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RAPID DETERMINATION OF SEVEN HERBICIDES IN WATER OR ISOOC-TANE USING C₁₈ AND FLORISIL SEP-PAK CARTRIDGES AND GAS CHROMATOGRAPHY WITH ELECTRON-CAPTURE DETECTION

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SUMMARY

Simple methods for the concentration and clean-up of seven herbicides in water or in isoocctane using a C₁₈ Sep-Pak cartridge and a Florisil Sep-Pak cartridge and subsequently determining the herbicides by gas chromatography with electron-capture detection have been developed. The conditions for stepwise or simultaneous desorption of these herbicides from the Sep-Pak cartridges are given.

INTRODUCTION

For the determination of trace amounts of pesticides and other environmental pollutants, enrichment and clean-up steps are generally required before analysis. Many kinds of adsorbent have been developed for this purpose, including Al₂O₃^{1,2}, mixtures of Al₂O₃ and silica gel³, silica gel^{4,5}, Bio-Beads S-X₃⁶, XAD-2 macroporous resin⁷, a mixture of MgO and cellulose⁸, graphitized carbon black⁹ and Florisil^{10,11}.

The traditional preconcentration and clean-up steps were performed by extracting a large water sample with a smaller amount of organic solvent, evaporating the extract to a concentrate, or partitioning between solvents for clean-up, or decanting onto a column of adsorbent followed by elution with suitable solvents. The disadvantages of these processes are that they are solvent consuming and time consuming and there is an increased possibility of contamination due to frequent transfers.

The Sep-Pak cartridge is a commercial product for enrichment and clean-up. It has the advantages of effecting time savings and solvent savings, having fewer transfers and being readily disposable. These advantages have led to its extensive use for sample pretreatment in many fields including the environment, biochemistry and food science, with substantial savings in the number of steps and total time. For example, Kuwata *et al.*¹² used a C₁₈ Sep-Pak cartridge to adsorb low-molecular-weight aliphatic amines from air; Kubo *et al.*¹³ determined disopyramide and its metabolites in serum using a silica Sep-Pak cartridge for clean-up; Bicchi *et al.*¹⁴ separated chlorothalonil, vinclozolin, captan and endosulfan from crops with a Florisil Sep-Pak cartridge; Hu *et al.*¹⁵ recovered polybrominated biphenyl from fat with C₁₈ and

Florisil Sep-Pak cartridges; and Nielson¹⁶ separated chlorophenols from municipal wastewater with a C₁₈ Sep-Pak cartridge.

In this paper, we report methods for the rapid determination of seven commonly used herbicides in aqueous or isooctane samples using C₁₈ Sep-Pak and Florisil Sep-Pak cartridges for enrichment and clean-up and subsequently using gas chromatography with electron-capture detection (GC-ECD) to determine the herbicides. The herbicides studied were 2,4-D methyl ester [methyl (2,4-dichlorophenoxy)acetate], 2,4-DB methyl ester [methyl 4-(2,4-dichlorophenoxy)butyrate], 2,4,5-T methyl ester [methyl (2,4,5-trichlorophenoxy)acetate], silvex methyl ester [methyl 2-(2,4,5-trichlorophenoxy)propionate], CIPC (chloropropham; isopropyl 3-chlorophenylcarbamate), ramrod (Propachlor; 2-chloro-N-isopropylacetanilide) and DEF (S,S,S-tributylphosphorotrithioate). The conditions for the stepwise or simultaneous desorption of these herbicides from the Sep-Pak cartridges are given. These techniques may also be applicable to the determination of trace amounts of the herbicides in other types of sample such as vegetable, meat and milk. However, to apply the procedure to the determination of these herbicides in dilute solutions may require further study that would take into account further phenomena, e.g., spurious adsorption and matrix effects, which may easily occur at the trace concentration level.

EXPERIMENTAL

Materials

All solvents were of analytical-reagent grade (Merck, Darmstadt, F.R.G.). The herbicides were standards from PolyScience (Niles, IL, U.S.A.). Florisil and C₁₈ Sep-Pak cartridges were obtained from Water Assoc. (Milford, MA, U.S.A.). Deionized water was prepared using a Milli-Q water purification system (Millepore, Bedford, MA, U.S.A.).

A stock solution was prepared by dissolving 360 mg of 2,4-D methyl ester, 72.0 mg of 2,4,5-T methyl ester, 3.6 mg of silvex methyl ester, 360 mg of CIPC, 14.4 mg of ramrod and 7.2 mg of DEF in 5 ml of methanol. Aqueous and isooctane sample solutions each containing 72 ppb^a of 2,4-D methyl ester, 144 ppb of 2,4-DB methyl ester, 14.4 ppb of 2,4,5-T methyl ester, 7.2 ppb silvex methyl ester, 720 ppb of CIPC, 28.8 ppb of ramrod and 14.4 ppb of DEF were prepared by dissolving 10 μ l of the above stock solution in 1000 ml of water or 1000 ml of isooctane.

C₁₈ and Florisil Sep-Pak cartridge chromatography for aqueous samples

The C₁₈ Sep-Pak cartridge was activated prior to use by prewetting the cartridge with 5 ml of methanol followed by washing with 2 ml of water¹². A 10-ml volume of aqueous sample was applied to a C₁₈ Sep-Pak cartridge or a Florisil Sep-Pak cartridge at a flow-rate of ca. 10 ml/min by means of a syringe. Room air (50 ml) was applied to the cartridge to remove residual water. The Sep-Pak cartridges were then eluted sequentially with 2-ml portions of solvent gradients and 4 μ l of the eluate were injected into the GC column for analysis.

The effluents from water samples passing through the Sep-Pak cartridges were extracted with three 2-ml volumes of isooctane and 4 μ l of the extracts were injected

^a Throughout this article, the American billion (10⁹) is meant.

into the GC column to study the adsorption efficiency. A preliminary study showed that extraction with three 2-ml volumes of isooctane can recover the herbicides quantitatively from water.

Florisil Sep-Pak cartridge chromatography for isooctane

A 10-ml volume of isooctane sample was forced to flow through a Florisil Sep-Pak cartridge at *ca.* 10 ml/min with a syringe. The residual herbicides in the effluent were determined by GC-ECD in order to study the adsorption efficiency. The Sep-Pak cartridge was purged with 50 ml of air to remove retained isooctane. The cartridge was then eluted sequentially with 2-ml portions of solvent gradients and 4 μ l of the eluates were injected into the GC column for analysis.

Florisil Sep-Pak cartridge chromatography for dilute aqueous samples

A 10-ml volume of the aqueous sample mentioned above was diluted to 10 l with purified water and the solution was forced to permeate through a Florisil Sep-Pak cartridge at *ca.* 10 ml/min under suction by an aspirator. The cartridge was purged with 50 ml of air and then eluted sequentially with 2-ml portions of solvent gradients. The herbicides in the eluates were determined by GC-ECD.

Instrumental

A Shimadzu GC-9AM gas-liquid chromatograph with a Shimadzu chemically bonded fused-silica capillary column (25 m \times 0.2 mm I.D.), coated with 0.25- μ m Shimadzu HiCap-CBPI liquid stationary phase, and a ^{63}Ni electron-capture detector were used. A Shimadzu C-R3A data processor was used for data analysis. The injector and the detector temperatures were 240 and 340°C, respectively. The column temperature was isothermal at 140°C for 22 min, programmed from 140 to 200°C at 40°C/min, and then isothermal at 200°C. The carrier gas was nitrogen of 99.99% purity, further purified by passing it through an Alltech gas purifier containing molecular sieve 5A and indicating Drierite and an oxygen-absorbing OxiClear gas purifier. The carrier gas pressure was 1.5 kg/cm² and the make-up gas flow-rate was 30 ml/min. The splitting ratio was 1:50. The range of the electron-capture detector was set at 10 and current was set at 1 nA.

RESULTS AND DISCUSSION

The chromatogram of the mixed herbicide standard in isooctane is shown in Fig. 1. The retention times and detection limits were 14.234 ± 0.089 min and 0.38 ppb for ramrod, 15.744 ± 0.085 min and 0.22 ppb for 2,4-D methyl ester, 17.707 ± 0.125 min and 2.6 ppb for CIPC, 23.893 ± 0.018 min and 0.032 ppb for silvex methyl ester, 24.332 ± 0.019 min and 0.074 ppb for 2,4,5-T methyl ester, 25.758 ± 0.016 min and 0.39 ppb for 2,4-DB methyl ester and 37.008 ± 0.046 min and 0.081 ppb for DEF. The means and the standard deviations of the retention times were obtained from triplicate injections. The detection limits correspond a signal-to-noise ratio of 2 with injection of 4 μ l of sample into the column.

Good resolutions were achieved under the above analytical conditions. The amounts of the herbicides absorbed when 10 ml of water sample permeated through the C₁₈ Sep-Pak cartridge were over 99% for all the herbicides. The amounts of

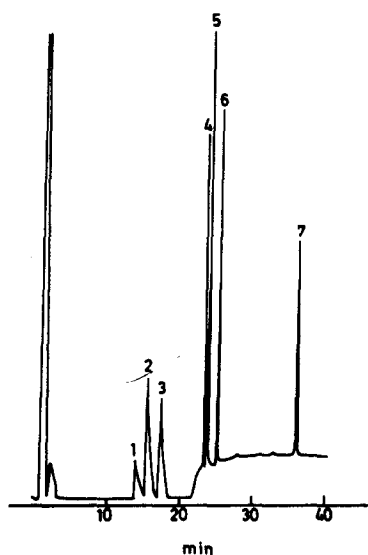


Fig. 1. Chromatogram of the herbicides. Column temperature: isothermal at 140°C for 22 min, programmed from 140 to 200°C at 40°C/min, then isothermal at 200°C. Sample: standard solution containing (1) ramrod, 288 ppb; (2) 2,4-D methyl ester, 719 ppb; (3) CIPC, 7190 ppb; (4) silvex methyl ester, 72 ppb; (5) 2,4,5-T methyl ester, 144 ppb; (6) 2,4-DB methyl ester, 1438 ppb; (7) DEF, 144 ppb.

herbicides recovered from the loaded C₁₈ Sep-Pak cartridge by eluting with sequential solvent gradients of acetonitrile–isooctane (100:0, 2:98 and 1:99) are given in Table I. The first two columns of data show the amounts of herbicides found in the first two 2-ml portions of the eluates [with acetonitrile–isooctane eluents] (100:0 and 2:98). Further elution of the cartridge with two 2-ml portions of the eluents (1:99 and 0:100) only desorbed 9.4% of DEF. The total recoveries of each herbicide were over 70%.

TABLE I

RECOVERY (%) OF HERBICIDES FROM A C₁₈ SEP-PAK CARTRIDGE WITH ACETONITRILE–ISOOCTANE

Results in all tables are means ± standard deviations for triplicate independent experiments.

Herbicide	Acetonitrile–isooctane			Total recovery (%)
	100:0	2:98	1:99	
Ramrod	83.8 ± 5.0	ND ^a	ND	83.8
2,4-D methyl ester	75.0 ± 3.7	ND	ND	75.0
CIPC	83.6 ± 2.0	ND	ND	83.6
Silvex methyl ester	ND	83.8 ± 3.3	ND	83.8
2,4,5-T methyl ester	73.8 ± 2.7	21.3 ± 2.4	ND	95.1
2,4-DB methyl ester	39.4 ± 3.0	31.2 ± 1.0	ND	70.6
DEF	31.9 ± 2.0	30.0 ± 1.6	9.4 ± 0.5	71.3

^a Concentration less than the detection limit (all tables).

Desorption of the herbicides from the loaded C₁₈ Sep-Pak cartridge with gradients of ethyl acetate–isooctane was also studied. The amounts of herbicides eluted by the first gradient of ethyl acetate–isooctane (5:95) were 99.0±4.3% for ramrod, 109.0±2.7% for 2,4-D methyl ester, 101.0±4.8% for CIPC, 82.0±2.4% for silvex methyl ester, 74.0±3.0% for 2,4,5-T methyl ester, 52.0±6.0% for 2,4-DB methyl ester and 87.0±7.0% for DEF. The amounts of herbicides found in the second 2-ml portion of eluate [with ethyl acetate–isooctane (3:97)] were 0.73±0.10% for silvex methyl ester, 6.2±1.7% for 2,4-DB methyl ester and 17.3±1.3% for DEF. The herbicides could not be desorbed further by eluting with a third 2-ml portion of eluent [ethyl acetate–isooctane (1:99)]. The total recoveries were over 80% for 2,4-D methyl ester, silvex methyl ester, CIPC, ramrod and DEF, 74.0% for 2,4,5-T methyl ester and 58.2% for 2,4-DB methyl ester.

The amounts of the herbicides adsorbed on the Florisil Sep-Pak cartridge were found to be over 99% when 10 ml of isooctane sample was passed through the cartridge. The conditions for the recovery of the herbicides from the Florisil cartridge were studied. Over 85% of each of the herbicides was recovered by eluting the loaded Florisil Sep-Pak cartridge with 2 ml of isooctane–acetone (30:70). The amounts of herbicides found in the eluate were 100% for ramrod, 110% for 2,4-D methyl ester, 110% for CIPC, 85% for silvex methyl ester, 89% for 2,4,5-T methyl ester, 87% for 2,4-DB methyl ester, and 100% for DEF. The herbicides could not be desorbed further by eluting with two additional 2-ml portions of isooctane–acetone gradient (10:90 and 5:95).

Interesting results were obtained on eluting the isooctane sample-loaded Florisil Sep-Pak cartridge with gradients of diethyl ether–isooctane, as shown in Table II. None of the herbicides was desorbed from the cartridge by eluting with 2 ml of diethyl ether–isooctane (10:90) solution. Eluting with 30:70 and 50:50 gradients of diethyl ether–isooctane desorbed only silvex methyl ester (39% and 43%). Further elution with a first 2-ml portion of 100% diethyl ether desorbed some fractions of 2,4-DB methyl ester (42.6%), 2,4,5-T methyl ester (22.0%) and DEF (23.6%); elution with second and third 2-ml portions of 100% diethyl ether desorbed all the herbicides. The total recoveries of the herbicides were over 80% except for 2,4-DB methyl ester (75%).

The results in Table II may provide valuable information for the clean-up steps

TABLE II

RECOVERY (%) OF HERBICIDES FROM ISOOCTANE SAMPLE-LOADED FLORISIL SEP-PAK CARTRIDGE WITH DIETHYL ETHER–ISOOCTANE

Herbicides	Diethyl ether–isooctane						Total recovery (%)
	10:90	30:70	50:50	100:0	100:0	100:0	
Ramrod	ND	ND	ND	ND	35.5±5.4	50.7±6.7	86.2
2,4-D methyl ester	ND	ND	ND	ND	52.0±1.7	30.0±1.3	82.0
CIPC	ND	ND	ND	ND	57.0±3.8	46.6±2.2	103.6
Silvex methyl ester	ND	39.0±2.0	43.0±2.0	ND	ND	ND	82.0
2,4,5-T methyl ester	ND	ND	ND	22.0±5.1	69.5±4.1	ND	91.5
2,4-DB methyl ester	ND	ND	ND	42.6±6.1	32.6±5.3	ND	75.2
DEF	ND	ND	ND	23.6±3.7	58.0±4.1	12.5±1.8	94.1

for the determination of these herbicides. For instance, by using the Florisil Sep-Pak cartridge, the determination in isooctane may be free from interference from similar substances if (1) the substance is not adsorbed on the cartridge, (2) the substance is adsorbed on the cartridge but can be desorbed by elution with 2 ml of diethyl ether-isooctane (10:90), (3) the substance is adsorbed on the cartridge but cannot be desorbed from the cartridge by the diethyl ether-isooctane gradient listed in Table II. For the determination of the herbicides apart from silvex methyl ester, the interference from those substances which are adsorbed on the cartridge but are desorbed by the first three portions of the gradients can also be eliminated.

The capillary column and the electron-capture detector may be protected from contamination by various types of substances if a Florisil Sep-Pak cartridge is used in the clean-up step. The clean-up ability of the Florisil Sep-Pak cartridge on loading an isooctane sample on the cartridge and desorbing the herbicides by elution with gradients of ethyl acetate-isooctane is also significant. A 2-ml volume of ethyl acetate-isooctane (5:95) eluted 93% of silvex methyl ester and 14% of 2,4,5-T methyl ester, but did not desorb the other herbicides. The next 2-ml portion of ethyl acetate-isooctane (10:90) gradient desorbed 56% of 2,4-D methyl ester, 59% of 2,4-DB methyl ester, 74% of 2,4,5-T methyl ester, 73% of CIPC and a small fraction (7%) of DEF; 92% of ramrod and 100% of DEF could be desorbed quantitatively with a further 2-ml portion of ethyl acetate-isooctane (50:50) gradient. The total recoveries of each herbicide were over 88%.

We also found that the herbicides adsorbed on the Florisil Sep-Pak cartridge on loading an isooctane sample on the cartridge cannot be desorbed from the cartridge by eluting with either three 2-ml portions of methanol-isooctane gradients or three 2-ml portions of acetonitrile-isooctane gradients (0:100, 1:99 and 2:98).

Over 99% of each of the herbicides was adsorbed on the Florisil Sep-Pak cartridge when 10 ml of aqueous sample were passed through the cartridge. The herbicides were desorbed from the aqueous sample-loaded cartridge by elution with diethyl ether-isooctane, (10:90, 30:70 and 50:50) as shown in Table III. Further elution with 2 ml of pure diethyl ether did not desorb any herbicide. The amount of each herbicide recovered by eluting with the diethyl ether-isooctane gradients was 75–95%.

The amounts of herbicides recovered by eluting with isooctane-acetone gra-

TABLE III

RECOVERY (%) OF HERBICIDES FROM AQUEOUS SAMPLE-LOADED FLORISIL SEP-PAK CARTRIDGE WITH DIETHYL ETHER-ISOOCTANE

<i>Herbicide</i>	<i>Diethyl ether-isooctane</i>			<i>Total recovery (%)</i>
	<i>10:90</i>	<i>30:70</i>	<i>50:50</i>	
Ramrod	50 ± 3	25 ± 4	ND	75
2,4-D methyl ester	60 ± 4	32 ± 3	ND	92
CIPC	75 ± 8	20 ± 5	ND	95
Silvex methyl ester	41 ± 1	38 ± 1	2.5 ± 0.3	82
2,4,5-T methyl ester	72 ± 2	5 ± 1	1.5 ± 0.3	79
2,4-DB methyl ester	51 ± 1	21 ± 1	6.0 ± 1.5	78
DEF	45 ± 9	34 ± 1	ND	79

TABLE IV

RECOVERY (%) OF HERBICIDES FROM AQUEOUS SAMPLE-LOADED FLORISIL SEP-PAK CARTRIDGE WITH ISOCTANE-ACETONE

Herbicide	Isooctane-acetone		Total recovery (%)
	30:70	10:90	
Ramrod	106.0 ± 6.9	ND	106.0
2,4-D methyl ester	93.0 ± 7.3	ND	93.0
CIPC	111.0 ± 5.8	ND	111.0
Silvex methyl ester	103.0 ± 14	8.7 ± 1.2	111.7
2,4,5-T methyl ester	84.0 ± 1.6	6.8 ± 0.7	90.8
2,4-DB methyl ester	84.0 ± 6.0	10.6 ± 1.7	94.6
DEF	105.0 ± 4.3	10.0 ± 2.0	115.0

dients (30:70 and 10:90) were over 90% for each of the herbicides, as shown in Table IV. Further elution with a 2-ml portion of isooctane-acetone gradient (5:95) did not desorb any herbicide.

The total recoveries of the herbicides by eluting the aqueous sample-loaded Florisil Sep-Pak cartridge with ethyl acetate-isooctane gradients (5:95, 10:90, 50:50 and 100:0) were over 95% except for CIPC (80%), as shown in Table V.

From the results in Tables III-V, it can be concluded that a Florisil Sep-Pak cartridge can be used to separate and enrich these herbicides from aqueous samples by loading the aqueous sample on the cartridge directly; extraction of the herbicides from aqueous samples with an organic solvent may not be required. However, there is a significant difference between the elution patterns of the isooctane sample-loaded (see Table II) and aqueous sample-loaded Florisil Sep-Pak cartridge (see Table III). None of the herbicides except silvex methyl ester can be desorbed from the isooctane sample-loaded cartridge by elution with three 2-ml portions of diethyl ether-isooctane gradients (10:90, 30:70 and 50:50) (these herbicides can be desorbed from the isooctane sample-loaded cartridge by elution with three 2-ml portions of pure diethyl ether). In contrast, all the herbicides were desorbed from the aqueous sample-loaded cartridge by elution with diethyl ether-isooctane gradients (10:90, 30:70 and 50:50).

TABLE V

RECOVERY (%) OF HERBICIDES FROM AQUEOUS SAMPLE-LOADED FLORISIL SEP-PAK CARTRIDGE WITH ETHYL ACETATE-ISOCTANE

Herbicide	Ethyl acetate-isooctane				Total recovery (%)
	5:95	10:90	50:50	100:0	
Ramrod	42.0 ± 3.9	27.8 ± 3.5	25.5 ± 3.8	ND	95.3
2,4-D methyl ester	82.0 ± 5.0	12.8 ± 1.4	5.1 ± 2.2	0.1 ± 0.05	100.0
CIPC	64.8 ± 5.4	11.3 ± 0.7	4.1 ± 0.3	ND	80.2
Silvex methyl ester	74.6 ± 0.5	30.2 ± 7.3	6.8 ± 0.9	1.45 ± 0.08	113.1
2,4,5-T methyl ester	83.7 ± 1.6	12.0 ± 2.1	0.91 ± 0.01	ND	96.6
2,4-DB methyl ester	71.8 ± 10.7	20.8 ± 4.8	7.8 ± 0.4	1.7 ± 0.6	102.1
DEF	95.9 ± 8.1	1.4 ± 0.5	ND	ND	97.3

TABLE VI

RECOVERY (%) OF HERBICIDES FROM DILUTED AQUEOUS SAMPLE-LOADED FLORISIL SEP-PAK CARTRIDGE WITH ETHYL ACETATE-ISOOCTANE

Volume of water sample loaded, 10 l. The results are average recoveries of triplicate independent experiments.

Herbicides	Concentration (ppb)	Ethyl acetate-isooctane		Total recovery (%)
		5:95	10:90	
Ramrod	0.0288	45.7 ± 2.8	5.0 ± 0.7	50.7
2,4-D methyl ester	0.0719	67.3 ± 4.6	9.6 ± 1.9	76.9
CIPC	0.719	50.0 ± 1.8	28.0 ± 3.1	78.0
Silvex methyl ester	0.072	67.3 ± 7.3	ND	67.3
2,4,5-T methyl ester	0.0144	57.4 ± 4.4	ND	57.4
2,4-DB methyl ester	0.1438	52.1 ± 3.7	5.8 ± 0.8	57.9
DEF	0.0144	53.8 ± 2.4	14.2 ± 2.8	68.0

The difference in elution patterns may be explained as follows. A dry loading solution (such as an isooctane sample) cannot deactivate the active sites on the Florisil surface such that the attractive force between the herbicides and the active sites of the Florisil surface is dependent on the polarity of the herbicide molecule, and a more polar solvent is required to desorb the more polar herbicides from the Florisil surface. Conversely, an aqueous sample may deactivate the Florisil¹⁰ by adsorption of water molecules on the active sites on the Florisil surface such that the attractive force between the Florisil surface and the herbicides is weaker and less dependent on the polarity of the herbicides, and the herbicides can be desorbed from the cartridge by a less polar solvent.

In order to examine the enrichment ability of a Florisil Sep-Pak cartridge for these herbicides using very dilute solution, 10 l of diluted aqueous sample (prepared by diluting 10 ml of aqueous sample to 10 l with water) was loaded on the cartridge. The amounts of herbicides recovered by elution with ethyl acetate-isooctane gradients are given in Table VI. The recoveries of the herbicides were from 51% (for ramrod) to 78% (for CIPC) on elution with two 3-ml portions of ethyl acetate-isooctane gradients (5:95 and 10:90). No herbicide was desorbed further by eluting with two additional 2-ml portions of ethyl acetate-isooctane gradients (50:50 and 100:0). The recoveries of the herbicides from a cartridge loaded with 10 ml of aqueous sample (without dilution) by elution with the same ethyl acetate-isooctane gradients were over 95%, except for CIPC (80%), as shown in Table V.

CONCLUSION

C₁₈ Sep-Pak and Florisil Sep-Pak cartridges may provide a simple and rapid method for the enrichment and clean-up of herbicides from aqueous or isooctane samples. For aqueous samples with a simple matrix that does not cause significant interferences in herbicide determinations, the aqueous sample may be loaded on the C₁₈ or Florisil cartridge directly, and then the herbicides can be recovered by elution with mixed solvents such as acetonitrile-isooctane, diethyl ether-isooctane, isooct-

tane-acetone or ethyl acetate-isooctane. The herbicides in the eluates can then be determined simultaneously by GC-ECD.

If the interferences cannot be eliminated effectively by the procedure suggested above, e.g., in the determination of herbicides in aqueous samples with a complicated matrix, the aqueous sample may be extracted with isooctane and then the isooctane sample loaded on the Florisil cartridge; the cartridge can be eluted with various kinds of solvent gradients (such as diethyl ether-isooctane, methanol-isooctane or acetonitrile-isooctane) to remove the interferences without desorbing the herbicides. The herbicides are then recovered from the cartridge by elution with three 2-ml portions of pure diethyl ether. The herbicides in the eluate can then be determined simultaneously by GC-ECD. The difference in the elution patterns of the herbicides (and hence the clean-up ability) between the isooctane and the aqueous sample-loaded cartridge is presumably due to deactivation of the active sites on the Florisil surface by adsorption of water molecule when an aqueous sample is loaded on the cartridge directly, such that the attractive force between the Florisil surface and the herbicides is weaker and less dependent on the polarity of the herbicides, and the herbicides can be desorbed from the cartridge by a less polar solvent if the aqueous sample is loaded on the cartridge directly.

The conditions for the stepwise or simultaneous desorption of the herbicides from C₁₈ and Florisil cartridges have been given. However, to be able to apply the procedure to the determination of herbicides in dilute solutions (or other types of sample such as milk or vegetables), further studies may be needed that take into account other phenomena, e.g., spurious adsorption and matrix effects, which may easily occur at the trace concentration level.

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