Solid-Phase Extraction Cleanup of Halogenated Organic Pesticides

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This study investigated the potential of solid-phase extraction (SPE) cartridges as replacements for Attagel in the cleanup procedure of halogenated organic pesticides in raw agricultural crops. Four commodities, broccoli, carrot, celery, and orange, were fortified with a total of 44 pesticides. Pesticides were analyzed by gas chromatography (GC) with electron capture detection (ECD). Cleanup with either C_{18} or Florisil SPE showed recoveries comparable to or better than that obtained by Attagel in most cases. Both C_{18} and Florisil SPEs showed significant differences in recoveries compared to that of Attagel.

The current California Department of Food and Agriculture (CDFA) multiresidue method (Joe, 1988) for screening of halogenated organic pesticides in raw agricultural crops includes an Attagel cleanup of the final benzene solution followed by GC-ECD and electrolytic conductivity detection (ELCD). Due to the nonspecific nature of electron capture detection and the low residue levels involved, matrix interference was evident in some of the commodities. Therefore, cleanup methods have been sought to substitute Attagel and benzene to minimize matrix interference and adsorption of pesticides on Attagel and to eliminate the usage of the suspected carcinogen benzene.

Since their introduction in the mid 1970s, SPE cartridges have been reported to separate organochlorine pesticides in sewage sludge samples (Anon., 1989), in seafood samples (Kohler and Su, 1986), in waters (Sherma, 1988), in sediment and fish (Marble and Delfino, 1988), and in environmental samples (Lopez-Avila et al., 1989). No comprehensive data are available on the cleanup of raw agricultural crops for the determination of halogenated pesticides. This study was conducted to evaluate the possibility of incorporating SPE cleanup in the routine multiresidue screening method.

Only C_{18} and Florisil SPE cartridges (J. T. Baker Chem-

Table I. Fortification Level and GC Retention Time (t_R) of Halogenated Pesticides

	fortn level, ppm	t_R, min		fortn level, ppm	t_R, min
			Fortification 1		
dichlobenil	0.2	1.59	*p,p'*-DDE	0.2	10.83
ethalfluralin	0.2	2.31	*p,p'*-DDD	0.2	12.27
lindane	0.2	5.71			
			Fortification 2		
trifluralin	0.2	2.31	endosulfan I	0.2	10.04
PCNB	0.2	5.28	endosulfan II	0.2	12.28
vinclozolin	0.2	6.9	endosulfan III	0.2	13.50
			Fortification 3		
pronamide	0.2	4.93	heptachlor epoxide	0.2	9.13
DCNA	0.2	5.46	endrin	0.2	11.78
heptachlor	0.2	6.61			
			Fortification 4		
benefin	0.2	2.11	*o,p'*-DDD	0.2	9.90
profluralin	0.2	3.00	iprodione	0.8	12.73
dichlone	0.4	5.45	bifenox	0.2	14.20
triadimefon	0.8	6.85	permethrin	0.8	15.73
o,p'-DDE	0.2	8.58			15.96
dieldrin	0.2	9.27	fenvalerate	1.0	20.15
					20.92
			Fortification 5		
sulfallate	0.2	4.88	oxadiazon	0.4	10.66
chlorothalonil	0.4	6.80	folpet	1.6	11.25
aldrin	0.2	7.51	ethylan	0.8	11.71
o,p'-dicofol	0.8	8.34	methoxychlor	0.8	15.25
p,p'-dicofol	0.8	8.85	tetradifon	0.4	15.55
			Fortification 6[a]		
alachlor	0.4	7.37	nitrofen	0.2	12.18
anilazine	1.0	9.41	chlorobenzilate	1.0	12.84
oxyfluorfen	0.2	11.52	*p,p'*-DDT	0.2	15.19
o,p'-DDT	0.2	13.57			

[a]Retention times were obtained from a 25-m methyl silicone capillary column.

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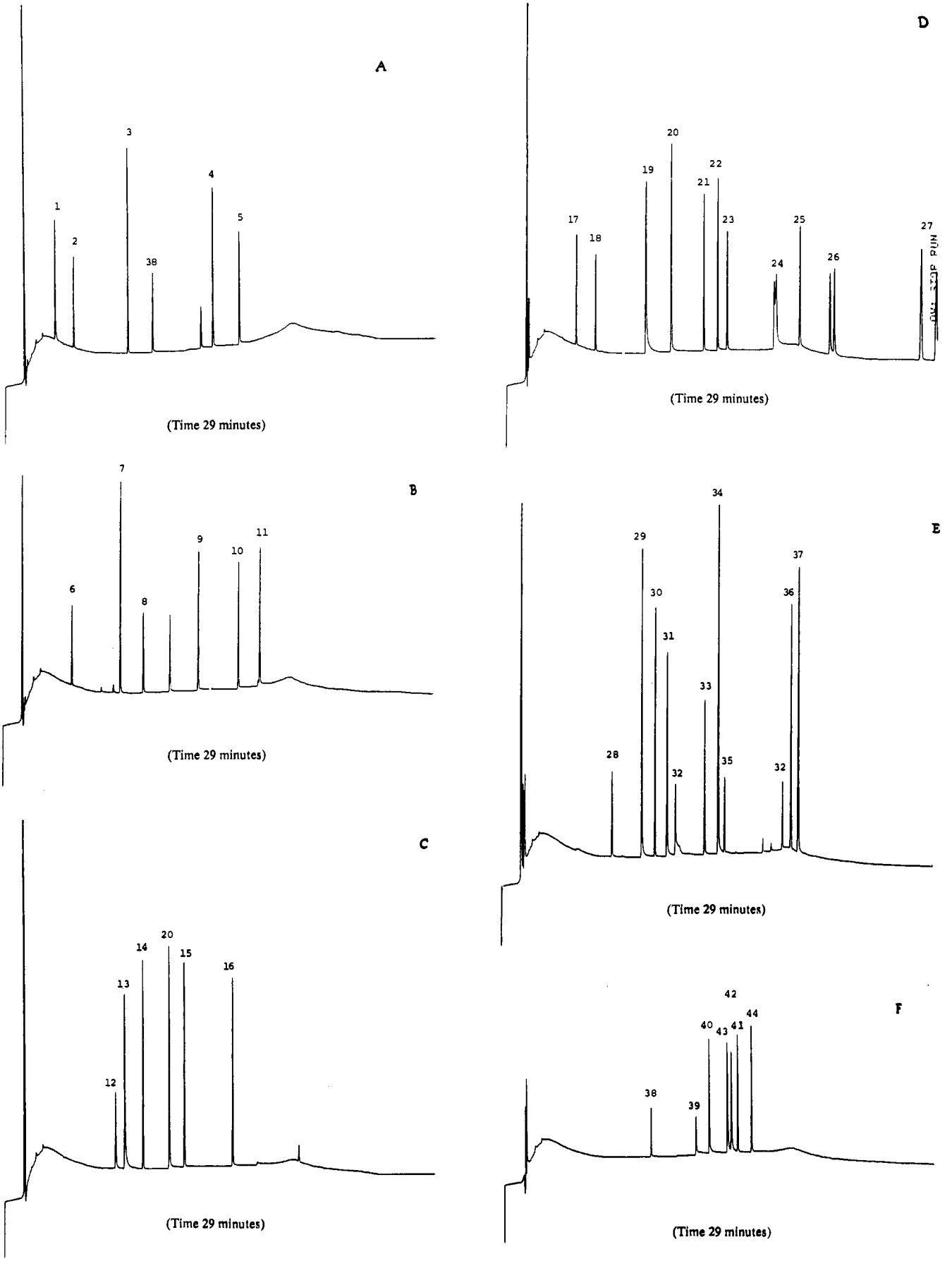

Figure 1. GC profiles of fortification standards. Column: 50% phenyl/methyl silicone, 30 m × 0.25 mm, 0.25-μm film thickness. Oven: 160 °C for 1 min, 160–270 °C at 6 °C/min, hold 10 min. Injector: 220 °C. Detector: ECD 350 °C. Peaks: 1, dichlobenil; 2, ethalfluralin; 3, lindane; 4, *p,p'*-DDE; 5, *p,p'*-DDD; 6, trifluralin; 7, PCNB; 8, vinclozolin; 9, endosulfan I; 10, endosulfan II; 11, endosulfan III; 12, pronamide; 13, DCNA; 14, heptachlor; 15, heptachlor epoxide; 16, endrin; 17, benefin; 18, profluralin; 19, dichlone; 20, triadimefon; 21, *o,p'*-DDE; 22, dieldrin; 23, *o,p'*-DDD; 24, iprodione; 25, bifenox; 26, permethrin; 27, fenvalerate; 28, sulfallate; 29, chlorothalonil; 30, aldrin; 31, *o,p'*-dicofol; 32, *p,p'*-dicofol; 33, oxadiazon; 34, folpet; 35, ethylan; 36, methoxychlor; 37, tetradifon; 38, alachlor; 39, anilazine; 40, oxyfluorfen; 41, *o,p'*-DDT; 42, nitrofen; 43, chlorobenzilate; 44, *p,p'*-DDT.

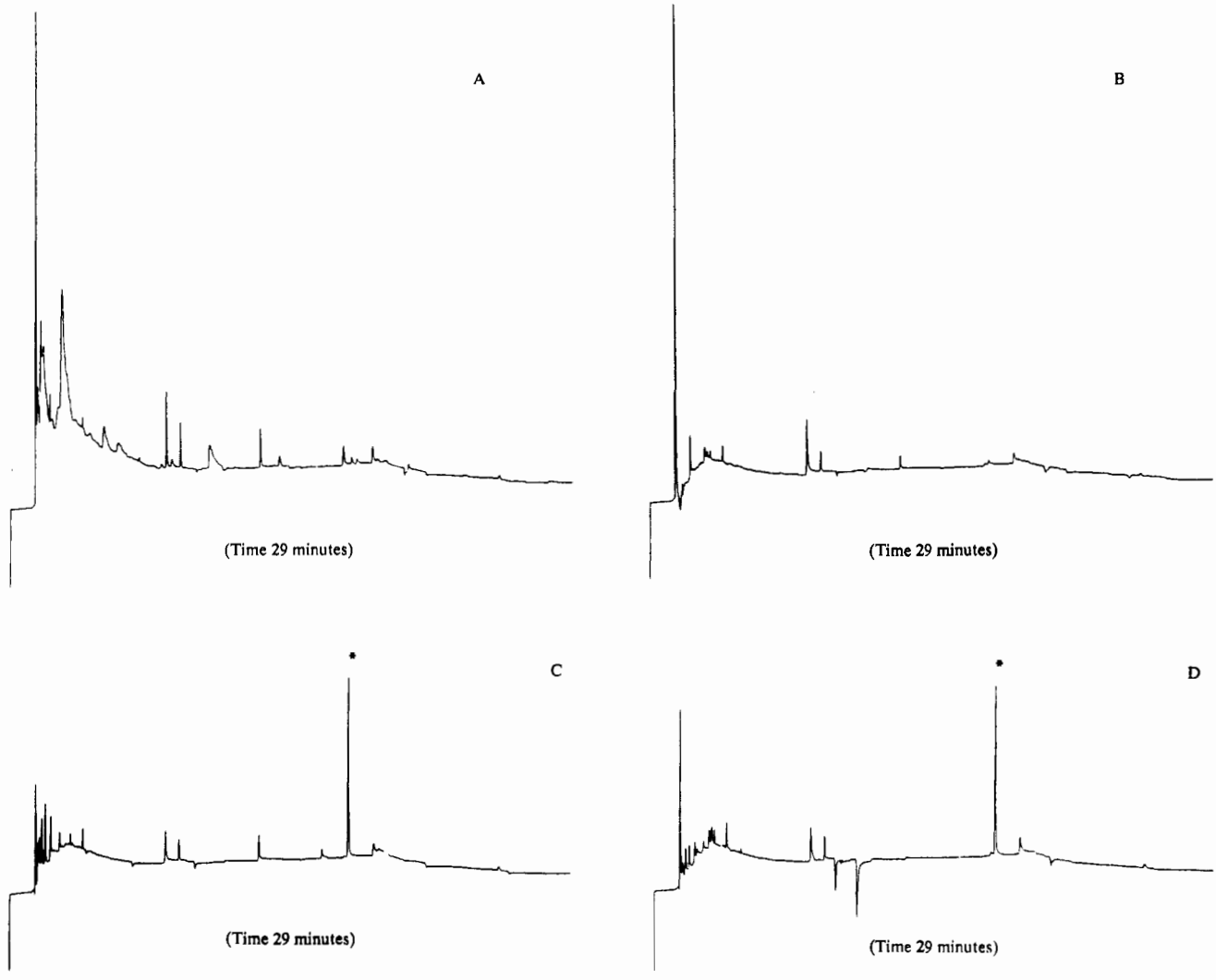

Figure 2. GC profiles of broccoli: (A) matrix blank; (B) with Attagel; (C) with Florisil SPE; (D) with C_{18} SPE. Asterisks indicate an extraneous peak, which appeared in one batch of cartridges only.

Table II. Recoveries of Pesticides and CV in Broccoli

	Attagel		C_{18}		Florisil			Attagel		C_{18}		Florisil	
	$\bar{x}$	CV, %	$\bar{x}$	CV, %	$\bar{x}$	CV, %		$\bar{x}$	CV, %	$\bar{x}$	CV, %	$\bar{x}$	CV, %
dichlobenil	59	16.0	108	1.7	62	8.2	*o,p'*-DDD	110	3.6	110	0.4	99	0.2
ethalfluralin	108	0.2	112	1.9	124	5.8	iprodione	124	7.2	160	0.6	133	10.6
lindane	111	1.5	108	2.3	118	2.5	bifenox	123	3.3	134	2.8	123	1.0
p,p'-DDE	117	4.4	103	1.6	122	1.5	permethrin	120	2.2	111	1.4	112	1.1
p,p'-DDD	122	4.4	111	3.1	129	2.3	fenvalerate	123	2.8	125	3.6	115	1.2
trifluralin	65	10.3	121	7.4	60	27.3	sulfallate	79	1.4	49	27.1	92	1.6
PCNB	59	10.2	113	7.7	66	21.6	chlorothalonil	77	2.6	108	0.9	92	0.5
vinclozolin	77	11.1	124	5.4	110	4.9	aldrin	94	1.3	88	6.9	98	2.7
endosulfan I	94	4.9	124	5.5	112	4.7	*o,p'*-dicofol	101	1.0	110	0.7	105	3.6
endosulfan II	90	4.8	125	7.0	123	2.6	*p,p'*-dicofol	65	2.9	42	4.3	99	6.1
endosulfan III	77	8.3	130	5.6	125	2.3	oxadiazon	114	0.8	113	1.6	106	4.1
pronamide	96	1.3	118	2.4	97	2.6	folpet	101	1.2	121	1.9	92	2.4
DCNA	92	3.1	113	4.5	93	3.4	ethylan	116	1.0	95	2.1	116	3.3
heptachlor	81	18.3	115	0.9	72	12.2	methoxychlor	118	2.6	115	0.4	109	4.0
heptachlor epoxide	104	3.6	115	0.4	95	2.1	tetradifon	116	3.0	115	0.8	111	2.4
endrin	111	1.7	121	0.2	104	1.0	alachlor	88	7.5	124	2.3	115	1.3
benefin	91	4.7	119	1.0	99	0.9	anilazine	102	3.0	143	4.5	101	3.7
profluralin	105	3.3	108	1.5	98	0.6	oxyfluorfen	125	1.7	132	0.8	127	2.2
dichlone	0		0		0		*o,p'*-DDT	58	1.6	131	2.7	125	2.2
triadimefon	97	7.7	135	0.6	97	4.2	nitrofen	127	1.9	137	1.7	117	3.6
o,p'-DDE	104	1.0	102	1.3	100	1.1	chlorobenzilate	111	2.5	117	1.2	117	1.1
dieldrin	108	1.7	108	0.4	100	0.5	*p,p'*-DDT	117	1.2	135	1.2	126	0.3

ical Co., 1982; 1984; Zief and Kiser, 1990) were evaluated for the cleanup of crop matrices extracted according to the CDFA method. Cleanup with Attagel was also included for comparison. Four commodities and 44 pesticides were tested for this study (see Table I). The commodities were carrot, broccoli, celery, and orange, which represent a root/tuber crop, a leafy brassica, a stem vegetable, and a citrus fruit, respectively.

Table III. Recoveries of Pesticides and CV in Carrot

	Attagel		C_{18}		Florisil			Attagel		C_{18}		Florisil	
	x	CV, %	x	CV, %	x	CV, %		x	CV, %	x	CV, %	x	CV, %
dichlobenil	40	7.4	81	2.1	38	12.9	*o,p'*-DDD	89	29.3	113	2.2	110	1.4
ethalfluralin	102	3.3	111	2.9	108	4.9	iprodione	135	1.8	157	2.3	149	2.4
lindane	107	2.0	107	2.9	107	2.9	bifenox	126	2.6	135	0.9	130	1.0
p,p'-DDE	113	1.3	106	1.9	118	3.8	permethrin	57	30.4	105	5.1	124	0.7
p,p'-DDD	115	0.2	109	2.7	117	2.1	fenvalerate	55	30.5	115	4.2	120	1.0
trifluralin	71	2.9	115	3.2	88	19.5	sulfallate	89	2.4	56	15.5	84	0.7
PCNB	69	3.8	108	3.6	84	19.1	chlorothalonil	93	4.1	128	0.5	99	1.3
vinclozolin	80	2.1	116	1.9	111	5.2	aldrin	101	0.8	103	3.5	98	1.1
endosulfan I	90	1.1	112	3.0	109	4.1	*o,p'*-dicofol	109	0.6	121	0.9	102	0.7
endosulfan II	89	1.2	114	1.4	120	2.5	*p,p'*-dicofol	80	1.0	44	3.9	80	0.5
endosulfan III	79	0.5	116	1.6	122	0.7	oxadiazon	119	1.4	122	0.6	101	0.5
pronamide	104	2.7	91	10.1	95	3.5	folpet	108	4.4	135	0.7	91	3.0
DCNA	91	6.4	109	3.0	86	6.7	ethylan	0		0		0	
heptachlor	97	2.6	112	2.3	73	17.8	methoxychlor	121	2.4	125	0.3	98	1.6
heptachlor epoxide	105	1.7	113	3.1	92	5.7	tetradifon	121	2.1	127	0.2	101	1.0
endrin	106	4.3	116	1.6	103	1.7	alachlor	102	4.7	132	0.8	107	0.8
benefin	94	8.8	103	3.5	101	1.5	anilazine	149	2.4	167	1.3	151	1.2
profluralin	98	12.6	113	3.6	102	1.8	oxyfluorfen	123	3.3	136	2.6	126	1.2
dichlone	41	5.3	50	1.7	45	1.6	*o,p'*-DDT	54	2.2	134	1.1	119	4.1
triadimefon	27	19.1	123	5.4	117	7.7	nitrofen	127	2.1	138	1.5	124	0.7
o,p'-DDE	104	11.3	105	3.2	108	1.4	chlorobenzilate	119	3.1	125	1.0	120	4.5
dieldrin	74	25.1	110	0.4	112	1.7	*p,p'*-DDT	109	2.6	154	1.3	128	3.0

Table IV. Recoveries of Pesticides and CV in Celery

	Attagel		C_{18}		Florisil			Attagel		C_{18}		Florisil	
	x	CV, %	x	CV, %	x	CV, %		x	CV, %	x	CV, %	x	CV, %
dichlobenil	51	6.9	118	2.8	43	16.8	*o,p'*-DDD	109	2.7	98	5.9	103	0.2
ethalfluralin	71	22.8	113	1.0	47	57.4	iprodione	139	1.8	151	1.1	151	2.2
lindane	87	11.4	109	1.3	65	37.4	bifenox	112	0.4	128	0.8	124	0.2
p,p'-DDE	120	2.3	105	1.4	106	7.1	permethrin	107	1.1	92	7.0	116	0
p,p'-DDD	117	2.0	109	1.7	110	3.5	fenvalerate	109	2.6	97	6.6	113	0.5
trifluralin	83	7.4	116	3.3	98	8.8	sulfallate	106	2.6	85	0	112	2.3
PCNB	88	7.0	117	7.3	109	9.9	chlorothalonil	94	7.8	121	1.2	106	1.5
vinclozolin	99	9.0	121	2.5	112	1.0	aldrin	101	3.8	81	14.3	101	1.9
endosulfan I	101	5.3	114	1.6	109	1.6	*o,p'*-dicofol	105	1.8	125	2.2	106	1.4
endosulfan II	103	9.0	118	1.3	118	0.5	*p,p'*-dicofol	92	3.2	49	2.2	96	1.1
endosulfan III	98	12.2	120	1.0	121	1.2	oxadiazon	122	2.8	124	1.6	113	1.4
pronamide	94	4.2	100	6.8	84	0.7	folpet	110	2.0	123	0.6	90	4.6
DCNA	101	8.4	113	0.6	71	10.6	ethylan	116	1.5	93	3.0	112	1.4
heptachlor	78	19.3	113	0.7	36	34.0	methoxychlor	116	3.3	120	1.1	105	0.9
heptachlor epoxide	103	7.9	115	0.2	76	9.3	tetradifon	122	0.3	119	0.3	109	1.5
endrin	112	5.5	112	1.8	99	5.2	alachlor	70	1.5	117	1.0	116	1.2
benefin	97	2.6	116	3.9	101	1.5	anilazine	142	1.4	158	2.1	153	0.4
profluralin	104	1.0	117	4.6	101	0.8	oxyfluorfen	115	0.7	129	0.8	127	1.0
dichlone	108	3.2	160	1.6	142	1.1	*o,p'*-DDT	50	2.7	119	2.0	127	1.2
triadimefon	92	6.3	107	6.9	102	3.2	nitrofen	116	2.3	135	1.4	129	2.2
o,p'-DDE	108	1.9	91	5.3	102	0.8	chlorobenzilate	107	1.0	115	0.6	116	0.8
dieldrin	108	1.9	98	4.0	101	0.2	*p,p'*-DDT	105	2.5	132	1.1	125	0.2

Table V. Recoveries of Pesticides and CV in Orange

	Attagel		C_{18}		Florisil			Attagel		C_{18}		Florisil	
	x	CV, %	x	CV, %	x	CV, %		x	CV, %	x	CV, %	x	CV, %
dichlobenil	83	2.0	132	1.7	100	8.3	*o,p'*-DDD	108	1.0	112	2.9	94	2.0
ethalfluralin	42	10.6	118	1.5	55	9.1	iprodione	106	11.2	156	1.5	108	0
lindane	33	13.5	111	1.7	57	5.6	bifenox	33	3.1	116	0.4	83	11.0
p,p'-DDE	49	8.2	111	2.0	79	9.4	permethrin	115	2.3	115	2.7	110	1.1
p,p'-DDD	42	7.2	113	1.5	75	6.9	fenvalerate	119	3.8	123	1.5	110	2.2
trifluralin	43	13.4	116	2.1	59	16.8	sulfallate	97	3.2	80	13.0	86	6.6
PCNB	35	14.4	104	3.0	62	9.9	chlorothalonil	85	11.2	122	2.0	88	12.4
vinclozolin	32	12.2	119	2.6	75	13.1	aldrin	100	2.5	95	1.5	93	2.6
endosulfan I	41	10.8	110	2.0	66	15.0	*o,p'*-dicofol	98	5.1	110	2.3	92	6.9
endosulfan II	37	9.2	116	1.9	73	14.3	*p,p'*-dicofol	40	4.8	31	8.7	79	4.8
endosulfan III	29	11.5	122	1.4	72	13.0	oxadiazon	108	4.2	115	3.5	95	3.6
pronamide	14	29.4	93	5.6	48	10.9	folpet	96	10.3	126	3.1	74	14.1
DCNA	13	29.3	109	0.7	59	8.5	ethylan	114	2.5	86	5.1	106	5.3
heptachlor	20	25.0	111	0.9	47	17.5	methoxychlor	114	6.1	114	2.5	89	7.5
heptachlor epoxide	20	30.6	110	0.7	50	12.6	tetradifon	103	6.1	116	4.1	92	6.2
endrin	22	30.3	113	1.0	50	14.2	alachlor	36	11.6	120	2.2	94	3.8
benefin	95	2.7	136	3.3	97	0.7	anilazine	89	1.1	137	2.9	92	7.2
profluralin	102	1.2	118	9.7	94	0.7	oxyfluorfen	90	3.2	108	3.0	88	5.7
dichlone	46	6.0	90	3.6	51	10.3	*o,p'*-DDT	36	3.1	122	1.0	114	0.2
triadimefon	92	9.6	131	4.3	95	9.9	nitrofen	83	2.0	108	5.2	84	8.3
o,p'-DDE	106	0.2	106	3.5	98	2.2	chlorobenzilate	84	2.7	107	2.4	86	6.4
dieldrin	104	1.7	108	3.2	95	3.1	*p,p'*-DDT	75	2.0	104	5.2	91	2.3

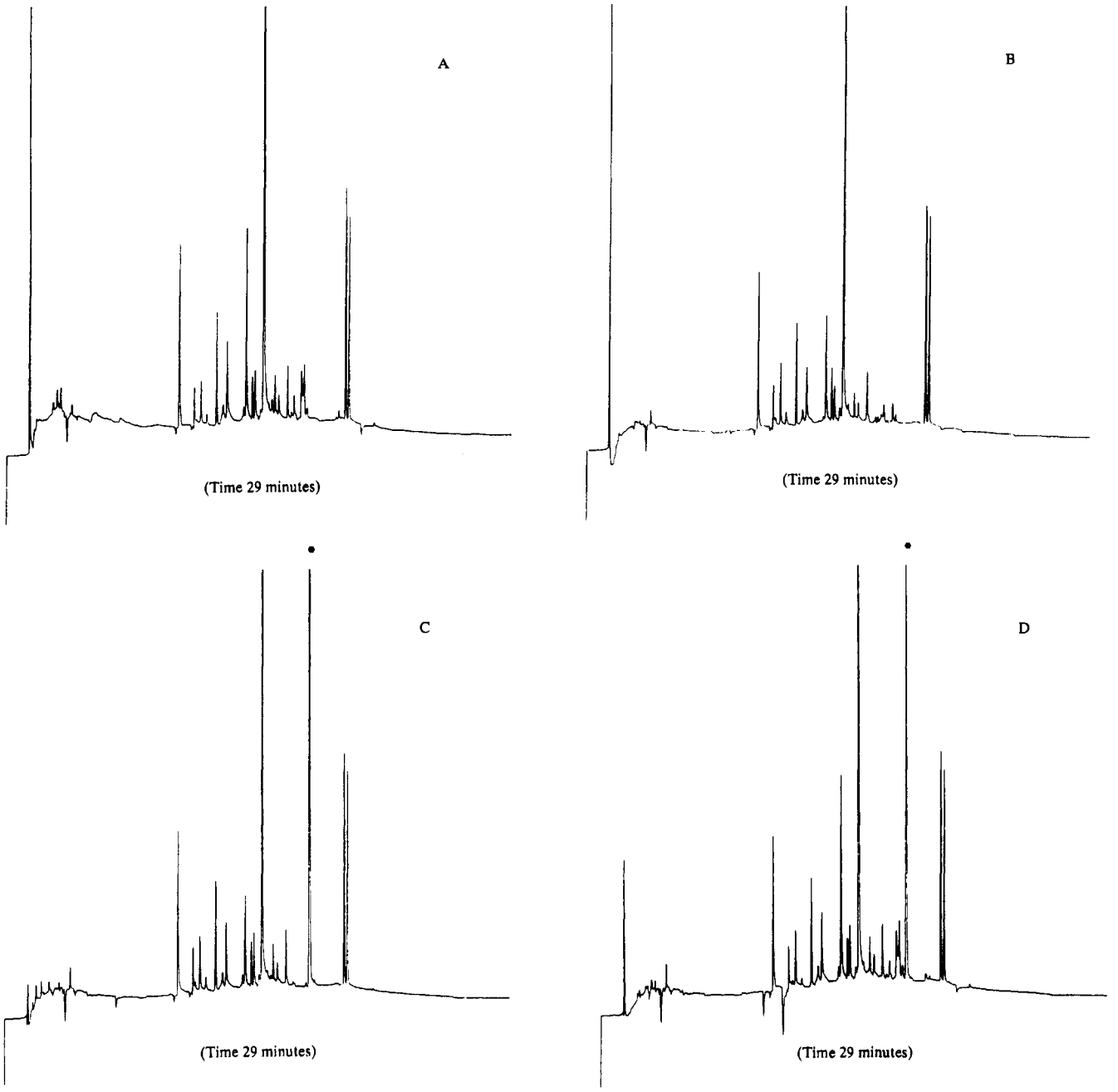

Figure 3. GC profiles of carrot: (A) matrix blank; (B) with Attagel; (C) with Florisil SPE; (D) with C_{18} SPE. Asterisks indicate an extraneous peak, which appeared in one batch of cartridges only.

Table VI. Number of Halogenated Organic Pesticides with 70–130% Recovery and a CV of <20% from Crops after Cleanup Procedure

	Attagel	C_{18}	Florisil
broccoli	38	33	39
carrot	32	31	39
celery	39	38	37
orange	25	38	33

MATERIALS AND METHODS

Description of Fortification. *Stock Solution.* Standards in 1 mg/mL were prepared in either *n*-hexane or benzene/*n*-hexane.

Fortification solutions were prepared from the stock solutions in the range 20–160 μg/mL each in *n*-hexane: fortification 1 consists of 5 pesticides (see Table I); fortification 2 consists of 6 pesticides (see Table I); fortification 3 consists of 5 pesticides (see Table I); fortification 4 consists of 11 pesticides (see Table I); fortification 5 consists of 10 pesticides (see Table I); fortification 6 consists of 7 pesticides (see Table I).

Table VII. General Statistics of the Percent Recoveries of All Pesticides from All Commodities Tested

	Attagel	C_{18}	Florisil
data elements[a]	525	525	525
95% confidence interval	88–94	111–115	97–101
SD	29.8	22.5	24.8
variance	886	504	614
SE	1.3	1.0	1.1
CV, %	33	20	25

[a] Excluding data from ethylan in carrot.

Extraction. The extraction method of Joe (1988) was adopted with doubling the sample size and the extracting solvent to accommodate the number of replicates needed. One milliliter of the above fortification solution was added to 100 g of produce sample in a quart-size Mason jar. Two hundred milliliters of acetonitrile was added, and the mixture was blended with an Omnimixer for 2–3 min at high speed. The resulting slurry was filtered through a Shark Skin (Schleicher & Schuell, Inc., Keene,

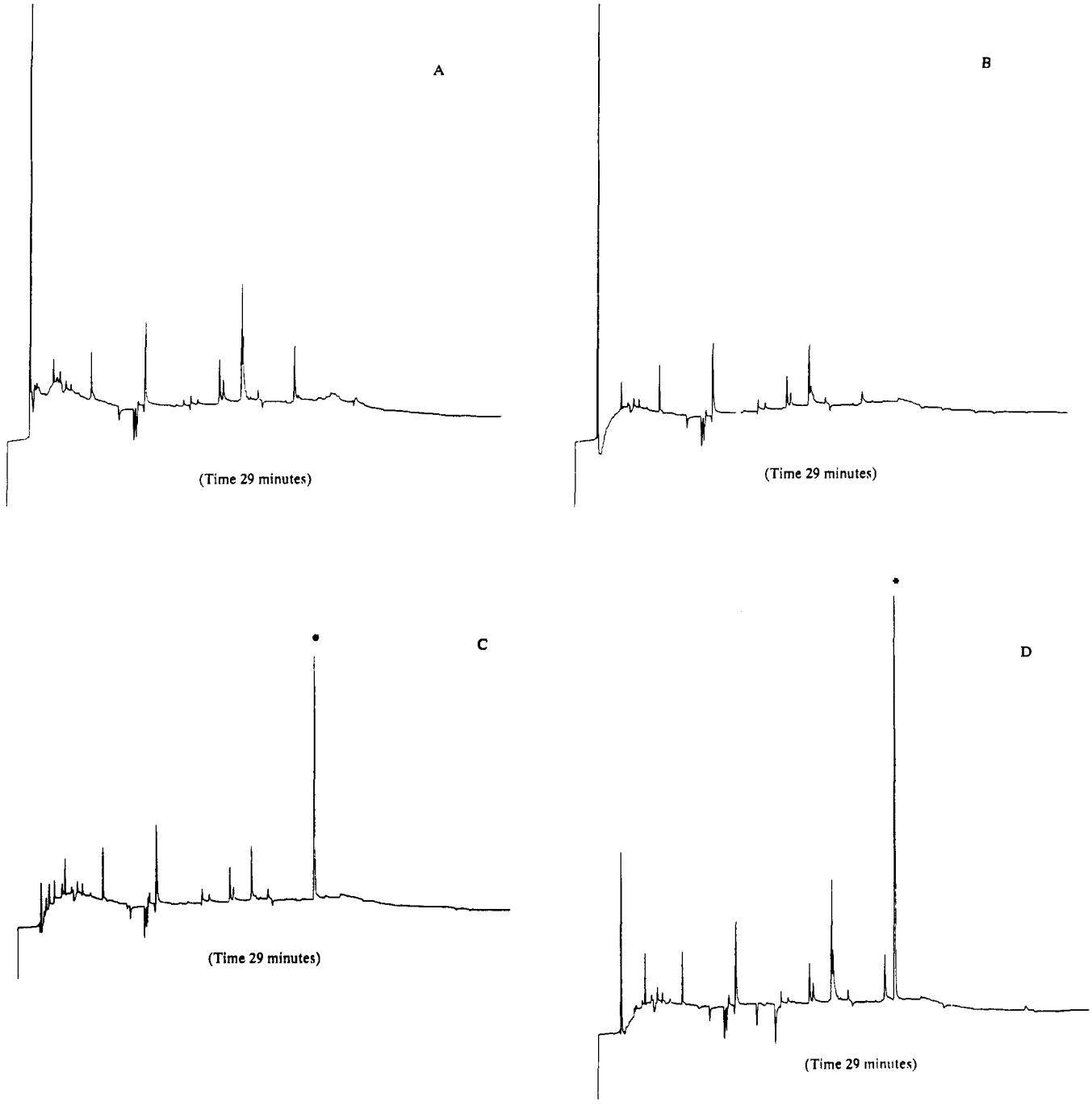

Figure 4. GC profiles of celery: (A) matrix blank; (B) with Attagel; (C) with Florisil SPE; (D) with C_{18} SPE. Asterisks indicate an extraneous peak, which appeared in one batch of cartridges only.

NH) filter paper into a 250-mL graduated cylinder containing ca. 20 g of sodium chloride. The cylinder was shaken vigorously for 1 min, and the phases were allowed to separate (salting out effect). For Attagel and Florisil SPE cleanups, the acetonitrile layer (5 mL, equivalent to 2.5 g of sample) in triplicates was evaporated just to dryness under a nitrogen stream in a 15-mL conical centrifuge tube and the residue was reconstituted in either benzene (Attagel) or *n*-hexane (Florisil SPE). For C_{18} cleanup, 5 mL of the acetonitrile extract in triplicates was evaporated to 3 mL.

Cleanup Procedure. *Attagel.* Benzene (5 mL) was added to the above residue followed by 0.5-mL equiv of Attagel (E. T. Horn Co., Oakland, CA; Attagel 40 dry grade). The tube was shaken and the supernatant transferred to an autosampler vial for GC analysis.

Florisil SPE. *n*-Hexane (2 mL) was added to the residue, mixed, and loaded onto a Florisil cartridge (Waters Associates, Milford MA; part no. 51960; save the effluent) which was conditioned with 5 mL of 10% acetone/hexane and 5 mL of hexane. The cartridge was eluted with 10 mL of 10% acetone/hexane (rinse the tube with this eluent), and the combined effluent was evaporated to 5 mL and transferred to an autosampler vial for GC analysis.

C_{18} SPE. The acetonitrile extract (5 mL) was evaporated to 3 mL in a graduated 15-mL conical centrifuge tube, and 7 mL of water was added. The mixture was loaded onto a C_{18} cartridge (Waters Associates, part no. 51910) which was conditioned with 2 mL of methanol and followed by 5 mL of water. The tube was rinsed with 1 mL of 30% acetonitrile/water, and the cartridge was further rinsed with 1 mL of water. The effluent was discarded. After the cartridge was dried for 15 min under vacuum, the halogenated pesticides were eluted with 2 mL of *n*-hexane and 2.5 mL of 5% acetone/hexane for spikes 1–3 and spikes 4–6, respectively. The effluent was then diluted to 5 mL with hexane, mixed on a vortex mixer, and transferred to an autosampler vial for GC analysis.

Gas Chromatographic Condition. Halogenated organic pesticides were analyzed on a Hewlett-Packard (HP) 5880A GC

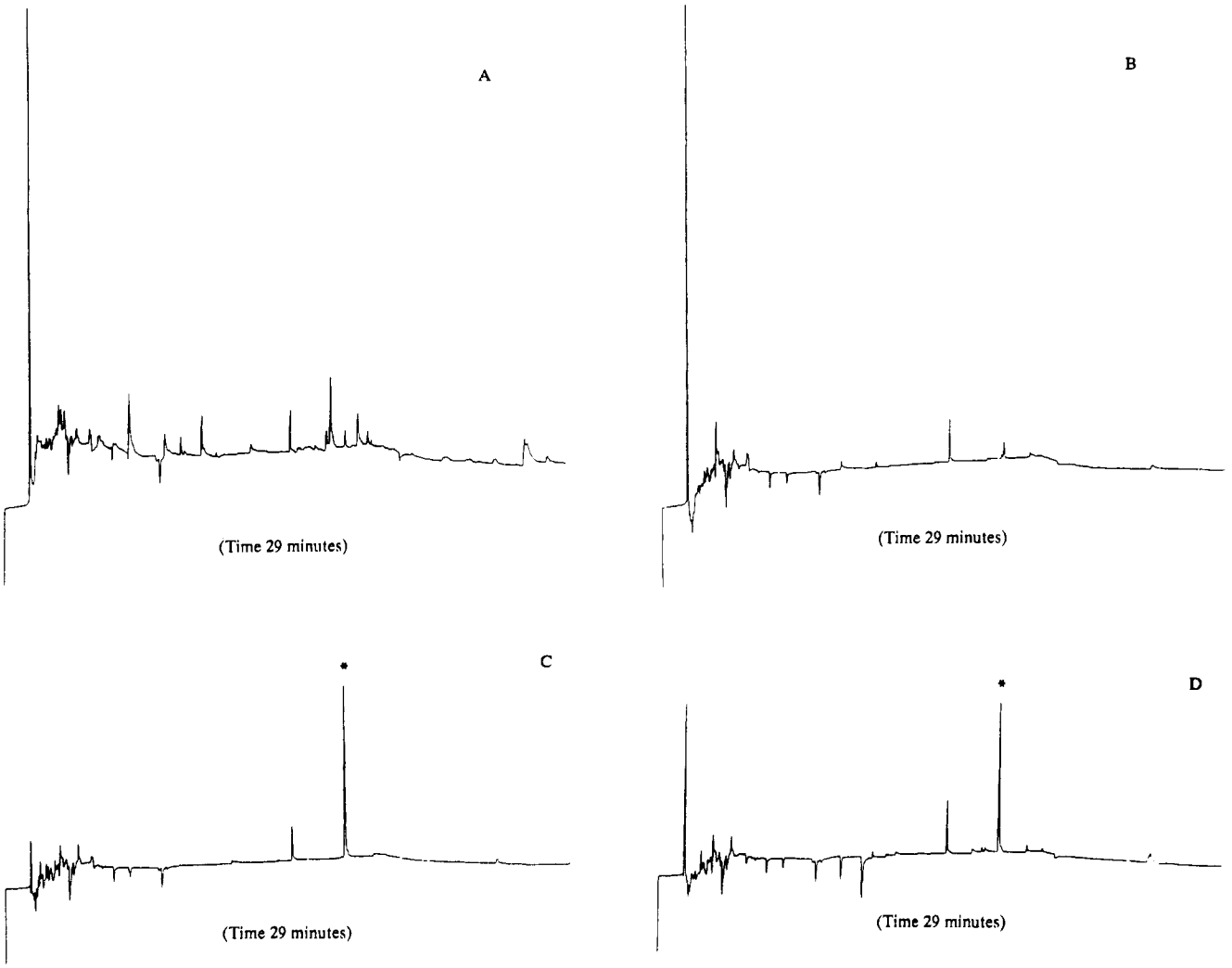

Figure 5. GC profiles of orange: (A) matrix blank; (B) with Attagel; (C) with Florisil SPE; (D) with C_{18} SPE. Asterisks indicate an extraneous peak, which appeared in one batch of cartridges only.

equipped with a 15 m × 0.25 mm 50% phenyl/methyl silicone, 0.25-μm film thickness capillary column (J&W Scientific, Folsom, CA), a ^{63}Ni-ECD, and an HP-7673A automatic sampler. Oven temperature was programmed from 170 °C, with an initial hold time of 4 min, to 240 °C at 8 °C/min and a final hold of 5 min. Injector and detector temperatures were set at 220 and 250 °C, respectively. Integration and quantitation was done by an HP-5880A GC level IV terminal using the external standard calibration method. Linear regressions of ECD response in peak height of three levels of each standard were used to calculate the amount of pesticides in sample. Extracts from fortification 6 were chromatographed on a 25 m × 0.2 mm methyl silicone, 0.33-μm film thickness capillary column with the following temperature program: initial temperature 210 °C with a 4-min hold increased at a rate of 5 °C/min to 240 °C with a final hold of 10 min.

RESULTS AND DISCUSSION

Due to the wide range of the tolerance levels of halogenated pesticides for the commodities tested (from no tolerance allowed in most cases up to 50 ppm; Duggan et al., 1990), fortification levels of 0.2–1.6 ppm of pesticides were used. At 0.2 ppm fortification level, ECD response is equivalent to that of a 0.1 ng/μL standard at full recovery (final concentration was 0.5 g of sample/mL).

Table I lists the fortification level and GC retention times of the pesticides. As indicated in Table I, some pesticides coelute under the chromatographic conditions used. However, our routine screening of the halogenated pesticides is carried out with dual columns, methyl silicone and 50% phenyl/methyl silicone. Coeluting peaks on one column usually can be resolved on the other, and any positive findings on the ECD are further confirmed on either electrolytic conductivity detector (ELCD) or GC/MS.

Mean percent recoveries and coefficients of variation (CV, %) for all cleanup procedures are listed in Tables II–V. Low recoveries were observed for dichlobenil from Attagel (40–83%), whereas C_{18} showed 81–132% recoveries. During the course of the C_{18} SPE experiment, it was noted that the recoveries of alachlor and triadimefon were improved with 5% acetone/*n*-hexane (2.5 mL) as eluent instead of *n*-hexane alone. The average percent recoveries of fortifications 1–3 from oranges were 35 ± 17%, 113 ± 8%, and 64 ± 14% for Attagel, C_{18}, and Florisil, respectively. This indicates sorption of pesticides on Attagel. With the exception of dichlone, *p,p'*-dicofol, alachlor, and *o,p'*-DDT, Attagel cleanup gave 74–119% recoveries from oranges in fortifications 4–6 (Table V). Attagel is a naturally occurring, highly porous mineral, which is a crystalline magnesium aluminum silicate with a three-dimensional chain structure that gives it unique colloidal and sorptive properties. Care should be taken not to overdo the evaporating steps to ensure proper recoveries of the pesticide. C_{18} SPE procedures offered an advantage over the Florisil SPE or Attagel, in which the sample solutions were never evaporated to dryness.

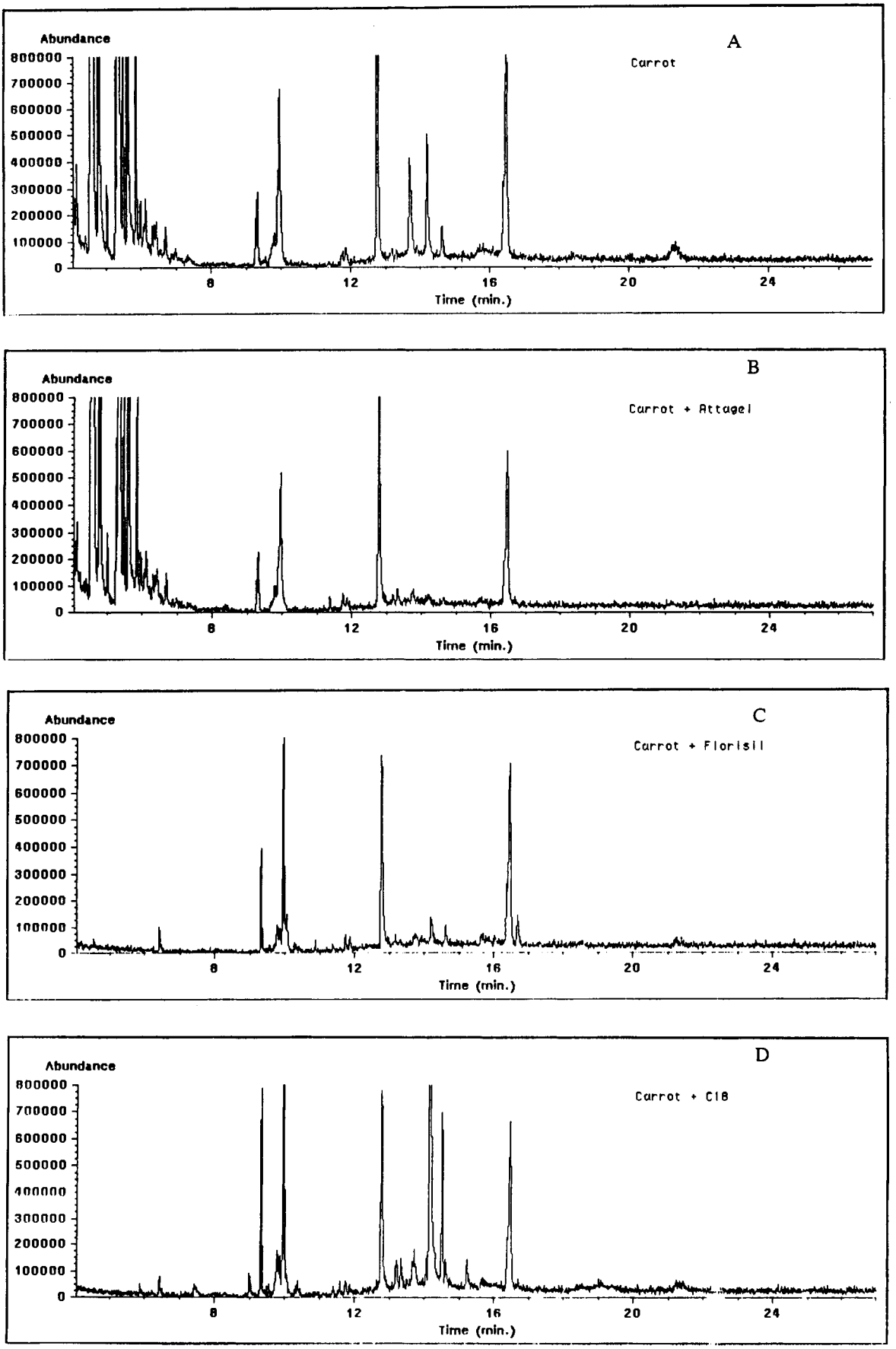

Figure 6. GC-MSD TIC profiles of carrot: (A) matrix blank; (B) with Attagel; (C) with Florisil SPE; (D) with C_{18} SPE. Instrument: HP 5970 GC-MSD. Column: methyl silicone, 25 m × 0.22 mm, 0.33-μm film thickness. Oven: 60 °C for 1 min, 60–280 °C at 20 °C/min, hold 15 min. Injector: 250 °C. Detector: 250 °C. Scan from 50 to 400 amu.

However, it was more time-consuming, and occasional water droplets were noticed if the cartridge were not completely dried before the final elution with 5% acetone/*n*-hexane. With the Attagel cleanup procedure, dichlone and *o,p'*-DDT showed average percent recoveries of 49 ± 45% and 50 ± 10%, respectively, for all four commodities tested (Tables II–V), indicating the adsorption of pesticides.

GC profiles of all pesticides tested are shown in Figure 1. They represent the standard responses at full recovery. Representative GC chromatograms of the sample matrices without any cleanups and with Attagel, Florisil SPE, and C_{18} SPE cleanups are shown in Figures 2–5 (run under the same conditions as in Figure 1). For both carrot and celery, there is no difference between the ECD chromatograms of the matrix blanks and the ones with C_{18} SPE. In addition, the final sample solutions from the C_{18} SPE showed only slight reduction in the color intensity. ECD chromatograms of the sample matrices were similar when the samples were treated with either Attagel or Florisil SPE, which in turn showed some differences from those of the matrix blanks. In the case of carrots, all chromatograms were similar. The final sample solutions were all clear in both Attagel and Florisil SPE treated samples, contrary to the intense coloration of the matrix blanks, except for the carrot with Florisil SPE, which was slightly colored.

Figure 6 shows the total ion chromatogram (TIC) of carrot extract before and after various cleanups, without further concentration, obtained from GC-MSD (mass selective detector). Since both the carrot blank and the Attagel treated matrix are in benzene, solvent interference can be seen initially for up to 6 min (Figure 6A,B, plot starts 4 min after injection). Attagel and Florisil SPE treated matrices again show similar chromatograms, which are somewhat cleaner than the carrot matrix itself. All C_{18} SPE treated matrices show additional common interferences in the region between 13 and 15 min (Figure 6D). Library search indicated some trimethylsilyl and siloxyl derivatives. Although the validated detection limit for most of the halogenated pesticides was 0.2 ppm, lower detection limits can be achieved on the basis of the relative peak response as shown for celery, orange, and broccoli.

Additional experiments with other SPEs, like alumina B and silica, were also tested for fortifications 1–3. For alumina B SPE, eluents such as 5 mL of 10% acetone/*n*-hexane, 5 mL of 5% ethyl acetate/toluene, or 10 mL of 25% ethyl ether/petroleum ether did not yield satisfactory recoveries (>70%) for most of the 16 pesticides. In the case of silica SPE, recoveries are comparable to that of the Attagel when 5% ethyl acetate/toluene was used as eluent.

Commodities like onions have been difficult to analyze on ECD due to their volatile flavor constituents, such as sulfides, thiophenes, and thiosulfonates (Boelens et al., 1971). Cleanups of onion extracts with C_{18} and Florisil SPEs using the same experimental conditions were attempted for fortifications 1–3. The resulting ECD chromatograms were still difficult to quantitate. For these onion extracts, ELCD was proven to be far superior to ECD in the analysis of halogenated pesticides, because no matrix interferences were observed. No significant differences in recoveries were noted among Attagel, C_{18}, and Florisil cleanups for these onion samples for fortifications 1–3.

Table VI shows the number of halogenated organic pesticides with recoveries between 70 and 130% and CV of <20% from crops after Attagel or SPE cleanups. General statistics and the analysis of variance (ANOVA) of the percent recoveries of all 44 pesticides from all commodities were carried out with the Quality Analyst program (Northwest Analytical, Inc., Portland, OR), and the results are shown in Table VII. It indicates a significant difference when either C_{18} or Florisil is compared with Attagel. Florisil SPE provides lower variation, narrower confidence interval, and higher recoveries in general than the Attagel. Considering the health hazard involved and the labor and high cost of segregation and disposal of benzene waste associated with the Attagel cleanup, the substitution of Florisil SPE for Attagel in the multiresidue screen procedure is warranted.

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LITERATURE CITED

Anon. Reliable Solid-Phase Extraction Procedure for Low Levels of Pesticides in Sludge Samples. *Supelco Rep.* **1989**, *8* (4), 7–8.

Baker, J. T., Chemical Co. *Baker-10 SPE Applications Guide*; Baker: Phillipsburg, NJ, 1982; Vol. I.

Baker, J. T., Chemical Co. *Baker-10 SPE Applications Guide*; Baker: Phillipsburg, NJ, 1984; Vol. II.

Boelens, M.; de Valois, P. J.; Wobben, H. J.; van der Gen, A. Volatile Flavor Compounds from Onion. *J. Agric. Food Chem.* 1971, *19*, 984–991.

Duggan, R., Duggan, P. D., Duggan, M. B., Eds. *Pesticide Chemical News Guide*; Rothschild: Washington, DC, 1990.

Joe, T. *Multi-Residue Pesticide Screens*; Department of Food and Agriculture, Division of Inspection Services, Chemistry Laboratory Services Branch: Sacramento, 1988.

Kohler, P. W.; Su, S. Y. Analysis of Some Organochlorine Pesticides in Seafood Samples by Solid-Phase Extraction-Gas Chromatography. *Chromatographia* **1986**, *21* (9), 531–537.

Lopez-Avila, V.; Milanes, J.; Dodhiwala, N. S.; Beckert, W. F. Cleanup of Environmental Sample Extracts Using Florisil Solid-Phase Extraction Cartridges. *J. Chromatogr. Sci.* **1989**, *27* (5), 209–215.

Marble, L. K.; Delfino, J. J. Extraction and Solid Phase Cleanup Methods for Pesticides in Sediment and Fish. *Am. Lab.* **1988**, *20* (11), 23–24, 26, 28, 30, 32.

Sherma, J. Determination of Organochlorine Insecticides in Waters by Quantitative TLC and C-18 Solid-Phase Extraction. *J. Liq. Chromatogr.* **1988**, *11* (9–10), 2121–2130.

Zief, M.; Kiser, R. An Overview of Solid Phase Extraction for Sample Preparation. *Am. Lab.* **1990**, Jan, 70–83.

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