository, Aldrich Chemical, and Ultra Scientific Incorporated. Purities were stated to be better than 98 percent. Stock solutions of each test compound were prepared at 1 mg/mL. Working calibration solutions were prepared in hexane by serial dilutions of a composite stock solution prepared from the individual stock solutions.

Samples – EPA WP-281 Samples 2 and 4 were analyzed for the 34 phenols; EPA WP-186 Sample 3, EPA WP-285 Samples 1, 2, and 3, and EPA WP-286 Sample 1 were analyzed for the 22 chlorinated hydrocarbons.

Matrices – Matrices 1 and 2 were soil samples taken from a farm in Northern California that was known to have used organochlorine pesticides, diazinon, ethion, ziram, carbaryl, benomyl, carbofenothion, and malathion. Matrix 3 was a wood sample that may have been contaminated with pesticides. Matrix 4 was a soil sample identified as "S2A Greenhouse South." Matrix 5 was a soil sample identified as GJ 230, EPA CLP Case 12449. Matrix 6 was a soil sample from an unknown source. These samples were extracted by sonication with methylene chloride/acetone (1:1) at least 10 months prior to this study, and the extracts were cleaned up by gel permeation chromatography. Following cleanup, the extracts were frozen at -20°C. Only the extracts spiked with the organochlorine pesticides were subjected to additional diol cartridge cleanup prior to analysis by gas chromatography.

Derivatization

Derivatization of phenols – Individual phenol stock solutions were prepared at 1 mg/mL in hexane. A composite solution at 20 µg/mL per

component was prepared by combining the individual stock solutions and by dilution with hexane. One hundred µL of the composite solution was added to 8 mL acetone in a 10-mL graduated concentrator tube with screw caps. To this solution, 100 µL of 5-percent pentafluorobenzyl bromide (PFBBR) reagent and 100 µL of 10-percent K₂CO₃ solution were added. The contents were mixed by shaking the capped tube gently. The capped tube was heated in a water bath at 60°C for one hour. The solution was cooled to room temperature and concentrated to 0.5 mL using nitrogen blowdown.

Results and Discussion

Phenols

The current EPA Method 8040 provides gas chromatographic procedures for the determination of 11 phenolic compounds. Analysis is performed either by gas chromatography using a flame ionization detector or by derivatization of the phenolic compounds with PFBBR and detection with an electron capture detector. We have expanded the list of the Method 8040 compounds to the 34 compounds presented in Table 1.

The 34 phenols listed in Table 1 were derivatized with PFBBR according to a method by Lee et al. (2). By examining the data in Table 1, we concluded that neither column could separate all 34 compounds. Five pairs were co-eluting on the DB-5 column and three pairs were co-eluting on the DB-1701 column. The pairs that were co-eluting (complete overlap) on the two columns are identified as follows:

DB-5: 2,6-dimethylphenol/
 2,5-dimethylphenol
 2,4-dimethylphenol/
 2-chlorophenol
 2,6-dichlorophenol/
 4-chloro-2-methylphenol
 2,4,5-trichlorophenol/
 2,3,5-trichlorophenol
 2,3,4,5-tetrachlorophenol
 /2,5-dinitrophenol

DB-1701: 3-chlorophenol
 /3,4-dimethylphenol
 2,4-dichlorophenol
 /3,5-dichlorophenol
 2,4,5-trichlorophenol
 /2,3,5-trichlorophenol

In addition, 3-methylphenol was only partially resolved from 4-methylphenol on the DB-5 and the DB-1701 columns, and 2-chlorophenol was only partially resolved from 2,3-dimethylphenol on the

Table 1. Retention Times of the PFB Derivatives of Phenols^a

Compound No.	Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
1	Phenol	108-95-2	4.69	6.36
2	2-Methylphenol	95-48-7	5.68	7.44
3	3-Methylphenol	108-39-4	6.05	7.99
4	4-Methylphenol	106-44-5	6.21	8.13
5	2,6-Dimethylphenol	255117-01-5	7.08	8.83
6	2,5-Dimethylphenol	66502-87-0	7.08	9.02
7	2,4-Dimethylphenol	105-67-9	7.34	9.27
8	2,3-Dimethylphenol	86260-39-1	7.96	10.11
9	2-Chlorophenol	95-97-8	7.34	10.24
10	3-Chlorophenol	108-43-0	7.86	10.78
11	3,4-Dimethylphenol	b	8.46	10.78
12	4-Chlorophenol	106-48-9	8.19	11.31
13	2-Chloro-5-methylphenol	80996-91-4	9.12	12.25
14	2,6-Dichlorophenol	87-65-0	9.73	12.52
15	4-Chloro-2-methylphenol	1570-64-5	9.73	12.89
16	4-Chloro-3-methylphenol	59-50-7	10.18	13.31
17	2,5-Dichlorophenol	583-78-8	10.71	14.37
18	3,5-Dichlorophenol	591-35-5	11.02	14.75
19	2,4-Dichlorophenol	120-83-2	11.02	14.75
20	2,4,6-Trichlorophenol	88-06-2	12.85	15.76
21	2,3-Dichlorophenol	576-24-9	12.01	16.22
22	3,4-Dichlorophenol	95-77-2	12.51	16.67
23	2,3,6-Trichlorophenol	933-75-5	13.93	17.36
24	2-Nitrophenol	88-75-5	12.51	19.19
25	2,4,5-Trichlorophenol	95-95-4	15.02	19.35
26	2,3,5-Trichlorophenol	933-78-8	15.02	19.35
27	3-Nitrophenol	554-84-7	13.69	20.06
28	2,3,5,6-Tetrachlorophenol	935-95-5	17.71	21.18
29	2,3,4,6-Tetrachlorophenol	58-90-2	17.96	21.49
30	2,3,4-Trichlorophenol	15950-66-0	16.81	21.76
31	4-Nitrophenol	100-02-7	15.69	22.93
32	2,3,4,5-Tetrachlorophenol	4901-51-3	20.51	25.52
33	Pentachlorophenol	87-86-5	22.96	26.81
34	2,5-Dinitrophenol	25550-58-7	20.51	30.15
IS-1 ^c	2,5-Dibromotoluene	b	3.16	3.18
IS-2 ^c	2,2',5,5'-Tetrabromobiphenyl	b	25.16	28.68
SU ^c	2,4-Dibromophenol	b	16.02	20.56

^a The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83- μ m film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0- μ m film thickness) connected to an 8-ln injection tee (Supelco Inc.). Temp. program: 150°C (1-min hold) to 275°C (2-min hold) at 3°C/min; injector temp. 250°C; detector temp. 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

^b Not available.

^c IS = internal standard; SU = surrogate compound.

DB-1701 column. Although the two columns are quite different in polarity, the elution order of the 34 compounds was not drastically altered when we compared the data from the two columns.

Twenty-four compounds were determined under the conditions established for the PFB derivatives of the phenolic compounds in order to select an internal standard. Two internal standards, one that elutes early (2,5-dibromotoluene) and one that elutes late (2,2',5,5'-tetrabromobiphenyl) were recommended. Nine

phenolic compounds containing either fluorine or bromine on the benzene ring, a naphthol, and a phenylphenol were derivatized with PFBB and analyzed under the conditions given in Table 1. All but one compound (2,4-dibromophenol) co-eluted with the target phenols; therefore, 2,4-dibromophenol was selected as the surrogate compound.

To determine the reproducibility of the injection technique (in terms of the individual retention times and detector responses) when using the dual-column/

dual-detector approach, we performed a series of 10 consecutive injections on the DB-5 and the DB-1701 column pair. The retention time reproducibility (percent RSD) was better than 0.33 percent for the DB-5 column and 0.34 percent on the DB-1701 column. The reproducibility of the detector response for the DB-5 column was better than 1.8 percent except for the 2,3-dimethylphenol/3-chlorophenol and the 2,3,4,5-tetrachlorophenol/2,5-dinitrophenol pairs at 14.7 and 13.8 percent, respectively. The

reproducibility of the detector response for the DB-1701 column was better than 8.2 percent, with 21 values under 4 percent, and with the exception of three compounds for which the RSD values were between 11.8 and 12.2 percent.

The method linearity was established from two sets of calibrations. The linear ranges for both the DB-5 and DB-1701 columns were found to lie between 20 pg and 160 pg, which was very narrow since it covered only one order of magnitude between the minimum quantifiable amounts and the maximum quantities before detector overloading occurred. Most correlation coefficients were greater than 0.95 but below 0.990 (for 24 of the 34 analytes) when the DB-1701 column was used. The daily variation of detector response factors (percent difference) were determined one day and two days after the multilevel calibration. Significant increases in the percent differences were observed for the DB-1701 column two days after the calibration was performed. These results indicate that the gas chromatographic system requires daily calibration

Organochlorine Pesticides

The current EPA Methods 8080/8081 provide gas chromatographic procedures for the determination of 18 organochlorine pesticides, toxaphene, and Aroclors. The analysis is performed by gas chromatography using an electron capture detector. We have expanded Methods 8080/8081 to cover the 45 compounds presented in Table 2. Standards of these 45 organochlorine pesticides were analyzed on two gas chromatographic systems. One system was equipped with a J&W Scientific press-fit Y-shaped splitter, a 30-m x 0.53-mm ID DB-5 column of 1.5- μ m film thickness, and a 30-m x 0.53-mm ID DB-1701 column of 1.0- μ m film thickness. The other system was equipped with a Supelco 8-in injection tee, a 30-m x 0.53-mm ID DB-5 column of 0.83- μ m film thickness, and a 30-m x 0.53-mm ID DB-1701 column of 1.0- μ m film thickness.

The pairs that were co-eluting (complete overlap) on the two columns using the first system are identified as follows:

DB-5: trans-permethrin/heptachlor epoxide
endosulfan I/alpha-chlordane
perthane/endrin
endosulfan II/chloropropylate/
chlorobenzilate
p,p'-DDT/endosulfan sulfate
methoxychlor/dicofol

DB-1701: chlorothalonil/beta-BHC
delta-BHC/DCPA/trans-
permethrin
alpha-chlordane/trans-nonachlor
captan/dieldrin
chlorobenzilate/chloropropylate

With the thinner-film DB-5 column, a different type of splitter, and the slower temperature programming rate, fewer compounds co-eluted on the DB-1701 column; however, on the DB-5 column there were still 6 pairs co-eluting (Table 2):

DB-5: diallate/alpha-BHC
perthane/endosulfan II
chlorobenzilate/chloropropylate
endrin/nitrofen
p,p'-DDT/endosulfan sulfate
methoxychlor/dicofol

DB-1701: alpha-chlordane/trans-nonachlor
(partially resolved)
p,p'-DDD/endosulfan II
(partially resolved)

Out of 10 compounds chromatographed under the conditions established for the organochlorine pesticides, α,α' -dibromo-m-xylene was recommended as the internal standard for the DB-5 (0.83- μ m film)/DB-1701 column pair, and 2-bromobiphenyl was recommended as the surrogate compound.

From the results of 10 consecutive injections, we determined the retention time reproducibility (percent RSD) to be better than 0.54 percent for both columns. The reproducibility of the detector response for the DB-5 column was better than 28.6 percent, with 32 of 43 values being under 6.7 percent, and the reproducibility of the detector response on the DB-1701 column was better than 21.1 percent, with 29 of the 43 values being under 5.6 percent.

The detector response for the DB-5 (0.83- μ m film)/DB-1701 column pair was linear for all target analytes from 10 pg to 100 pg per column, with linear correlation coefficients being greater than 0.95 for all compounds on the DB-5 column and for 26 out of 40 compounds on the DB-1701 column. Percent differences for RFs determined one day after the gas chromatographic system was calibrated ranged from 17.7 to -37.8 percent for the DB-5 column and from 33.4 to -45.8 percent for the DB-1701 column indicating that the gas chromatographic system requires daily calibration.

Nitroaromatics

Thirty-six nitroaromatic compounds were determined on the DB-5/DB-1701 column pair (Table 3). By examining the

retention time data in Table 3, we concluded that neither column can separate all 36 compounds. The co-eluting compounds among the 36 test compounds were:

DB-5: 2,4,6-trichloronitrobenzene/
1,3-dinitrobenzene
1-chloro-2,4-dinitrobenzene/
1-chloro-3,4-dinitrobenzene/
1,2,3-trichloro-4-nitrobenzene
DB-1701: 2,4-dichloronitrobenzene/
4-chloro-3-nitrotoluene
2,4,6-trichloronitrobenzene/
1,4-naphthoquinone
1-chloro-2,4-dinitro-
benzene/2,3,4,5-tetra-
chloronitrobenzene

In addition, on the DB-5 column 2,5-dichloronitrobenzene partially overlapped with 4-chloro-3-nitrotoluene and trifluralin partially overlapped with benefin. On the DB-1701 column, compounds that partially overlapped include p-nitrotoluene/1-chloro-3-nitrobenzene and trifluralin/benefin.

Out of 22 compounds, hexachlorobenzene was selected as the internal standard and 1-chloro-3-nitrobenzene was selected as the surrogate compound.

From the results of 10 consecutive injections, we determined the retention time reproducibility (percent RSD) to be better than 0.22 percent for both columns, with most values less than 0.07 percent. The reproducibility of the detector response was better than 9.4 percent on the DB-5 column, with the exception of 1,2,3-trichloro-4-nitrobenzene, 1-chloro-2,4-nitrobenzene and 1-chloro-3,4-dinitrobenzene which were co-eluting on the DB-5 column and for which the RSD was 10.56 percent. The reproducibility of the detector response for the DB-1701 column was better than 9.13 percent for all target compounds.

The detector response was linear for all target analytes in the 25- to 500-pg range, with correlation coefficients greater than 0.99 for 33 out of the 36 compounds on the DB-5 column. The correlation coefficients for the DB-1701 column were greater than 0.99 for all compounds, with the exception of 2,4,6-trichloronitrobenzene and 1,4-naphthoquinone, which coelute, and 1-chloro-3,4-dinitrobenzene. Percent differences for RFs determined on consecutive days indicate that the gas chromatographic system requires daily calibration.

Haloethers

Nineteen haloethers were determined on the DB-5/DB-1701 column pair each connected to an electron capture detector

Table 2. Retention Times of the Organochlorine Pesticides^a

Compound No.	Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
1	DBCP	96-12-8	2.14	2.84
2	Hexachlorocyclopentadiene	77-47-4	4.49	4.88
3	Etridiazole	2593-15-9	6.38	8.42
4	Chloroneb	2675-77-6	7.46	10.60
5	Hexachlorobenzene	118-74-1	12.79	14.58
6	Diallate	2303-16-4	12.35	15.07
7	Propachlor	1918-16-17	9.96	15.43
8	Trifluralin	1582-09-8	11.87	16.26
9	alpha-BHC	319-84-6	12.35	17.42
10	PCNB	82-68-8	14.47	18.20
11	gamma-BHC	58-89-9	14.14	20.00
12	Heptachlor	76-44-8	18.34	21.16
13	Aldrin	309-00-2	20.37	22.78
14	Alachlor	15972-60-8	18.58	24.18
15	Chlorothalonil	1897-45-6	15.81	24.42
14	Alachlor	15972-60-8	18.58	24.18
16	beta-BHC	319-85-7	13.80	25.04
17	Isodrin	465-73-6	22.08	25.29
18	DCPA	1861-32-1	21.38	26.11
19	delta-BHC	319-86-8	15.49	26.37
20	Heptachlor epoxide	1024-57-3	22.83	27.31
21	Endosulfan I	959-98-8	25.00	28.88
22	gamma-Chlordane	5103-74-2	24.29	29.32
23	alpha-Chlordane	5103-71-9	25.25	29.82
24	trans-Nonachlor	39765-80-5	25.58	30.01
25	p,p'-DDE	72-55-9	26.80	30.40
26	Dieldrin	60-57-1	26.60	31.20
27	Captan	133-06-2	23.29	31.47
28	Perthane	72-56-0	28.45	32.18
29	Endrin	72-20-8	27.86	32.44
30	Chloropropylate	b	28.92	34.14
31	Chlorobenzilate	510-15-6	28.92	34.42
32	Nitrofen	1836-75-5	27.86	34.42
33	33 p,p'-DDD	72-54-8	29.32	35.32
34	Endosulfan II	33213-65-9	28.45	35.51
35	p,p'-DDT	50-29-3	31.62	36.30
36	Endrin aldehyde	7421-93-4	29.63	38.08
37	Mirex	2385-85-5	37.15	38.79
38	Endosulfan sulfate	1031-07-8	31.62	40.05
39	Methoxychlor	72-43-5	35.33	40.31
40	Captafol	2425-06-1	32.65	41.42
41	Endrin ketone	53494-70-5	33.79	42.26
42	trans-Permethrin	51877-74-8	41.50	45.81
43	Kepone	143-50-0	31.10	c
44	Dicofol	115-32-2	35.33	c
45	Dichlone	117-80-6	15.17	c
IS ^d	alpha,alpha-Dibromo-m-xylene	b	9.17	11.51
SU ^d	2-Bromobiphenyl	b	8.54	12.49

^a The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83- μ m film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0- μ m film thickness) connected to an 8-lin injection tee (Supelco Inc.). Temperature program: 140°C (2-min hold) to 270°C (1-min hold) at 2.8°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

^b Not available.

^c IS = internal standard; SU = surrogate compound.

using the gas chromatographic conditions given in Table 4. By examining the data in Table 4, we concluded that the best separation of the 19 compounds was achieved on the DB-1701 column. The elution order of the 19 compounds on the two columns was identical, with the exception of 2,4-dichlorophenyl-3'-methyl-4'-nitrophenyl ether. The co-eluting compounds on the DB-5 column were:

DB-5: 3,5-dichlorophenyl-4'-nitrophenyl ether
3,4,5-trichlorophenyl-4'-nitrophenyl ether
2,5-dichlorophenyl-4'-nitrophenyl ether
2,4-dichlorophenyl-3'-methyl-4'-nitrophenyl ether

On the DB-1701, 3,5-dichlorophenyl-4'-nitrophenyl ether was partially resolved from 2,5-dichlorophenyl-4'-nitrophenyl ether, and 2,3,6-trichlorophenyl-4'-nitrophenyl ether was partially resolved from 2,3,5-trichlorophenyl-4'-nitrophenyl ether. So far, we have not experienced any problems in detecting the two pairs that were only partially resolved.

Out of 10 compounds evaluated as possible internal standards and surrogates, 4,4'-dibromobiphenyl was recommended as the internal standard, and 2,4-dichlorodiphenyl ether and 2,3,4-trichlorodiphenyl ether were recommended as the surrogate compounds.

From the results of 10 consecutive injections, we determined the retention time reproducibility (percent RSD) to be better than 0.12 percent for the DB-5 column, and better than 0.06 percent for the DB-1701 column. The reproducibility of the detector response was better than 2.4 percent on the DB-5 column and 1.55 percent or better on the DB-1701 column for all target compounds.

The detector response was linear for all target analytes in the 50- to 400-pg range, with correlation coefficients greater than 0.99 for all compounds on the DB-5 column. The correlation coefficients for the DB-1701 column were greater than 0.99 for all compounds. Percent differences for RFs determined on two consecutive days after the gas chromatographic system was calibrated ranged from 19.2 to -0.93 percent on day 1 and from 0.61 to -15.5 percent on day 2 for the DB-5 column and from -2.24 to -12.5 percent on day 1 and from -10.8 to -20.4 percent on day 2 for the DB-1701 column indicating that the gas chromatographic system requires daily calibration.

Chlorinated Hydrocarbons

Twenty-two chlorinated hydrocarbons (Table 5) were determined on the DB-5/DB-1701 column pair with dual-ECD using the temperature program given in Table 5. By examining the data in Table 5, we concluded that neither column can separate all target analytes. The co-eluting compounds among the 22 test compounds were:

DB-5: 1,4-dichlorobenzene/benzyl chloride
1,2,3,5-tetrachlorobenzene/
1,2,4,5-tetrachlorobenzene
1,2,3,4-tetrachlorobenzene/2-chloronaphthalene
DB-1701: benzyl chloride/1,2-dichlorobenzene/
hexachloroethane
benzal chloride/1,2,4-trichlorobenzene/hexachlorobutadiene

Out of 10 compounds evaluated as possible internal standards and surrogates, 1,3,5-tribromobenzene was recommended as the internal standard and 1,4-dichloronaphthalene was recommended as the surrogate compound.

From the results of 10 consecutive injections, we determined the retention time reproducibility (percent RSD) to be equal to or better than 0.08 percent for both columns. The reproducibility of the detector response was better than 11.1 percent on the DB-5 column and that for the DB-1701 column was better than 17.1 percent for all compounds.

The method linearity was determined for two sets of calibrations and the results were compared. The first calibration covered a range from 50 to 250 pg. The detector response was linear, with correlation coefficients being greater than 0.97 for the DB-5 column and between 0.83 and 0.99 for the DB-1701 column. The second calibration was only performed for the DB-1701 column and covered the range between 50 pg and 125 pg. Linear correlation coefficients were 0.99 for most compounds. The daily variation of compound RFs was determined one day after the multilevel calibration. The daily variation was below 10 percent for most compounds on the DB-5 column, and below 20 percent for most compounds on the DB-1701 column.

Organophosphorus Pesticides

Preliminary experiments to chromatograph the 50 compounds listed in Table 6 were performed with a DB-5/DB-1701 column pair and nitrogen/phosphorus detectors. Because of excessive back-

ground noise, the DB-1701 column was replaced with a DB-210 column. All experiments were then carried out with the DB-5/DB-210 column pair and two nitrogen phosphorus detectors. By examining the data in Table 6, we concluded that neither column can resolve all 50 compounds. The co-eluting compounds were:

DB-5: terbufos/tricresyl phosphate
naled/simazine/atrazine
dichlorophenthion/demeton-O
trichloronate/aspon
bolstar/stirophos/
carbophenothion
phosphamidon/crotoxyphos
fensulfothion/EPN
DB-210: terbufos/tricresyl phosphate
dichlorophenthion/
phosphamidon
chlorpyrifos methyl/
parathion methyl
chlorpyrifos/parathion ethyl
aspon/fenthion demeton-O/dimethoate
leptophos/azinphos methyl
EPN/phosmet
famphur/carbophenothion

Out of 17 compounds tested for suitability as internal standards and surrogates, 1-bromo-2-nitrobenzene was suggested as the internal standard, and 4-chloro-3-nitrobenzotrifluoride as the surrogate.

From the results of 10 consecutive injections, we determined the retention time reproducibility (percent RSD) to be better than 0.38 percent for the DB-5 column and better than 0.57 percent for the DB-210 column. The reproducibility of the detector response was better than 12.1 percent on the DB-5 column and better than 13.5 percent on the DB-210 column for all 50 compounds.

The detector response was linear for all the target analytes from 1 to 10 ng per column, with correlation coefficients greater than 0.95 for most of the compounds on both columns. The daily variation of detector RFs were determined one day and two days after the multilevel calibration was performed. The daily variation of the detector response was less than 20 percent for most of the compounds on both columns. However, a few compounds showed significantly higher deviations from linearity. Also, the deviation from linearity was higher on the second day.

Method Evaluation

Two aspects of the dual-column/dual-detector method were addressed in this study. One aspect dealt with how well the target analytes were identified and

Table 3. Retention Times of the Nitroaromatics^a

Compound No.	Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
1	Nitrobenzene	95-95-3	4.71	4.23
2	o-Nitrotoluene	88-72-2	6.08	5.32
3	m-Nitrotoluene	99-08-1	6.93	6.22
4	p-Nitrotoluene	99-99-0	7.35	6.73
5	1-Chloro-3 nitrobenzene ^b	121-73-3	7.66	6.85
6	1-Chloro-4-nitrobenzene	100-00-5	7.9	7.15
7	1-Chloro-2-nitrobenzene	88-73-3	8.09	7.78
8	2-Chloro-6-nitrotoluene	83-42-1	9.61	8.32
9	4-Chloro-2-nitrotoluene	89-59-8	9.76	8.62
10	3,5-Dichloronitrobenzene	618-62-2	10.42	8.84
11	2,5-Dichloronitrobenzene	89-61-2	11.46	10.62
12	2,4-Dichloronitrobenzene	611-06-3	11.73	10.84
13	4-Chloro-3-nitrotoluene	89-60-1	11.31	10.84
14	3,4-Dichloronitrobenzene	99-54-7	12.24	11.04
15	2,3-Dichloronitrobenzene	3209-22-1	12.58	12.01
16	2,4,6-Trichloronitrobenzene	c	13.97	12.31
17	1,4-Naphthoquinone	130-15-4	12.98	12.31
18	1,2,4-Trichloro-5-nitrobenzene	89-69-0	15.97	14.46
19	1,4-Dinitrobenzene	100-25-4	13.41	14.72
20	2,6-Dinitrotoluene	606-20-2	14.44	15.16
21	1,3-Dinitrobenzene	99-65-0	13.97	15.68
22	1,,2,3-Trichloro-4-nitrobenzene	17700-09-3	17.61	16.51
23	2,3,5,6-Tetrachloronitrobenzene	117-18-0	19.41	17.11
24	1,2-Dinitrobenzene	528-29-0	14.76	17.51
25	2,4-Dinitrotoluene	121-14-2	16.92	18.16
26	1-Chloro-2,4-dinitrobenzene	97-00-7	17.85	19.55
27	2,3,4,5-Tetrachloronitrobenzene	c	21.51	19.55
28	1-Chloro-3,4-dinitrobenzene	610-40-2	17.85	19.85
29	Trifluralin	1582-09-8	21.81	20.31
30	Benefin	1861-40-1	21.94	20.46
31	Pentachloronitrobenzene	82-68-8	25.13	22.33
32	Profluralin	26399-36-0	25.39	23.81
33	Dinitramine	29091-05-2	26.45	27.06
34	Butralin	33629-47-9	32.41	31.03
35	Isopropalin	33820-53-0	32.71	31.33
36	Penoxalin (Pendimethalin)	40318-45-4	33.05	31.67
IS ^d	Hexchlorobenzene	118-74-1	23.18	18.72

^a The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (1.5- μ m film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0- μ m film thickness) connected to a J&W Scientific press-fit Y-shaped Inlet splitter. Temperature program: 120°C (1-min hold) to 200°C (1-min hold) at 3°C/min then to 250°C (4-min hold) at 8°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

^b Recommended as surrogate compound.

^c Not available.

^dIS = internal standard.

quantified by the dual-column/dual-detector approach when no matrix interferences were present. For this purpose, we selected a set of blind performance evaluation samples which were available from EPA-Cincinnati and contained not only the target analytes but also other compounds of environmental significance. The other aspect dealt with how well the target analytes were identified

and quantified by the dual-column/dual-detector approach in real matrix extracts. For this purpose, we prepared a few matrix extracts (mostly from soils contaminated with pesticides), spiked these extracts with known amounts of the target analytes, and analyzed the spiked extracts

The samples that we were able to obtain contained only a limited number of

the target phenols and of the target chlorinated hydrocarbons. For example, EPA WP-281 Sample 2 was reported to contain 9 phenols at levels ranging from 8.3 to 20 ng/ μ L, and EPA WP-281 Sample 4 was reported to contain the same compounds but at higher levels (70.0 to 175 ng/ μ L). Using the DB-5/DB-1701 column pair, we were able to identify all 9 compounds correctly. The

Table 4. Retention Times of the Haloethers^a

Compound No.	Compound	DB-5 RT(min)	DB-1701 RT(min)
1	4-Bromophenyl-phenyl ether	4.28	5.57
2	Phenyl-4'-nitrophenyl ether	6.85	10.86
3	2-Chlorophenyl-4'-nitrophenyl ether	10.44	16.31
4	3-Chlorophenyl-4'-nitrophenyl ether	10.78	16.70
5	4-Chlorophenyl-4'-nitrophenyl ether	11.37	17.68
6	2,6-Dichlorophenyl-4'-nitrophenyl ether	14.02	20.84
7	3,5-Dichlorophenyl-4'-nitrophenyl ether	14.55	21.33
8	2,5-Dichlorophenyl-4'-nitrophenyl ether	14.55	21.54
9	2,4-Dichlorophenyl-4'-nitrophenyl ether	15.08	22.30
10	2,3-Dichlorophenyl-4'-nitrophenyl ether	16.11	23.87
11	3,4-Dichlorophenyl-4'-nitrophenyl ether	16.65	24.54
12	2,4,6-Trichlorophenyl-4'-nitrophenyl ether	17.89	24.93
13	2,3,6-Trichlorophenyl-4'-nitrophenyl ether	19.40	27.27
14	2,3,5-Trichlorophenyl-4'-nitrophenyl ether	19.70	27.56
15	2,4,5-Trichlorophenyl-4'-nitrophenyl ether	20.03	28.05
16	2,4-Dibromophenyl-4'-nitrophenyl ether	21.63	30.03
17	3,4,5-Trichlorophenyl-4'-nitrophenyl ether	21.83	30.42
18	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	22.28	31.18
19	2,4-Dichlorophenyl-3'-methyl-4'-nitrophenyl ether	21.83	31.60
IS ^b	4,4'-Dibromobiphenyl	9.44	12.66
SU-1 ^b	2,4-Dichlorodiphenyl ether	4.82	6.17
SU-2 ^b	2,3,4-Trichlorodiphenyl ether	8.31	10.95

^a The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83- μ m film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0- μ m film thickness) connected to an 8-in injection tee (Supelco Inc.). Temperature program: 180°C (0.5-min hold) to 260°C (1.0-min hold) at 2°C/min injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min. CAS Registry numbers are not available for any of these compounds.

^b IS = internal standard; SU = surrogate compound.

percent biases are satisfactory considering the fact that the samples had to be diluted and then derivatized with PFBBR prior to the GC/ECD analysis.

Five blind performance evaluation samples were available for the chlorinated hydrocarbons. Two of these samples were reported to contain compounds such as nitroaromatics, phthalate esters, polynuclear aromatic hydrocarbons, etc. The four chlorinated hydrocarbons that were present in EPA WP-186 Sample 3 were identified correctly. Pentachlorobenzene was not confirmed in WP-286 Sample 1 (although it was reportedly to be present in the sample).

The results from 6 different, spiked matrix extracts showed that all compounds were identified correctly, even when matrix interferences were present in the sample. This further indicates that compound retention times were reproducible and that any nonvolatile residue that might have been present in these matrix extracts did not cause any problems during sample injection. Biases were quite high in the

case of the organochlorine pesticides, possibly because the extracts had to be subjected to diol cartridge cleanup prior to gas chromatographic analysis. Furthermore, the Matrix 1 and 2 extracts contained high levels of endrin, endosulfan II, and p,p'-DDT. Since the spiking levels were significantly lower than the background levels for these three compounds, the errors had to be quite high.

Conclusion

The results of this study indicate that the dual-column/dual-detector approach using two 30-m x 0.53-mm ID fused-silica open-tubular columns coated with dissimilar stationary phases and connected to either an 8-in injection tee or a press-fit Y-shaped splitter is reliable for the gas chromatographic determination of Method 8040 phenols, Methods 8080/8081 organochlorine pesticides, Method 8090 nitroaromatics, Method 8110 haloethers, Method 8120 chlorinated hydrocarbons, and Method 8140/8141 organophosphorus pesticides.

The lists of compounds targeted by the methods identified in this study have been expanded to cover additional isomers of the target compounds, and internal standards and surrogate compounds have been selected for each method.

Blind performance evaluation samples and matrix extracts of environmental samples (spiked with the target analytes) were analyzed by the dual-column/dual-detector procedure to establish how well the target analytes are identified and quantified in the presence of matrix interferences.

Notice

Although the research described in this paper has been supported by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 5. Retention Times of the Chlorinated Hydrocarbons^a

Compound No.	Compound	CAS No.	DB-5 RT(min)	DB-1701 RT(min)
1	1,3-Dichlorobenzene	541-73-1	5.82	7.22
2	1,4-Dichlorobenzene	106-46-1	6.00	7.53
3	Benzyl chloride	100-44-7	6.00	8.47
4	1,2-Dichlorobenzene	95-50-1	6.64	8.58
5	Hexachloroethane	67-72-1	7.91	8.58
6	1,3,5-Trichlorobenzene	108-70-3	10.07	11.55
7	Benzal chloride	98-87-2	10.27	14.41
8	1,2,4-Trichlorobenzene	120-82-1	11.97	14.54
9	1,2,3-Trichlorobenzene	87-61-6	13.58	16.93
10	Hexachlorobutadiene	87-68-3	13.88	14.41
11	Benzotrichloride	98-07-7	14.09	17.12
12	1,2,3,5-Tetrachlorobenzene	634-90-2	19.35	21.85
13	1,2,4,5-Tetrachlorobenzene	95-94-2	19.35	22.07
14	Hexachlorocyclopentadiene	77-47-4	19.85	21.17
15	1,2,3,4-Tetrachlorobenzene	634-66-2	21.97	25.71
16	2-Chloronaphthalene	91-58-7	21.77	26.60
17	Pentachlorobenzene	608-93-5	29.02	31.05
18	alpha-BHC	619-84-6	34.64	38.79
19	Hexachlorobenzene	118-74-1	34.98	36.52
20	beta-BHC	619-85-7	35.99	43.77
21	gamma-BHC	58-89-9	36.25	40.59
22	delta-BHC	319-86-8	37.39	44.62
IS ^b	1,3,5-Tribromobenzene	626-39-1	11.83	13.34
SU ^b	1,4-Dichloronaphthalene	^c	15.42	17.71

^a The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83- μ m film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0- μ m film thickness) connected to an 8-in injection tee (Supelco Inc.). Temperature program: 80°C (1.5-min hold) to 125°C (1-min hold) at 2°C/min then to 240°C (2-min hold) at 5°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

^b IS = internal standard; SU = surrogate compound.

^c Not available.

Table 6. Retention Times of the Organophosphorus Pesticides^a

Compound No.	Compound	CAS No	DB-5 RT(min)	DB-210 RT(min)	References
1	Trimethylphosphate	512-56-1	b	2.36	1. Test Methods for Evaluating Solid Waste; Laboratory Manual – Physical/Chemical Methods, SW-846, 3rd Edition, Vol 1B, U.S. Environmental Protection Agency, Washington, DC, November 1986. 2. Lee, H. B., Weng, L. D., and Chau, A. S. Y., "Chemical Derivatization Analysis of Pesticide Residues. IX. Analysis of Phenol and 21 Chlorinated Phenols in Natural Waters by Formation of Pentafluorobenzyl Ether Derivatives," J. Assoc. Off. Anal. Chem. 41:375-387, 1988.
2	Dichlorvos	62-73-7	7.45	6.99	
3	Hexamethylphosphoramide	680-31-9	b	7.97	
4	Trichlorfon	52-68-6	11.22	11.63	
5	TEPP	21646-99-1	b	13.82	
6	Thionazin	297-97-2	12.32	14.71	
7	Mevinphos	7786-34-7	12.20	10.82	
8	Ethoprop	13194-48-4	12.57	15.29	
9	Diazinon	333-41-5	13.23	18.60	
10	Sulfotepp	3689-25-5	13.39	16.32	
11	Terbufos	13071-79-9	13.69	18.23	
12	Tricresyl phosphate	78-30-8	13.69	18.23	
13	Naled	300-76-5	14.18	15.85	
14	Phorate	298-02-2	12.27	16.57	
15	Fonophos	944-22-9	14.44	18.38	
16	Disulfoton	298-04-4	14.74	18.84	
17	Merphos	150-50-5	14.89	23.22 ^c	
18	Dichlorofenthion	97-17-6	15.55	20.09	
19	Chlorpyrifos-methyl	5598-13-1	15.94	20.45	
20	Ronnel	299-84-3	16.30	21.01	
21	Chlorpyrifos	2921-88-2	17.06	22.22	
22	Trichloronate	327-98-0	17.29	22.73	
23	Aspon	3244-90-4	17.29	21.98	
24	Fenthion	55-38-9	17.87	22.11	
25	Demeton-S	8065-48-3	11.10	14.86	
	Demeton-O	8065-48-3	15.57	17.21	
26	Monochrotophos	6923-22-4	19.08	15.98	
27	Dimethoate	60-51-5	18.11	17.21	
28	Tokuthion	34643-46-4	19.29	24.77	
29	Malathion	121-75-5	19.83	21.75	
30	Parathion-methyl	298-00-0	20.15	20.45	
31	Fenithrothion	122-14-5	20.63	21.42	
32	Chlorfevinphos	470-90-6	21.07	23.66	
33	Parathion-ethyl	56-38-2	21.38	22.22	
34	Bolstar	35400-43-2	22.09	27.57	
35	Stirophos	22248-79-9	22.06	24.63	
36	Ethion	563-12-2	22.55	27.12	
37	Phosphamidon	13171-21-6	22.77	20.09	
38	Crotoxyphos	7700-17-6	22.77	23.85	
39	Leptophos	21609-90-5	24.62	31.32	
40	Fensulfothion	115-90-2	27.54	26.76	
41	EPN	2104-64-5	27.58	29.99	
42	Phosmet	732-11-6	27.89	29.89	
43	Azinphos-methyl	86-50-0	28.70	31.25	
44	Azinphos-ethyl	2642-71-9	29.27	32.36	
45	Famphur	52-85-7	29.41	27.79	
46	Coumaphos	56-72-4	33.22	33.64	
47	Atrazine ^d	1912-24-9	13.98	17.63	
48	Simazine ^d	122-34-9	13.85	17.41	
49	Carbophenothion ^d	786-19-6	22.14	27.92	
50	Dioxathion	78-34-2	e	e	
IS ^f	1-Bromo-2-nitrobenzene	g	8.11	9.07	
SU ^f	4-Chloro-3-nitrobenzotrifluoride	g	5.73	5.40	

^a The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (1.50- μ m film thickness) and 30-m x 0.53-mm ID DB-210 (1.0- μ m film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 120°C (3-min hold) to 270°C (10-min hold) at 5°C/min; injector temperature 250°C; detector temperature 300°C; bead temperature 400°C; bias voltage 4.0; hydrogen gas pressure 20 psi; helium carrier gas 6 mL/min; helium makeup gas 20 mL/min.

^b Not detected at 20 ng per injection.

^c Merphos shows another peak at 20.25 min on DB-5 and 24.87 min on DB-210.

^d Originally in the organochlorine pesticide list but were added to the organophosphorus pesticide list because they gave very poor detector responses when analyzed with an electron capture detector.

^e Shows multiple peaks.

^f IS = internal standard; SU = surrogate compound.

^g Not available.

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The complete report, entitled "Application of Open-Tubular Columns to SW-846 GC Methods," (Order No. PB 90-259 847/AS; Cost: \$39.00, subject to change) will be available only from:

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