RESIDUES AND TRACE ELEMENTS

Multiresidue Screening of Pesticides in Foods Using Retention Time Locking, GC–AED, Database Search, and GC/MS Identification

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Fruit and vegetable extracts were screened for over 400 pesticides by gas chromatography with atomic emission detection (GC–AED) and an experimental database. A technique called retention time locking was used to match GC–AED and GC with mass spectrometry (MS) retention times to those of the database. Samples were analyzed for sulfur, nitrogen, phosphorus, and chlorine by GC–AED. Possible pesticides were suggested by database search and identified by GC/MS. Forty-four pesticide standards were analyzed to determine the precision of retention time matching and the accuracy of the database search. Analytical retention times matched database retention times within 0.32 min. Using elemental criteria, the database search identified the correct compound for 41 of 44 pesticide standards. For blind spikes of fruit and vegetable extracts, the database suggested 22 of 26 spiked pesticides as matches. Nineteen were identified by GC/MS. The combination of retention time locking, GC–AED, database search, and GC/MS can be a powerful tool for identifying pesticides in a complex matrix.

Passage of the Food Quality Protection Act in 1997 highlighted the need to assure consumers of a wholesome and safe food supply, free from harmful levels of pesticides (1). With the passage of the North American Free Trade Agreement, public concern over the safety of imported foods has increased (2). In 1999, Congress will consider passage of the National Organic Program (3). To address pesticide safety concerns, regulatory programs need to screen for an increasingly complex array of agricultural chemicals in a greater variety of domestic and international foods.

Several multiresidue pesticide methods have been published (4–6). Most depend on multiple gas chromatographic (GC) selective detectors and dual-column confirmations to identify pesticides containing chlorine (Cl), bromine (Br), fluorine (F), nitrogen (N), phosphorus (P), and sulfur (S). Unidentified analytical responses (UARs) such as other pesticides, food contaminants, and naturally occurring compounds are also detected. Some methods use GC/mass spectrometry (MS) with selected ion monitoring (SIM) to detect 200 or more pesticides and provide legally defensible confirmations (7). However, GC/MS methods detect only those compounds that are part of the SIM screen. Although multiresidue screens have become increasingly large, it is impossible for regulatory laboratories to screen for every known pesticide by injecting every standard with each set of analyses.

The usefulness of GC with atomic emission detection (AED) for the selective detection of pesticides has been described (8, 9). With elemental detection, GC–AED can screen for the same pesticides seen by several GC selective detectors. Investigation of UARs containing multiple heteroatoms such as Cl, S, N, and/or P can lead to detection of food contaminants that are not identified during routine analysis.

The purpose of this research was to determine the usefulness of retention time locking (RTL) and a GC–AED database (DB) application for identifying pesticide residues in foods (10). A proprietary, experimental DB containing more than 400 pesticide retention times and molecular formulas and a search application (RT_Search) were developed by Hewlett Packard. DB retention times for the 0.25 mm HP5MS capillary column were translated from literature values (11) generated on the same column phase but with a different oven temperature program by using the software HP Method Translation (12). RT_Search uses the selectivity and compositional information of GC–AED analysis, library searching with the aid of RTL, and GC/MS identification and confirmation to identify pesticides in food extracts. GC–AED retention times were compared to DB retention times to determine the precision of RTL. A mixture of pesticides was analyzed by GC–AED and identified by RT_Search to determine the selectivity of the application. Blind spikes of fruit and vegetable extracts were analyzed to determine the ability of the technique to identify pesticides in a sample matrix. Quantitative analyses were not conducted during this initial investigation. The data will be used to develop a new

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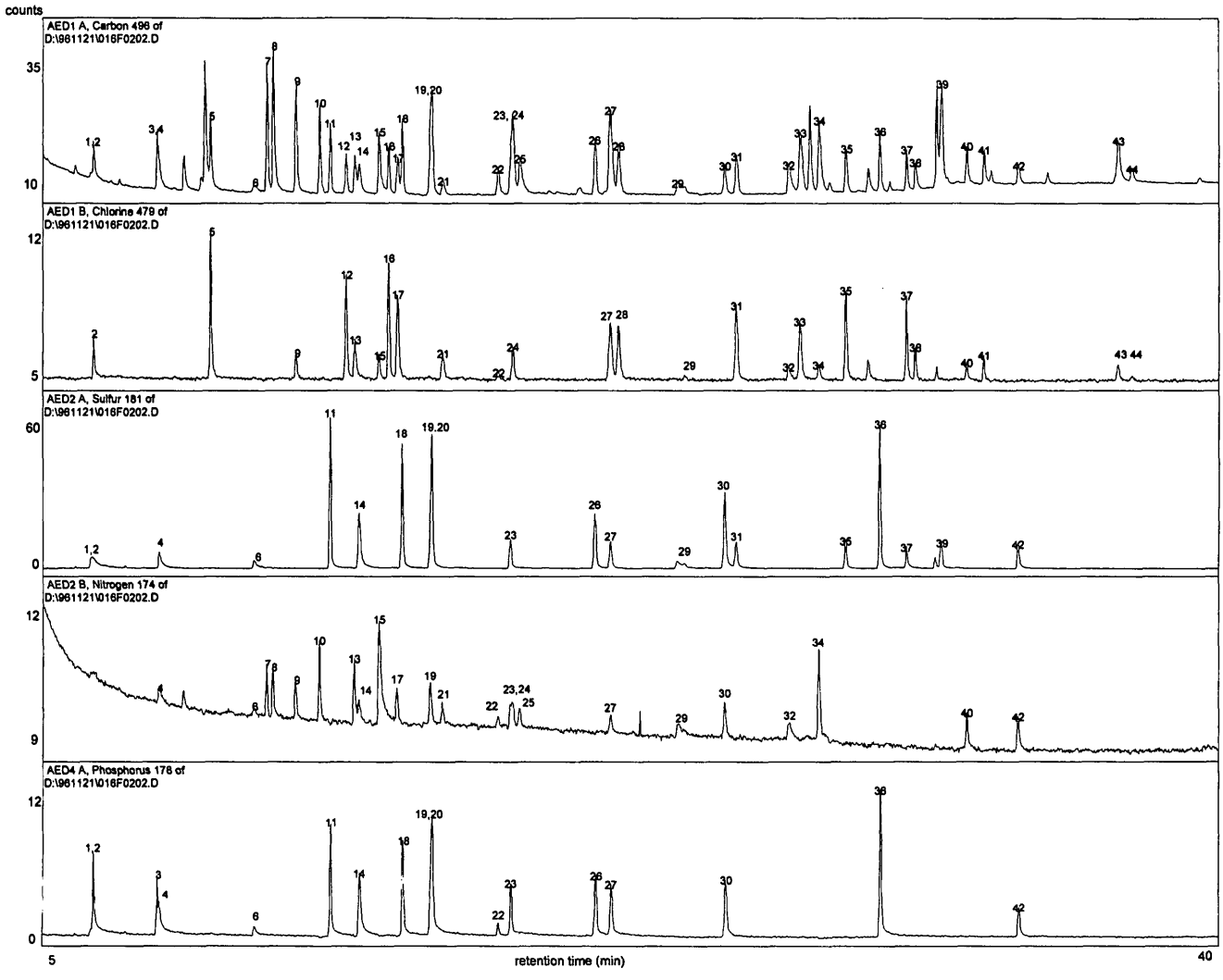

Figure 1. GC–AED chromatograms of a mixure of 44 pesticide compounds each at 1 ng/μL. Carbon, chlorine, sulfur, nitrogen, and phosphorus responses are shown. Compounds are identified in Table 1.

pesticide DB application that can accurately screen for hundreds of compounds.

Experimental

Apparatus

(a) *GC–AED system.*—HP 5890 Series II gas chromatograph equipped with electronic pressure control (EPC; 13, 14), HP 5921 AED (15), dual HP 7673 autosamplers, HPIB interface, Dell Pentium computer, and Windows 3.11-based GC–AED ChemStation version A.01.00 (Hewlet Packard, Avondale, PA). GC operating conditions: He carrier gas in constant-pressure mode, ca 22 psig (varies with RTL adjustments); splitless injection of 3 μL; purge valve, 1.5 min; injector temperature, 250°C; detector B for column transfer to AED, 280°C. AED operating conditions: He, 95 psig; O_2, 25 psig; H_2, 80 psig; spectrometer purge, N_2 at 3 L/min; water temperature, 65°C; He supply, 30 psig; cavity pressure, 1.5 psig; cavity temperature 300°C; peak width, 0.216; data rate, 1.250 Hz; solvent vent on 0.01 to 3.00 min; element groups: injection 1: C at 496 nm, Cl at 479 nm, Br at 478 nm; injection 2: S at 181 nm, N at 174 nm; injection 3: P at 178 nm; injection 4: F at 690 nm (15). In the initial investigations of DB precision and accuracy and the first set of blind spikes, C, S, N, P, and Cl channels were analyzed. In the second set of blind spikes, Br and F were added to the analysis.

(b) *GC selective detectors.*—Provided for identification of detector type only. No analytical data presented. Multiresidue screens are routinely performed in this laboratory using HP 5890 Series II gas chromatographs equipped with EPC, DB-5, and DB-17 megabore columns, and several different selective detectors: electron capture detector (ECD), HP Model 19223; electrolytic conductivity detector (ELCD), Model 4420, OI Analytical, College, TX; nitrogen phosphorus detector (NPD), HP Model 19234; flame photometric detector (FPD), HP Model 19256A; halogen specific detector (XSD), Model 5360, OI.

(c) *GC/MS system.*—HP 5890 Series II gas chromatograph equipped with EPC, Model HP 5972 GC/MS detector equipped with autosampler, HP 7673 autosampler, and ChemStation G1036 rev. C software. GC operating conditions: splitless injector, 280°C; septum purge flow, 1 mL/min; inlet purge flow, 50 mL/min; injector purge time, 0.5 min; He carrier gas

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Data File C:\HPCHEM\1\DATA\961121\016F0202.D Sample Name: GC MSD 1
Instrument 1 9/4/97 3:30:19 PM

Injection Date : 11/22/96 2:30:40 AM Seq. Line : 2
Sample Name : GC MSD 1 Vial : 16
Acq. Operator : JMC Inj : 2
Acq. Method : HP5MS254.M

Results of Pesticide Data Base Search

#5. Search results for 8.368 to 9.168 minutes
Must have: CL: Must not have: S:P:

RetTime	Molecular Formula	Compound Name	Molecular Weight
8.490	C:8,H:8,Cl:2,O:2,	Chloroneb	207.06
8.690	C:6,H:1,Cl:5,	Pentachlorobenzene	250.34
9.140	C:11,H:13,Cl:1,O:3,	Mercoprop-methyl	228.68

#10 Search results for 11.411 to 12.211 minutes
Must have: N: Must not have: CL:P:S:

RetTime	Molecular Formula	Compound Name	Molecular Weight
11.460	C:13,H:14,F:3,N:3,O:4,	Ethalfluralin	333.27
11.680	C:19,H:11,F:5,N:2,O:2,	Diflufenican	394.30
11.700	C:13,H:16,F:3,N:3,O:4,	Trifluralin	335.28
11.790	C:11,H:13,N:1,O:4,	Bendiocarb	223.23
11.850	C:7,H:3,Br:2,N:1,O:1,	Bromoxynil	276.91
11.880	C:13,H:16,F:3,N:3,O:4,	Benfluralin	335.28
12.030	C:15,H:23,N:1,O:1,	Tebutam	233.35
12.160	C:12,H:17,N:1,O:2,	Promecarb	207.27

#22 Search results for 16.422 to 17.222 minutes
Must have: CL:P: Must not have: S:

RetTime	Molecular Formula	Compound Name	Molecular Weight
16.860	C:10,H:19,Cl:1,N:1,O:5,P:1,	Phosphamidon II	299.69

#36 Search results for 27.100 to 27.900 minutes
Must have: P:S: Must not have: CL:N:

RetTime	Molecular Formula	Compound Name	Molecular Weight
27.500	C:9,H:22,O:4,P:2,S:4,	Ethion	384.46
27.510	C:12,H:27,P:1,S:3,	Merphos III	298.50
27.880	C:12,H:19,O:2,P:1,S:3,	Sulprofos	322.44

#15 Search results for 13.102 to 13.902 minutes
Must have: CL:N: Must not have: P:S:

RetTime	Molecular Formula	Compound Name	Molecular Weight
13.360	C:7,H:12,Cl:1,N:5,	Simazine	201.66
13.470	C:11,H:10,Cl:1,N:1,O:2,	Chlorbufam	223.66
13.510	C:9,H:11,Cl:1,N:2,O:2,	Monolinuron	214.65
13.530	C:8,H:7,Cl:2,N:1,O:2,	SWEP	220.06
13.590	C:8,H:14,Cl:1,N:5,	Atrazine	215.69
13.830	C:9,H:16,Cl:1,N:5,	Propazine	229.71

Figure 2. Example of some results obtained by searching the pesticide DB. Table 1 summarizes the search results for all 44 compounds in the standard mixture.

in constant-pressure mode at ca 10 psi at 50°C (varies with RTL adjustments). MS operating conditions: electron impact mode, transfer line, 280°C; ion source temperature, 280°C; electron energy, 70 eV; mass calibration, peak widths (typically 0.5 mass unit), and electron multiplier voltage (typically 2400 V) set during the instrument tuning to meet U.S. Environmental Protection Agency decaflurotriphenylphosphine (DTFPP) 625 criteria (16); data acquisition in full-scan mode; mass scan range, 50 to 550 *m/z*; library searches using CRUSDA, Wiley 138K, and HPPEST.

(**d**) *GC–AED and GC/MS column.*—HP5MS column, cross-linked 5% phenylmethylsiloxane, 30 m × 0.25 mm id, 0.25 μm film thickness.

(**e**) *GC–AED and GC/MS oven program.*—Oven temperature program: 50°C (1.13 min), 30°C/min to 150°C (2 min), 3°C/min to 205°C (0 min), 10°C/min to 250°C (20 min).

Reagents, Standards, and Samples

(**a**) *Solvents.*—Pesticide grade or better (Optima grade, Fisher, Pittsburgh, PA).

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Table 1. Results of retention time locking and database search to identify mix of 44 pesticides[a]

Sample No.	Compound	Composition	Database RT, min	AED RT, min	Elemental search criteria		Search results: RT fit
					Must have	Doesn't have	
1	Methamidophos	N, P, S	5.24	5.40	S	Cl, P	No match
2	Dichlorvos	Cl, P	5.28	5.40	Cl, P	—	1
3	Mevinphos	P	7.27	7.25	P	Cl, N, S	1
4	Acephate	N, P, S	7.65	7.30	S, P	Cl	1
5	PCB	Cl	8.69	8.73	Cl	P, S	1
6	Omethoate	N, P, S	10.05	9.95	S, P	Cl	1
7	Propoxur	N	10.27	10.31	N	Cl, P	2
8	Diphenylamine	N	10.55	10.48	N	Cl, N, S	3
9	Chlorpropham	Cl, N	11.21	11.12	Cl, N	S, P	1
10	Trifluralin	F, N	11.70	11.79	N	Cl, P, S	2
11	Phorate	P, S	12.15	12.08	P, S	Cl, N	1
12	HCB	Cl	12.71	12.52	Cl	P, S	1
13	Dichloran	Cl, N	12.93	12.76	Cl, N	P, S	1
14	Dimethoate	N, P, S	13.09	12.89	N, P, S	Cl	1
15	Atrazine	Cl, N	13.59	13.45	Cl, N	P, S	5
16	Lindane	Cl	13.82	13.71	Cl	N, P, S	4
17	PCNB-quintozene	Cl, N	4.08	13.96	Cl, N	P, S	1
18	Terbufos	P, S	14.18	14.10	P, S	Cl, N	1
19	Diazinon	N, P, S	14.93	14.92	N, P, S	Cl	1
20	Disulfoton	P, S	15.02	14.92	P, S	—	No match
21	Chlorthalonil	Cl, N	15.41	15.22	Cl, N	P, S	2
22	Phosphamidon II	Cl, N, P	6.86	16.80	Cl, P	S	1
23	Methyl parathion	N, P, S	17.32	17.13	N, S	Cl	2
24	Vinclozalin	Cl, N	17.32	17.19	Cl	S	2
25	Carbaryl	N	17.68	17.38	N	Cl, P, S	1
26	Malathion	P, S	19.61	19.50	S	Cl	2
27	Chlorpyrifos	Cl, N, P, S	20.08	19.93	Cl, N, P, S	—	1
28	Dichlorobenzophenone	Cl	0.14	20.16	Cl	N, P, S	1
29	Captan	Cl, N, S	22.23	21.97	S	P	6
30	Methidathion	N, P, S	23.36	23.13	N, P, S	Cl	1
31	Endosulfan-α	Cl, S	3.42	23.45	Cl, S	N, P	1
32	Imazalil	Cl, N	25.13	24.95	Cl, N	P, S	2
33	*p,p'*-DDE	Cl	25.22	25.24	Cl	N, P, S	1
34	Myclobutanil	Cl, N	25.86	25.78	Cl, N	P, S	2
35	Endosulfan-β	Cl, S	26.57	26.54	Cl, S	N, P	1
36	Ethion	P, S	27.50	27.49	P, S	Cl, N	1
37	Endosulfan sulfate	Cl, S	28.26	28.24	Cl, S	N, P	1
38	*p,p'*-DDT	Cl	28.50	28.50	Cl	N, P, S	1
39	Propargite	S	29.22	29.23	S	Cl, N, P	1
40	Iprodione	Cl, N	29.89	29.93	Cl, N	P, S	1
41	Methoxychlor	Cl	30.37	30.41	Cl	N, P, S	1
42	Azinphos-methyl	N, P, S	31.46	31.36	N, P, S	Cl	1
43	Permethrin-*cis*	Cl	34.23	34.16	Cl	N, P, S	1
44	Permethrin-*trans*	Cl	34.63	Not detected	—	—	—

[a] AED retention time (RT), elements detected, and elements not detected were entered as search criteria. Suggested matches are ranked by retention time fit. Pesticides identified by the search were ranked in increasing order by the absolute retention time difference from the standard. (The minimum difference = 1, the next largest difference = 2, etc.)

(**b**) *Background correction solution.*—10 ng/μL hexadecane (99% pure, Fisher), 100 ng/μL octadecane, and 200 ng/μL nonadecane (99% pure, ChemService, West Chester, PA) prepared in acetone.

(**c**) *Standards.*—Stock standard solutions were prepared from certified, neat materials (ChemService) in either isooctane or acetone. Working standard mixtures were prepared from dilutions of stock solutions in acetone.

(**d**) *Extracts.*—Luke extracts in acetone were analyzed at the sample extract concentration of 1.95 g/mL (4, 6).

(**e**) *Spikes.*—Blind spikes were prepared in another section of the laboratory by chemists who were not assigned to this

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Table 2. Retention time comparisons of DB, AED, and MS[a]

			AED retention time data					MS RTL data			
Compound	Composition	Database	Sulfur mean[b]	Nitrogen mean[b]	Phosphorus mean[b]	Chlorine mean[b]	AED mean[c]	Daily diff[d]	Dbase diff[e]	RT, min[f]	Dbase diff[g]
Methamidophos	N, P, S	5.24	5.39	5.46			5.42	0.24	0.32	5.40	0.16
Dichlorvos	Cl, P	5.28			5.47	5.46	5.46	0.16	0.29	5.48	0.20
Mevinphos	P	7.27			7.27		7.27	0.16	0.10	7.29	0.02
Acephate	N, P, S	7.65	7.43	7.43	7.46		7.44	0.24	0.28	7.53	0.12
PCB	Cl	8.69				8.75	8.75	0.19	0.19	8.77	0.08
Omethoate	N, P, S	10.05	9.98	9.99	10.01		9.99	0.20	0.12	10.03	0.02
Propoxur	N	10.27		10.33			10.33	0.12	0.14	10.38	0.11
Diphenylamine	N	10.55		10.51			10.51	0.16	0.09	10.52	0.03
Chlorpropham	Cl, N	11.21		11.15		11.15	11.15	0.13	0.11	11.16	0.05
Trifluralin	F, N	11.70		11.76			11.76	0.06	0.10	11.80	0.10
Phorate	P, S	12.15	12.07		12.10		12.09	0.16	0.12	12.12	0.03
HCB	Cl	12.71				12.53	12.53	0.18	0.25	12.55	0.16
Dichloran	Cl, N	12.93		12.79		12.80	12.79	0.17	0.19	12.81	0.12
Dimethoate	N, P, S	13.09	12.93	12.93	12.96		12.94	0.18	0.21	12.97	0.12
Atrazine	Cl, N	13.59		13.51		13.51	13.51	0.12	0.13	13.54	0.05
Lindane	Cl	13.82				13.73	13.73	0.17	0.15	13.75	0.07
PCNB-quintozene	Cl, N	14.08		13.96		13.97	13.96	0.16	0.17		
Terbufos	P, S	14.18	14.08		14.11		14.09	0.14	0.14	14.12	0.06
Diazinon	N, P, S	14.93	14.87	14.86	14.88		14.87	0.07	0.09	14.90	0.03
Disulfoton	P, S	15.02	14.90		14.91		14.91	0.15	0.16	14.96	0.06
Chlorthalonil	Cl, N	15.41		15.25		15.25	15.25	0.14	0.21	15.24	0.17
Phosphamidon II	Cl, N, P	16.86		16.76	16.78	16.76	16.77	0.10	0.13		
Methyl parathion	N, P, S	17.32	17.12	17.14	17.16		17.14	0.13	0.23	17.18	0.14
Vinclozalin	Cl, N	17.32		17.18		17.19	17.18	0.09	0.17	17.24	0.08
Carbaryl	N	17.68		17.41			17.41	0.08	0.30	17.44	0.24
Malathion	P, S	19.61	19.46		19.49		19.48	0.06	0.16	19.52	0.09
Chlorpyrifos	Cl, N, P, S	20.08	19.91	19.91	19.94	19.91	19.92	0.11	0.20		
Dichlorobenzophenone	Cl	20.14				20.13	20.13	0.07	0.04		
Captan	C, N, S	22.23	21.99	22.00		22.00	22.00	0.10	0.27	22.01	0.22
Methidathion	N, P, S	23.36	23.11	23.12	23.15		23.13	0.12	0.27	23.15	0.21
Endosulfan-α	Cl, S	23.42	23.43			23.44	23.43	0.13	0.10	23.47	0.05
Imazalil	Cl, N	25.13		25.05		24.92	24.98	0.21	0.23	24.90	0.23
p,p′-DDE	Cl	25.22				25.22	25.22	0.05	0.03	25.24	0.02
Myclobutanil	Cl, N	25.86		25.82		25.81	25.81	0.05	0.07	25.80	0.06
Endosulfan-β	Cl, S	26.57	26.54			26.54	26.54	0.11	0.06	26.54	0.03

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Table 2. (*continued*)

			AED retention time data					MS RTL data			
Compound	Composition	Database	Sulfur mean[b]	Nitrogen mean[b]	Phosphorus mean[b]	Chlorine mean[b]	AED mean[c]	Daily diff[d]	Dbase diff[e]	RT, min[f]	Dbase diff[g]
Ethion	P, S	27.50	27.47		27.50		27.49	0.07	0.04	27.50	0.00
Endosulfan sulfate	Cl, S	28.26	28.25			28.26	28.26	0.11	0.07	28.25	0.01
p,p'-DDT	Cl	28.50				28.50	28.50	0.08	0.05	28.48	0.02
Propargite	S	29.22	29.22				29.22	0.06	0.04	29.22	0.00
Iprodione	Cl, N	29.89		29.96		29.97	29.96	0.09	0.14	29.91	0.02
Methoxychlor	Cl	30.37				30.42	30.42	0.12	0.13	30.39	0.02
Azinphos-methyl	N, P, S	31.46	31.40	31.39	31.43		31.41	0.20	0.12	31.33	0.13
Permethrin-*cis*	Cl	34.23				34.17	34.17	0.14	0.11	34.09	0.14
Permethrin-*trans*	Cl	34.63				34.54	34.54	0.13	0.13	34.46	0.17
Cypermethrin I	Cl, N	37.32		37.18		37.19	37.19	0.15	0.20	37.05	0.27
Cypermethrin II	Cl, N	37.74		37.61		37.61	37.61	0.12	0.18	37.47	0.27
Cypermethrin III	Cl, N	37.99		37.86		37.87	37.87	0.12	0.16	37.73	0.26
Cypermethrin IV	Cl, N	38.20		38.07		38.05	38.06	0.12	0.19	37.90	0.30
Maximum absolute retention time difference								0.24	0.32		0.30

[a] Retention times after RTL, *p,p'*-DDE = 25.216 min.
[b] Average of results from 3 analyses on 3 days for each element.
[c] Average for all elements for 3 days.
[d] Maximum difference between daily RTL locked retention times.
[e] Maximum difference between any individual daily value and the DB value.
[f] Retention time after RTL in constant pressure mode, *p,p'*-DDE = 25.216 min, single analysis.
[g] Difference of MS retention time from DB value.

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Table 3. Identification of unknown analytical responses (UARs) in blind spikes 1–5, using RTL[a], GC–AED analysis, RT_Search, and GC/MS confirmation

Blind spike[b]	Commodity[c]	Pesticide spiked[d]	Concentration, ng/μL	GC–AED rank[e]	GC/MS match[f] quality
1	Carrot roots	Simazine	2.50	1	99
		Chlorfenvinphos	5.00	1	89
		Bifenthrin	5.00	3	Not in library
2	Radish roots	Ethalfluralin	3.75	NS[g]	98
		Tetrachlorvinphos	2.50	1	Failed match
		Folpet	5.00	2	Weak response
		Dieldrin	2.50	2	95
3	Leeks	Metalaxyl	2.50	2	In-house standard
					Not in library
4	Blackberry	Pendimethalin	5.00	2	98
		Chlorpropham	1.50	1	97
5	Eggplant	Sulprofos	1.50	1	95
		Chlorobenzilate	3.00	1	91
		Disulfoton	2.50	2	97
		Profenofos	2.50	1	Interference
		Tolyfluanid	5.00	1	58

[a] RTL using linear equation, set *p,p'*-DDE = 25.216 min.
[b] Other chemists were asked to spike fruit or vegetable Luke extracts that would challenge the identification technique. GC–AED and GC/MS operators were not given identifications until all analyses and evaluations were made.
[c] Some spiked commodities have a lot of interfering, naturally occurring compounds that are problematic in residue analysis by both GC selective detectors and GC/MS.
[d] Chemists were asked to spike fruit or vegetable Luke extracts with nonroutine pesticides at concentrations between 1 and 5 ng/μL. Most pesticides spiked are not routinely analyzed by either GC or GC/MS.
[e] Pesticides identified by GC–AED search were ranked in increasing order by the absolute retention time difference from the standard. (The minimum difference = 1, the next largest difference = 2, etc.)
[f] Goodness of fit to the GC/MS library of spectra is calculated by the library software.
[g] NS = fluorine ethalfluralin not screened.

project. They spiked fruit and vegetable sample extracts with nonroutine pesticides at levels between 1 and 5 ng/μL. Each spike could contain 1 to 5 pesticides. Pesticides, like those in real samples, were not limited to those present in the DB. The identities of the spikes were kept secret until all GC–AED and GC/MS analyses were completed.

Data Handling

(a) *RTL procedure.*—The following procedure was followed to adjust the column head pressure so that GC–AED and GC/MS retention times of *p,p'*-DDE matched the DB retention time of 25.216 min. Prior to each set of runs, a 1 ng/μL *p,p'*-DDE standard was analyzed. The retention time was entered into the RTL equation supplied by Hewlett Packard and adjusted to the suggested pressure. The change in GC–AED column head pressure in pounds per square inch (psi) equals $(25.216 - RT_{DDE})/(-0.27509)$. The change in GC/MS column head pressure equals $(25.216 - RT_{DDE})/(-0.2288)$. *p,p'*-DDE was reanalyzed, and the pressure adjustment was repeated if necessary. After initial determination of the appropriate pressure for a given GC–column combination, periodic adjustments of only a few tenths of a psi were needed to account for column maintenance and aging.

(b) *GC–AED and DB data processing.*—HP GC–AED ChemStation version A.01.00 was used to prepare sequences, integrate and rescale chromatograms, and select peaks of interest for DB search. Background due to carbon response was corrected by using background correction solution and the Chemstation "backamount" function. The Hewlett Packard proprietary DB contained the retention times of 400 pesticides for a given oven temperature program, as well as each compound's molecular formula and molecular weight. The proprietary macro RT_Search was used to search DB. Using the application while in the data analysis portion of ChemStation, the analyst selected a peak of interest by clicking at the peak apex. The retention time of the selected compound was shown. Elements that were present or absent from the peak were added to the search parameters. A report of pesticides that had the same elemental composition within a window of 0.8 min was produced. The procedure was repeated for each additional search. The report was saved as a file or printed. New compounds could be added to the DB or in-house DBs could be built.

(c) *Compound-independent calibration (CIC).*—With GC–AED ChemStation A.01.00, the response of chlorpyrifos at 1 ng/μL was used to calibrate Cl, N, S, and P responses to their corresponding 3:1:1:1 elemental composition. Unknown peaks were then analyzed. Once calibrated, CIC analysis returns the approximate elemental composition, and ratios can be calculated from these results (9).

(d) *GC/MS identification.*—A GC–AED sample chromatogram, an integration report, and a printed RT_Search report were submitted to GC/MS for pesticide identification. GC–

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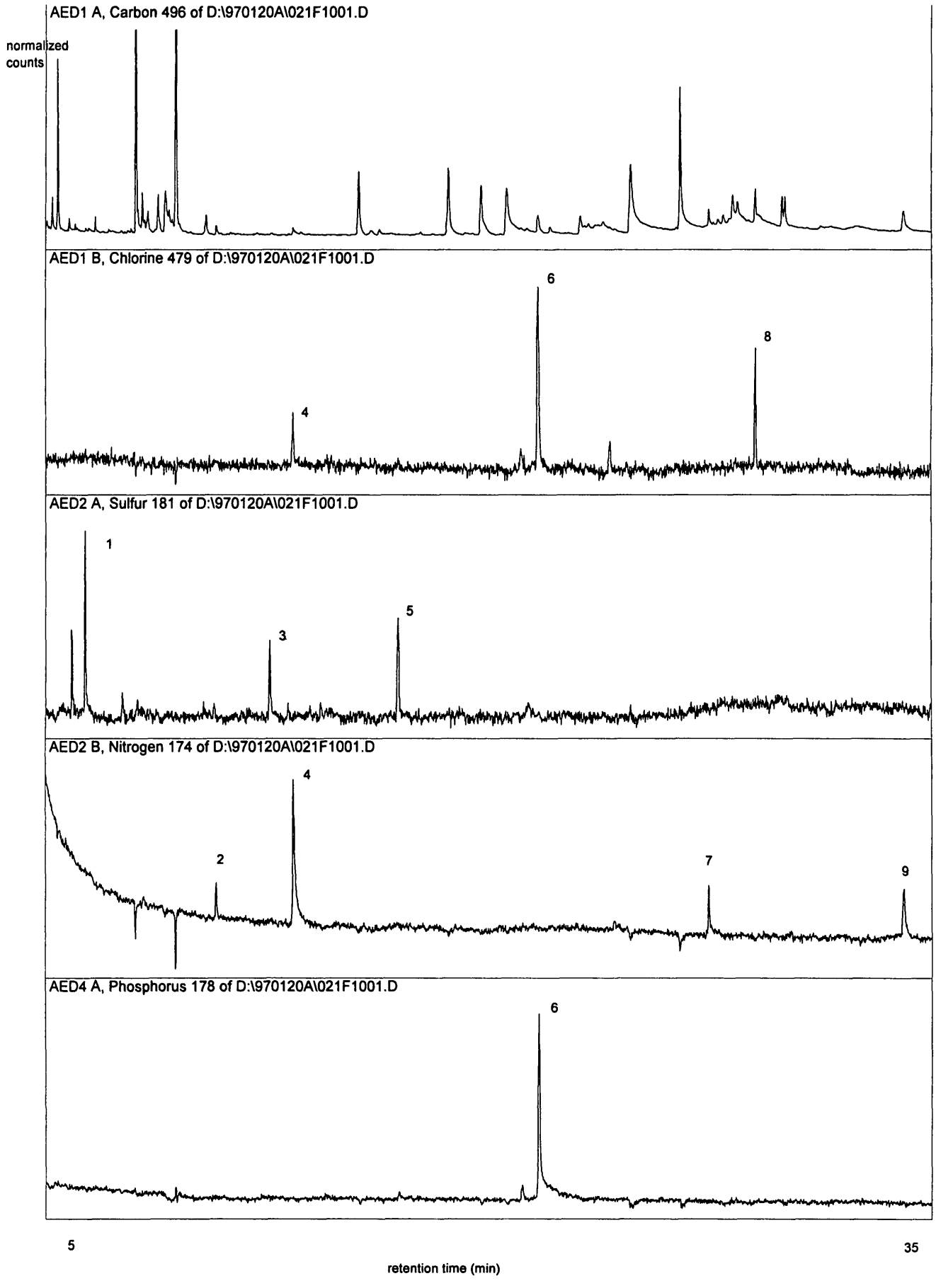

Figure 3. GC–AED chromatograms of a carrot extract spiked with simazine (4), chlorfenvinphos (6), and bifenthrin (8). Carbon, chlorine, sulfur, nitrogen, and phosphorus responses are shown.

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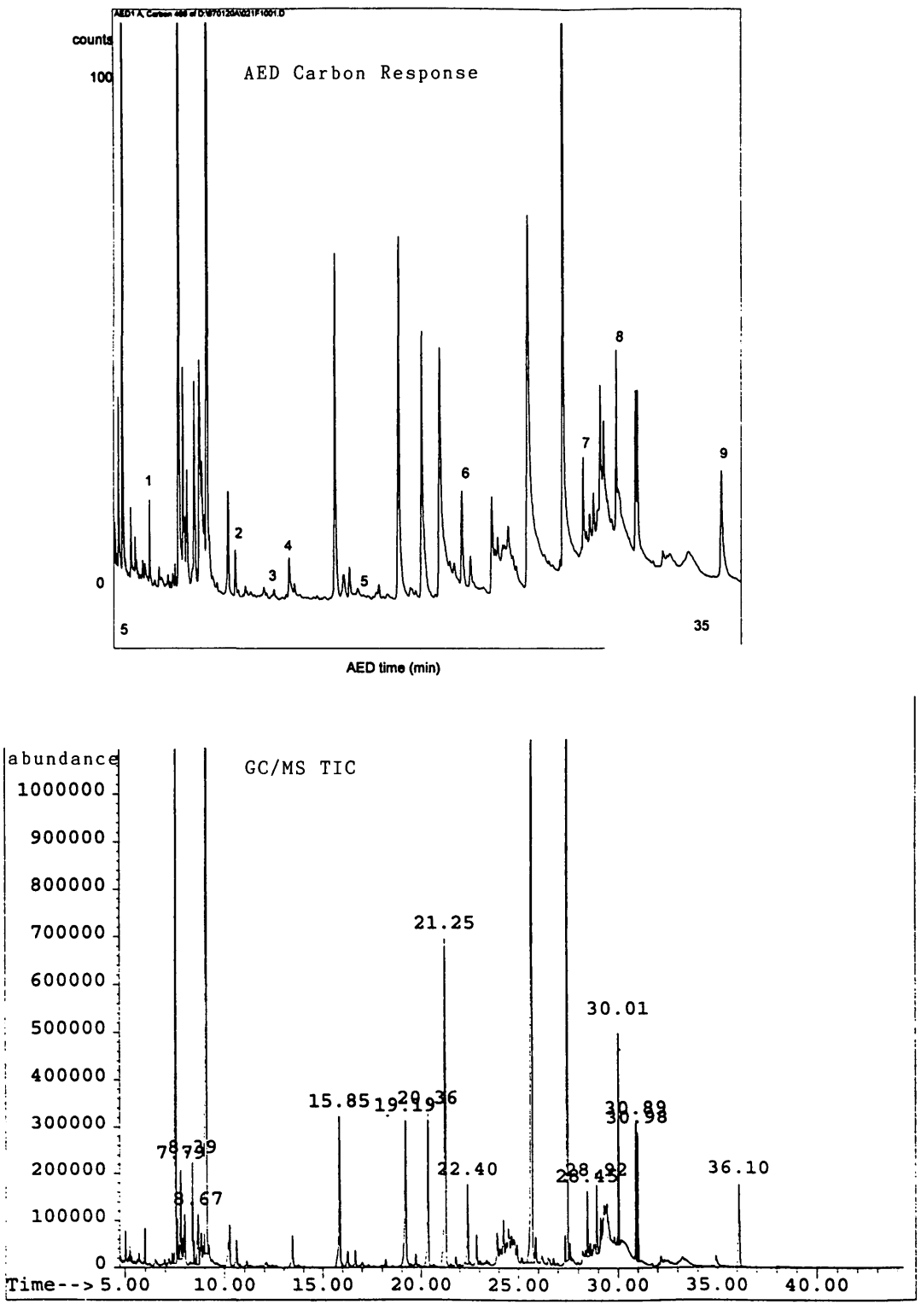

Figure 4. GC–AED carbon-channel chromatogram of carrot spike (top) and GC/MS TIC of carrot spike (bottom).

AED carbon-channel chromatograms, scaled to approximate GC/MS total ion chromatograms (TICs), were provided for blind spikes 6–10. RTL was used to adjust GC/MS retention times to match the GC–AED and DB retention times, and then GC/MS full-scan data were analyzed to confirm the presence of pesticides suggested by the RT_Search report. By comparing the TIC to the GC–AED carbon-channel trace, the GC/MS operator zeroed in on the peak of interest and obtained a full-scan spectrum of the peak. If a library search did not identify the peak, a GC/MS extracted ion chromatogram was generated by using appropriate ions for a particular pesticide suggested by RT_Search. Pesticides were identified in the presence of significant background interference by using extracted ions.

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Table 4. Identification of unknown analytical responses (UARs) in blind spikes 6–10, using RTL[a], GC–AED analysis, RT_Search, and GC/MS confirmation

Blind spike[b]	Commodity[c]	Pesticide spiked[d]	Concentration, ng/μL	GC–AED rank[e]	GC/MS match[f] quality
6	Spinach	Fenitrothion	5.00	1	38
		Terbacil	5.00	1	93
		Allethrin	2.50	(C, H, O only)	NS, 46
7	Oranges	Fenchlorphos	5.00	1	70
		Triadimefon	5.00	3	91
8	Tomatoes	Fenarimol	5.00	1	Interference
9	Tomatoes	Monocrotophos	5.00	1	78
		Naled as dichlorvos	5.00	1	38
		Thiabendazole	0.25	Not in DB	NS[g]
10	Tomatoes	Oxadixyl	5.00	1	72
		Bendiocarb	5.00	No match (searched for S)	96

[a] RTL using linear equation, set *p,p'*-DDE = 25.216 min.
[b] Other chemists were asked to spike fruit or vegetable Luke extracts that would challenge the identification technique. GC–AED and GC/MS operators were not given identifications until all analyses and evaluations were made.
[c] Some spiked commodities have a lot of interfering, naturally occurring compounds that are problematic in residue analysis by both GC selective detectors and GC/MS.
[d] Chemists were asked to spike fruit or vegetable Luke extracts with nonroutine pesticides at concentrations between 1 and 5 ng/μL. Most pesticides spiked are not routinely analyzed by either GC or GC/MS.
[e] Pesticides identified by GC–AED search were ranked in increasing order by the absolute retention time difference from the standard. (The minimum difference = 1, the next largest difference = 2, etc.)
[f] Goodness of fit to the GC/MS library of spectra is calculated by the library software.
[g] NS = allethrin and thiabendazole not screened by GC/MS. Allethrin screened by GC/MS after spike identifications revealed.

Results and Discussion

Selectivity of DB Search

Through RTL and the DB oven program, a mixture containing 44 pesticide standards was analyzed to determine if the RT_Search algorithm could identify known pesticides. Figure 1 shows GC–AED chromatograms for the C, CL, S, N, and P channels. RT_Search was used to identify the compounds in the mixture. An example of some search results for this mixture is shown in Figure 2.

Table 1 lists the parameters used in RT_Search, including the elements noted as present or absent. The search produced a list of possible matches in retention time order. The suggestions were ranked by closeness of the DB and analytical retention times. The correct pesticide was ranked first in 29 of 44 searches. Eight pesticides were identified by the second choice. Eighty-four percent of the pesticides were correctly identified in the first 2 choices.

Of the remaining pesticides, coelutions interfered with accurate identification of methamidophos (sample 1) and disulfoton (sample 20). The poorer rankings for diphenylamine (sample 8), atrazine (sample 15), and lindane (sample 16) appeared to be due only to the large number of other pesticides in the DB in the same retention time window. Extremely low responses to Cl and N and poor peak shape contributed to the poor ranking of captan (sample 29). These low responses were probably due to injector discrimination and not to poor GC–AED response. If Cl and N elemental responses had been detected, the correct identification would have been ranked 3. Retention time appears to be the most significant factor in correct DB identifications.

Very low GC–AED N response was noted for acephate (sample 4), omethoate (sample 6), phosphamidon (sample 22), methyl parathion (sample 23), vinclozolin (sample 24), carbaryl (sample 25), captan (sample 29), and imazalil (sample 32). The low N response may be disguised easily by naturally occurring nitrogen compounds in real samples.

RT_Search peak selection and search were initiated manually for each compound of interest. Search results could be evaluated and immediately rerun with different parameters. Multiple searches on questionable peaks could be made. Very low Cl was detected in the case of captan. An additional search that included Cl as a possibility would have suggested captan as the first choice. If sulfur peaks are present in a sample, searches both with and without S can be made. As described in a later section, bendiocarb was not identified in blind spike 10 because it was mistakenly thought to contain sulfur.

Precision of RTL

Critical to the success of DB screening is the ability to match analytical retention times to the DB values reproducibly. To determine how precisely RTL analytical retention times compare with each other and with DB, the standard mixture including cypermethrin was analyzed by GC–AED on 3 separate days approximately one week apart. Routine injector maintenance including column cutting and liner and septa replacement was performed between analyses. As seen in Table 2, the maximum difference in day-to-day retention times across the entire length of the temperature program was 0.2 min. Day-to-day retention time differences of less than 0.1 min were observed for 65% of the compounds. Nonsymmetrical peaks and closely eluting compounds affected the retention time slightly.

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Table 5. Identification of suspected pesticides in blind spikes 11–14, using DB reference and retention time (RT) locked[a] GC/MS identification

Blind spike[b]	Commodity[c]	Pesticides suspected[d]	Spiked identified Y/N[e]	DB RT, min	GC/MS RT, min
11	Cucumber	Ethoprop	Y/Y	10.83	10.77
		Cycloate		10.84	
		Terbacil		15.26	
		Metalaxyl		18.13	
		Fenthion	Y/Y	20.02	19.79
		Parathion		20.21	
		Propyzamide	Y/N	20.60	14.32
12	Cucumber	Molinate		9.00	
		Dialte		12.07	
		Fenchlorphos	Y/Y	18.05	17.89
		Fenitrothion	Y/Y	18.91	18.70
		Triademefon		20.31	
		Gardona		24.11	
		Sulprofos	Y/Y	27.80	27.80
		Methoxychlor		30.33	
13	Carrot	Cycloate	Y/Y	10.84	10.79
		Trifluralin	Y/Y	11.70	11.80
		Demeton		12.90	
		Methyl chlorpyrifos		17.25	
		Fenchlorphos		18.05	
		Aldrin		19.29	
14	Carrot	Simazine		13.63	
		Diazinon	Y/Y	14.93	14.91
		Fenthion		20.02	
		Dacthal	Y/Y	—	20.18
		Captafol		29.16	
		Methoxychlor	Y/Y	30.37	30.40

[a] RTL using linear equation, set *p,p'*-DDE = 25.216 min.
[b] Chemists were asked to spike fruit or vegetable Luke extracts that would challenge the identification technique. GC/MS operator was not given identifications until all analyses and evaluations were made.
[c] Some spiked commodities have a lot of interfering, naturally occurring compounds that are problematic in residue analysis by GC/MS.
[d] Two to 3 pesticides were spiked into each sample. GC/MS operator was told to look for 6–8 pesticides.
[e] Chemists were asked to spike fruit or vegetable Luke extracts with nonroutine pesticides at concentrations between 2 and 5 ng/μL. Most pesticides spiked are not routinely analyzed by GC/MS.

For the HP 5890 gas chromatograph, head pressure adjustments were limited to changes of 0.1 psi, resulting in retention time changes of approximately 0.03 min.

Table 2 also shows that 48% of GC–AED retention times were within 0.1 min of the DB value and 85% were within 0.2 min. The maximum difference between retention time and the DB value was 0.32 min. For the RT_Search to capture all possible pesticide identifications, a window of 0.8 min was used for searches. In most cases, the correct identification was found within 0.2 min. Equally critical to the success of this screening technique was the ability to predict analyte retention time for GC/MS. GC–AED detects naturally occurring nitrogen and phosphorus compounds as well as pesticides. The RT_Search can suggest only possible pesticides that elute near the unknown compound. With RTL retention time, elemental composition, and a list of up to 8 possible pesticides, the GC/MS operator was asked to identify any pesticides present in the sample. With RTL, GC/MS retention times matched DB values within 0.30 min, and GC–AED retention times matched DB values within 0.16 min. The agreement between the GC–AED and GC/MS instruments is better than the day-to-day variability of the GC–AED itself.

Sensitivity of GC–AED Elemental Analysis

Although the GC–AED is very selective, it is not as sensitive as some other GC selective detectors, especially for N. Of the 44 pesticides analyzed in Table 1, most could be detected at 1 ng/μL. Some pesticides containing N could be detected only at higher concentrations. All 44 pesticides could be detected at 10 ng/μL.

Because the purpose of the investigation was to test the ability of RTL and DB matching to identify pesticides, blind spikes were prepared at detectable concentrations from 1 to 5 ng/μL. In UAR investigations of real samples, extracts are concentrated to approximately 10 g/mL to detect lower levels of pesticides. Most pesticides can be detected at 0.1–0.5 ppm in these extracts. UARs such as linuron in carrots, procymidon in grapes, and folpet in onions were all identified with GC–AED and

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RT_Search at approximately these levels. Large-volume injection may enable GC–AED to detect lower levels of pesticides.

Identifying standards in solvent is not as difficult a task for RT_Search as identification of pesticides in fruit and vegetable matrixes. Coextractables in complicated food extracts can make it more difficult to evaluate the chromatography and elemental composition. Resolution, detection limit, and selectivity become critical issues.

Identification of Unknowns in Blind Spikes 1–5

The first set of blind spikes contained 3–5 pesticides at 1–5 ng/μL. These extracts were analyzed by GC–AED in the C, Cl, N, S, and P mode. An RT_Search was made of all significant peaks. CIC was used for multielement peaks to narrow the possibilities returned by RT_Search. Results are summarized in Table 3.

The first spike was prepared in carrot matrix. Coextractables in carrots interfere with the analysis of most pesticides by ECD. Some matrix interferences are noted even with ELCD and XSD. As shown in Figure 3, 9 peaks were seen clearly in the GC–AED chromatogram. N- and S-containing peaks 1, 2, 3, 5, 7, and 9 were searched but not identified as pesticides. Peaks 4 and 6—simazine and chlorfenvinphos, respectively—were listed as the RT_Search's first choice and were identified easily by GC/MS. Peak 8—bifenthrin, containing Cl and F—was identified as the RT_Search's third of 5 choices. It would have been ranked first if F had been analyzed. Bifenthrin was not identified by GC/MS because it was not in the MS library, suggesting that a larger, more inclusive MS library than what already exists is needed. Figure 4 compares the GC–AED carbon-channel chromatogram to the GC/MS TIC. Using the GC–AED as a "fingerprint" when requesting UAR identifications helps GC/MS to identify the peak of interest.

The second spike was prepared in radish root extract. Six major peaks were searched. RT_Search correctly suggested the identity of 3 Cl responses. Dieldrin was identified by GC/MS. Folpet did not yield a strong enough spectrum for a reliable GC/MS library search. The MS library search algorithm failed to identify tetrachlorvinphos. Identification of pesticides by GC/MS library search is affected by concentration, interfering compounds, and the ability of the GC/MS spectrum to match the library spectrum among other things. With the pesticide suggestions made by RT_Search, ions can be chosen and GC/MS extracted ion analysis may identify pesticides missed by library search. Ethalfluralin was not detected by GC–AED but was identified by GC/MS because it was close to one of the S peaks. If the F channel had been analyzed, this compound would probably have been detected easily by GC–AED. Pesticides in radish root are difficult to analyze by NPD because of coextractables. Many GC–AED S peaks were seen in this sample. Two other S peaks were searched but not identified as pesticides. Captan and folpet were both suggested by RT_Search. CIC did not help distinguish captan from folpet because they have the same Cl:N:S ratios. In spike 2, only 1 of 4 pesticides was detected by both GC–AED and GC/MS; however, all 4 pesticides were detected by either GC–AED or GC/MS.

Leeks, the third commodity spiked, is one of the worst commodities analyzed by traditional GC detectors. It has strong interferences on ECD and NPD throughout the entire chromatogram. Strong S and early eluting P responses but few N interferences were seen on the GC–AED. Of 6 peaks searched, one N pesticide, metalaxyl, was identified easily by RT_Search. Although this pesticide was not present in the MS library, it was identified by matching an in-house standard.

Blackberry extract is a relatively interference-free matrix to analyze with GC selective detectors. Nine GC–AED peaks were searched, each of which resulted in lists of 1–11 suggestions. Some peaks were searched with and without "must not have" criteria, leading to an even longer and more confusing list of suggestions than usual for the GC/MS operator. Despite the long list of possibilities, GC–AED, RT_Search, and GC/MS identified both of the pesticides present.

Eggplant is also a relatively interference-free matrix for GC analysis. Eight peaks were identified by GC–AED, resulting in searches with up to 12 suggestions. CIC predicted the correct N:S ratio for tolylfluanid but did not predict the P:S ratio in disulfoton. If the F channel had been analyzed, identification of tolylfluanid would have been a lot clearer. RT_Search suggested that 5 of the 8 peaks were pesticides; 4 were identified by GC/MS. Profenofos was not identified by GC/MS because it coeluted with a large organic acid peak.

In this initial set of blind spikes, the GC/MS operator searched all 38 peaks submitted by the GC–AED operator. RT_Search suggested 2 to 12 possibilities for each of these peaks. The GC/MS operator, either by library identification or by using spectra obtained from a standard, identified 11 of the 15 spikes. GC–AED and RT_Search suggested 14 of the 15 spikes.

Identification of Unknowns in Blind Spikes 6–10

After analysis of the first spike set, it was clear that the number of suggested pesticides submitted to GC/MS for identification should be reduced to a minimum. If RT_Search identifies 6–8 peaks as possible pesticides and suggests 2–8 possibilities and less than half of the peaks are actually pesticides, the GC/MS operator would have to search at least 4 suggested identifications to identify one pesticide. For the second set of blind spikes, summarized in Table 4, Br and F were added to the GC–AED screen. Special care was taken to ensure that background correction eliminated misleading background response due to carbon response. Early eluting S peaks known to be naturally occurring extract peaks were not included in the search. On the RT_Search report, the analyst highlighted the most probable matches based on RTL and CIC criteria. A full-page, carbon-channel chromatogram, scaled to approximate a GC/MS TIC was provided for each sample with the peaks of interest identified.

For spike 6, the spinach GC–AED chromatogram was comparatively clean. Small S, N, and P peaks were not searched. Terbacil was suggested by GC–AED and identified by GC/MS. The GC/MS library match for fenitothion was 38%. A third pesticide, allethrin, did not contain any heteroatoms to distinguish it from naturally occurring compounds. It was not sug-

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gested by the GC–AED for search. The investigators had not considered the possibility of pesticides that did not contain any heteroatoms. These compounds would not be detected by GC selective detectors either. The GC–AED technique would not be a good choice for identification of these pesticides. When asked to find allethrin, GC/MS identified it with a 46% match quality. Library matches for allethrin and fenitothion were good enough to pursue confirmations with a standard.

For spike 7, 2 pesticides in oranges were suggested correctly by GC–AED and identified by GC/MS.

For spike 8, tomatoes, 5 peaks were submitted for identification. One Cl peak was identified as fenarimol by GC–AED but could not be identified by GC/MS library matching.

For spike 9, 4 peaks were submitted for GC/MS identification. Dichlorvos and monocrotophos were the clear choices of RT_Search. Although naled was spiked, it breaks down to dichlorvos in the GC injectors of both GC–AED and GC/MS. Thiabendazole was not suggested by GC–AED because it was not present in DB. No pesticide DB is going to include all the possibilities. However, pesticides with heteroatoms will be detected by GC–AED and can then be investigated and possibly identified by RTL GC/MS. DB did not contain metabolites and breakdown products, although these compounds could be added easily.

For spike 10, 5 GC–AED peaks were submitted to MS for identification. Oxadixyl was identified by GC/MS. Bendiocarb was not identified by RT_Search because it was thought to contain S. The S response on the GC–AED was misleading and may have been due to background from the large N peak. This needs to be investigated further. The S peak was identified as bendiocarb by GC/MS.

In the second set of blind spikes, 18 peaks were submitted to GC/MS for identification. Eleven pesticides were spiked. Two were not screened because they were not present in the database. Seven out of 9 spikes were identified as pesticides by GC–AED, RT_Search, and GC/MS. Seven of these pesticides were ranked as the first choice by RT_Search.

Identification of Unknowns Using RTL and DB Reference

Routine GC residue analysis using selective detectors frequently results in unidentified peaks. If a particular pesticide is suspected, RTL and GC/MS can be used to identify the unknown. Using RTL and the DB, mass spectra from the retention time of interest can be extracted to perform a library search. If a reasonable library match is made, comparison with an analytical standard can complete confirmation. As indicated in Table 2, agreement between MS and DB retention times was very good. This set of analyses also tested the usefulness of RTL and GC/MS for residue screening.

To test this technique, blind spikes of up to 5 pesticides were prepared. The GC/MS analyst was given a list of suspected residues, some of which were not necessarily spiked into the sample.

As shown in Table 5, RTL GC/MS retention times matched DB values within 0.23 min except for propyzamide, which appears to have an incorrect retention time in the DB, and dacthal, which is not in the DB. Propyzamide was not identified in spike 11 until its retention time was compared with the RTL retention time of a single standard. All spiked pesticides in spikes 12 and 13 were identified. For spike 14, fenthion was listed as a suspected pesticide. Dacthal is not in DB, but it coelutes with fenthion and was identified when the fenthion peak was searched by GC/MS.

Conclusions

RTL can reliably and precisely reproduce analytical retention times in both GC–AED and GC/MS. The ability to match retention times between instruments allows analysts to collaborate in the analysis of a single sample. RTL also enables analysts to compare analytical retention times without any mathematical conversions such as relative retention time or linear interpolation.

Analytical retention times closely matched experimental retention times in the DB, which was created by a mathematical conversion of literature data. Method translation and linear interpolation were successfully used to convert data collected under different conditions (17). Perhaps if a DB were developed for cases using the same analytical column and conditions, the agreement between instrument and DB RTL would be even better than it is now.

With GC–AED followed by DB searching, pesticides containing heteroatoms can be detected selectively in food matrixes. However, additional information was needed to reduce the large number of RT_Search-suggested pesticides presented to GC/MS for identification. Good GC–AED and GC/MS RTL matching minimizes DB mismatches. Retention times closest to the DB RTL were highlighted in the RT_Search report as the most probable choices. CIC estimates of elemental ratios can narrow the RT_Search to the correct choice or eliminate unlikely candidates. GC–AED/C chromatograms provide a "fingerprint" similar to GC/MS TIC so that the exact peak of interest can be identified. GC–AED is not selective for pesticides with C, H, and O only.

Compounds present at levels close to the detection limit of the GC–AED yield less desirable results. Our analysis of more than 50 pesticides indicated that if the correct elemental search criteria are used, any of the 400 pesticides present in the DB will be correctly suggested by a search. Although further validation is required, we anticipate that hundreds of pesticides may be screened by using the combination of RTL, GC–AED, and GC/MS. The GC instrumentation used in this work allowed pressure adjustments of only within 0.1 psi, leading to a possible variation in retention time of approximately 0.03 min. Improvements in instrumental pressure regulation may lead to more precise RTL, resulting in searches of smaller retention time windows and leading to a shorter list of possibilities in the same search window.

RTL helps GC/MS to identify UARs by narrowing the search window. This increases the success rate and reduces the analysis time. MS libraries did not contain many of the pesticides in the DB. This technique would be more useful than it already is if there were an MS library that contained all of the

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residues found in the pesticide DB. The RT_Search report would be more useful to the GC/MS analyst if it listed 2 or 3 characteristic ions for suggested compounds. This would enable the GC/MS operator to generate extracted ion chromatograms for pesticides suggested by RT_Search without using an external source to identify appropriate ions. Using extracted ion chromatograms aids identification of compounds hidden by matrix interferences.

The techniques described in this paper are very useful for identification of unknown compounds in complex matrix. Refinements in RTL and customization of DBs for specific applications will make the procedures even more efficient than it is at present. It is exciting to contemplate the collaborative possibilities of reproducing the exact conditions of other researchers' work by using RTL techniques.

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