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Potential of Solid Phase Extraction Disks to Aid Determination of Dislodgeable Foliar Residues of Chlorpyriphos, Malathion, Diazinon, and Acephate

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Abstract. The utility of solid phase extraction (SPE) for concentrating four organophosphate insecticides from solutions of water and sodium dioctyl sulfosuccinate, a surfactant, was evaluated. Reverse phase (C18, octadecyl bonded silica) sorbent in the form of a disk was the SPE medium evaluated. Chlorpyriphos, malathion, and diazinon, but not acephate, were retained on and eluted from the SPE disks. For pesticides that were retained on SPE disks, recoveries from the disks were equal to or higher than recoveries achieved by solvent partitioning. Dislodgeable foliar residues of acephate were successfully concentrated for analysis by lyophilization of water–surfactant solutions. Recoveries of pesticides from SPE disks stored at −15°C for one week were equal to or higher than those of pesticides stored in water–surfactant for one week at −15°C. Malathion- and diazinon-fortified samples in water–surfactant and on SPE disks were prepared in one state and shipped for analysis in another state. Pesticides in the water–surfactant samples were concentrated by solvent partitioning and were underestimated by 41% (diazinon) and 16% (malathion). Conversely, diazinon samples on the SPE disks were on average underestimated by 3% and malathion was overestimated by an average of 55%. The overestimation of malathion was attributed to a matrix effect during analysis associated with the presence of surfactant, which was retained on and subsequently eluted from the SPE disks. The retention of surfactant by the SPE disks and its subsequent elution may considerably limit their usefulness in determination of dislodgeable foliar residues.

During the early 1960s, it became evident that agricultural workers were potentially exposed to pesticides during pesticide application and upon reentry into treated fields for maintenance or harvesting operations. The majority of these exposures were associated with transfer of pesticide from the foliage to the skin (Durham and Wolfe 1962). Pesticide exposures of workers performing manual harvesting of crops still is of concern to public health organizations. The United States Environmental Protection Agency (EPA) has recently curtailed the use of certain pesticides and is evaluating others because of the potential exposure to not only consumers but also workers during reentry and harvesting activities (US EPA 1999a, b, 2000). Together with toxicological reviews, the conduct of risk assessments requires having objective exposure assessment data obtained by reliable measurement methods.

Foliar pesticide residue analysis has been used for decades as a means to assess the potential for transfer of pesticides from foliage to workers entering previously treated fields. Although the retention and fate of pesticides applied to the surface of plants remains somewhat uncertain, it has long been recognized that the potential for worker exposure does correlate with the amount of pesticide remaining on the surface. First Gunther *et al.* (1973) and later Iwata *et al.* (1977) described methods utilizing a mechanical leaf disk-sampling device to collect leaf material in a systematic, reproducible manner. Iwata *et al.* (1977) focused on using this device by defining field sampling strategies to obtain representative samples.

Gunther *et al.* (1974) refined their initial method which consisted of taking a large number of leaf punch discs from several plants, washing the leaf discs in an aqueous surfactant solution to dislodge removable pesticides from the leaf surface, and performing a liquid–liquid extraction to recover the pesticide. This method is still used in worker exposure studies, as recommended by the EPA (US EPA 1996). A large number of articles on dislodgeable and total foliar residues of pesticides have been published (Willis and McDowell 1989).

In order to prevent poisoning of harvest workers, research focused on accurate determination of reentry interval is needed. The reentry interval provides in most situations the minimum time that must elapse before workers may safely work unprotected (with no personal protective equipment) in a previously treated field, based on available health effects information. The reentry interval may vary depending on the toxicity and persistence of the pesticide, the crop to which it is applied, and the geographic region where applied.

In practice, the leaf wash and liquid–liquid extraction is performed shortly after collection, making it necessary to have

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separatory funnels and adequate volumes of solvents for extraction available nearby. Alternatively, if storage stability is not a problem, the wash solution samples may be frozen and shipped to a laboratory where the extraction and analysis are performed. Losses may be experienced using the latter approach if the pesticide is not stable in water (Barcelo and Alpendurada 1996). Also, the possibility of analyte loss exists if the frozen samples thaw during shipment. The use of solid-phase extraction could eliminate some of these drawbacks. Consequently, the utility of solid-phase extraction for determination of dislodgeable foliar residues of chlorpyriphos, malathion, diazinon, and acephate was evaluated.

Materials and Methods

Supplies and Equipment

Pesticides obtained from Chem Service Inc. (West Chester, PA) were: chlorpyriphos (phosphorothioic acid, O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl)ester), purity 98%; diazinon (phosphorothioic acid, O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester), purity 99.5%; malathion (butanedioic acid, ([(dimethoxyphosphinothioyl) thio]-, diethyl ester), purity 99%; and acephate (phosphoramidothioic acid, acetyl-, O,S-dimethyl ester), purity 99.6%. Each pesticide was dissolved in methanol at a concentration of 10 mg/mL. These solutions were used for spiking, generation of standard curves, and when appropriately diluted, as external standards. Purities were those reported by the supplier and were not considered in calculation of recoveries.

The surfactant used was sodium dioctyl sulfosuccinate (Aldrich Chemical Co., Milwaukee, WI). Throughout this report, water–surfactant solution refers to a concentration of four drops of a 2% solution (vol/vol) of surfactant in water per 100 mL of water, the concentration used by Gunther *et al.* (1974).

All solvents used were HPLC grade. 3M Empore C18 extraction disks (octadecyl bonded silicon) were obtained from Fisher Scientific (Florence, KY). Except for the blind-spike and other samples discussed later in this manuscript, 47-mm disks were used. For the other samples, 90-mm disks were used. Larger disks were used because the blind spike samples were included as part of an actual field sampling of dislodgeable foliar residues in California. These field samples were larger (had more leaf area) than those prepared in the lab, and use of larger disks avoided potential problems with low flow rates that could occur with some of the leaf disk washes. Data from the actual field sampling for dislodgeable residues are not included in this report.

The gas chromatograph was a Hewlett-Packard 5890, equipped with a nitrogen–phosphorous (NP) detector. The column used for diazinon, chlorpyriphos, and malathion was 15 m $\times$ 0.53 mm I.D., with a 1.5-μ bonded phase of dimethylpolysiloxane (Ohio Valley Specialty Chemical, Marietta, OH). The column used for acephate was 15 m $\times$ 0.53 mm I.D. with a 1.0-μ bonded phase of 50:50 dimethyl-diphenylpolysiloxane (J and W Scientific, Folsom, CA).

Conditions for analysis of diazinon, chlorpyriphos, and malathion were identical. Helium was the carrier gas (3 mL/min) and make-up gas (27 mL/min). The injector was maintained at 250°C, the detector at 280°C, and the oven at 200°C (isothermal). Under these conditions, the retention times were: diazinon, 1.70 min; malathion, 3.83 min; and chlorpyriphos, 4.22 min.

Conditions for analysis of acephate were similar. Helium was the carrier gas (10 mL/min) and make-up gas (45 mL/min). The injector was maintained at 190°C, the detector at 275°C, and the oven at 170°C (isothermal). The retention time was 1.58 min.

The performance of the NP detector was evaluated using methods outlined in American Society of Testing and Materials (ASTM) specification E1140-95 (ASTM 1999). For procedures that used leaf disks (discussed later), recovery was calculated as relative and actual recovery. Relative recovery was the amount of pesticide recovered from the treatment containing leaf disks divided by the amount of pesticide recovered from a similar treatment, but without leaf disks, expressed as a percentage. Actual recovery was the amount of pesticide recovered from a treatment divided by the amount of pesticide in an appropriate dilution of the spiking solution, expressed as a percentage. Quantitation relied on external standards and all determinations were made in triplicate. Sample standard deviations were calculated for each average relative and actual recovery value.

Evaluation of Surfactant Effect on Recovery of Pesticides from SPE Disks

To determine the effect of surfactant on recovery of acephate, chlorpyriphos, diazinon, and malathion from SPE disks, flasks containing water–surfactant (3 $\times$ 300 mL) and flasks containing water only (3 $\times$ 300 mL) were prepared for each pesticide. A pesticide (250 μg) was then added to each flask. After mixing, the contents of a flask were passed through an SPE disk that had been activated using methods outlined by the manufacturer (3M Corporation 1998). After drying, the SPE disk was eluted with methanol (3, 3, and 4 mL). The eluate was concentrated by a stream of N_2 to $<$0.5 mL, then made to volume in a volumetric flask. Actual recoveries were determined using procedures outlined above.

Preparation of Leaf Disks

Four combinations of crop species and pesticide were used. The particular crop species/pesticide combinations were chosen because they are commonly used in production. For chlorpyriphos, broccoli (*Brassica oleracea* L.) was the test species, obtained from a local commercial field. For diazinon, spinach (*Spinacea oleracea* L.) was the test species acquired from a local experimental field (250-μg spike) or from a local supermarket (4-μg spike). For malathion, strawberry (*Fragaria* $\times$ *ananassa* Duch.) was the test species and locally grown plants were used. For acephate, Romaine lettuce (*Lactuca sativa* L.) was the test species, purchased from a local supermarket.

Disks were cut from leaves with cork borers. Because leaf size differed among test species, different sized borers were used. For broccoli, lettuce, and spinach—crops having large leaves—a 2.22-cm diameter borer was used. For strawberry—which has small leaves—a 1.59-cm diameter borer was used.

Evaluation of Pesticide Recoveries from Water–Surfactant Containing Leaf Disks

Each crop species/pesticide combination was evaluated at two pesticide doses, 4 and 250 μg. These doses were chosen because they would result in a concentration range typical for dislodgeable foliar residues. For each dose, five flasks, each containing water–surfactant (100 mL) were prepared for each crop species/pesticide combination. Pesticide (4 or 250 μg) was added to each of four flasks. After mixing, an equal number of leaf disks of the appropriate crop species was added to each of three spiked flasks and to the unspiked flask, which allowed assessment of field-applied pesticide residues after analysis. Leaf disks were not added to the fourth spiked flask, allowing an assessment of pesticide absorption by the leaf disks. In the flasks containing leaf disks, leaf load (cm^2 of leaf area per mL of initial wash

solution) was maintained at approximately 4 cm^2/mL. For the strawberry/malathion combination 104 leaf disks per flask were used. Likewise, 52 leaf disks were used for each of the other combinations (broccoli/chlorpyriphos, spinach/diazinon, and lettuce/acephate). Leaf load was 4.1 cm^2/mL for strawberry and 4.0 cm^2/mL for the other crops. After adding leaf disks, flasks were rotated on a shaker (200 rpm, 20 min), decanted, and the leaf disks were washed twice more with water–surfactant (100 mL, 200 rpm, 20 min) each time. The wash solutions for each flask were pooled, and chlorpyriphos, diazinon, and malathion were trapped on and eluted from SPE disks using procedures outlined above, except that glass fiber prefilters (Fisherbrand G6, Fisher Scientific, Cincinnati, OH), which had no effect on recovery (data not shown), were used to aid filtration.

Because SPE disks retained little of the acephate, another isolation procedure was developed. Pooled wash solutions from each flask were frozen and then lyophilized. Just after all of the ice was sublimated from the sample, judged visually, samples were removed from the lyophilizer. The residues were quantitatively transferred to a volumetric flask and recovery of acephate was determined.

For comparison to isolation of pesticides from leaf disk washes by SPE, pesticides were also isolated by solvent extraction, the method used by Gunther *et al.* (1973) and Iwata *et al.* (1977). Leaf disk washes of each species/pesticide combination, except acephate/lettuce, were prepared using procedures identical to those outlined above, except that flasks were spiked with 125 μg of pesticide. Leaf loads were identical to those used previously. Pesticide residues were isolated by partitioning the pooled washes against ethyl acetate (3 × 10 mL). The organic (upper) phases were combined, reduced by rotary evaporation, and recoveries were determined as outlined above. Solvent partitioning of acephate was not attempted because of its high water solubility.

Evaluating Losses of Chlorpyriphos, Diazinon, and Malathion During Storage

For evaluation of storage loss on SPE disks, diazinon, chlorpyriphos, or malathion (125 μg) in water–surfactant was loaded onto each of three conditioned SPE disks, aided by vacuum. After drying, the SPE disks were placed in a petri dish that was then sealed with Parafilm and placed in a freezer at −15°C. After seven days the SPE disks were eluted in the usual fashion with methanol and the pesticides were quantified. Storage of acephate on SPE disks was not evaluated because it was not retained on the disks.

For comparison to storage on SPE disks, storage in water–surfactant was also evaluated. Three flasks, each containing water–surfactant (25 mL) were prepared for each pesticide. A pesticide (250 μg of diazinon, or 150 μg of chlorpyriphos or malathion) was added to each of the three flasks. Flasks were swirled, sealed with a double layer of Parafilm, and then placed in a freezer (−15°C). After seven days the stored solutions were partitioned against ethyl acetate (3 × 10 mL). The volumes of the combined ethyl acetate fractions were reduced by rotary evaporation. Residues were then determined in the normal fashion.

Preparation and Analysis of Blind Samples

To further evaluate the potential of SPE disks for determination of dislodgeable residues, blind spikes of malathion and diazinon were prepared in Cincinnati, Ohio and shipped on ice to California, and then sent on ice to Kentucky for analysis. Expected concentrations of these blind samples were revealed only after analysis.

On September 9, 1999, water–surfactant solutions (3 × 100 mL) containing diazinon (176 or 17.6 μg) and solutions (3 × 100 mL) containing malathion (189 and 18.9 μg) were prepared in triplicate in Cincinnati. After conditioning the 90-mm SPE disks, a diazinon solution (176 μg) was passed through a prefilter (Fisherbrand G6) and an SPE disk, followed by a solution containing malathion (189 μg). The solutions of the low concentrations of pesticides were handled likewise. Non-spiked solutions were also prepared and passed through the SPE disks for use as blanks. Disks and prefilters were dried with the aid of vacuum, and were then stored frozen. On September 26 the samples were shipped on ice to California, and on September 29 they were shipped on ice to the University of Kentucky for elution and analysis. A similar set of water–surfactant solutions—spiked as outlined above, except for blanks—were prepared on the same date and shipped to California as frozen aqueous solutions and then to Kentucky on October 12, 1999.

The blind spike samples on the SPE disks were received at the University of Kentucky on September 30, 1999 and eluted the same day. The prefilter and SPE disks were eluted sequentially with methanol (30, 20, and 20 mL). The volume of the eluate was reduced with the aid of a rotary evaporator and then made to volume (1.0 mL). Prior to analysis these samples were diluted 1:10 with methanol.

The frozen blind-spike aqueous samples were received at the University of Kentucky on October 13, 1999. They were immediately placed in a freezer upon arrival. For analysis, conducted on the day of arrival, a sample was thawed, the contents of the bottle were swirled, and the volume was measured. Each sample was partitioned against ethyl acetate (3 × 40 mL). The volume of the pooled ethyl acetate was reduced with the aid of a rotary evaporator and then made to volume (10.0 mL).

Residues of diazinon and malathion in the blind samples were quantified using procedures outlined herein, based on external standards. Concentrations of diazinon and malathion from the SPE disks were corrected for recovery based on lab spikes recovered from SPE disks, processed at the same time as the blind samples. Concentrations of pesticides in the frozen water–surfactant samples were also corrected for recovery based on the lab spikes processed with these experimental samples.

Evaluation of Effect of Surfactant on Quantitation

Because our results indicated that the surfactant might have impaired the quantitation of malathion, we investigated the effect of surfactant on malathion quantitation. We first verified that surfactant altered malathion quantitation by quantifying samples of malathion (0.06 and 0.6 ng/μL) that were free of surfactant or contained 2% surfactant.

The amount of surfactant that was retained on and subsequently eluted from the SPE disks was determined gravimetrically. Using a similar approach, we also determined the fate of surfactant when water–surfactant solution was partitioned against ethyl acetate. For the SPE disks, water–surfactant (3 × 300 mL) was passed through 90-mm SPE disks. Larger disks were used because they might retain more surfactant than smaller disks. The disks were eluted in the normal fashion with methanol, which was then completely evaporated from the eluate, and the residue was weighed. Weight of residues present in lyophilized water–surfactant that had passed through the SPE disk and, in 300 mL of lyophilized water–surfactant starting solution, were also determined. The location of surfactant after partitioning water–surfactant against ethyl acetate was also evaluated gravimetrically. Water–surfactant (3 × 300 mL) was partitioned against ethyl acetate (3 × 40 mL) in the usual fashion. The ethyl acetate was evaporated from the combined washes and the residue present was weighed. Also, the water–surfactant that had been partitioned against ethyl acetate was lyophilized and its residue was weighed.

After determining the approximate weight of surfactant that would likely be present in the blind samples obtained by SPE, standard curves for diazinon and malathion determined in the absence and presence of surfactant at its normal concentration were generated.

Results

The presence of surfactant appeared to improve the recovery of chlorpyriphos and malathion from SPE disks, perhaps indicating that surfactant may aid elution of these pesticides from the disks (Table 1). Recovery of diazinon was unaffected by the presence of surfactant. The SPE disks retained very little acephate.

For chlorpyriphos, recovery from SPE disks in the presence of broccoli leaf disks was about the same as that obtained with solvent extraction (Table 2). When leaf disks were not present, recovery was somewhat greater indicating that the leaf disks themselves probably absorbed some of the chlorpyriphos. Ethyl acetate extraction of the leaf disks that had been washed with spiked water–surfactant confirmed that the leaf disks had absorbed at least 15.2 ± 5.3% of the chlorpyriphos. No chlorpyriphos was detected in any of the unspiked samples (data not shown).

For malathion, recovery using SPE disks was equal to or greater than recovery using solvent partitioning (Table 3). In fact, recoveries greater than 100% supported the idea that malathion was overestimated, a topic addressed later in this report. The presence of strawberry leaf disks had no consistent effect on malathion recovery. No malathion was detected in any of the unspiked samples (data not shown).

For diazinon, recovery in the presence of spinach leaf disks using SPE disks was similar to that obtained with solvent partitioning (Table 4). Recoveries obtained in the presence of leaf disks were numerically, but not significantly, less than those obtained in the absence of leaf disks. No diazinon was detected in any of the unspiked samples (data not shown).

As stated previously, very little acephate was retained on SPE disks (Table 1). However, lyophilization of water solutions of acephate permitted recovery of about 50% of the acephate (Table 5). Furthermore, lyophilization of water–surfactant solutions resulted in greater recovery of acephate, possibly because of the solvent ability of the surfactant. The presence of leaf disks had no consistent effect on recovery. No acephate was detected in the unspiked samples (data not shown).

Recoveries of pesticides stored on SPE disks were equal to or higher than recoveries of pesticides stored in frozen water–surfactant. For malathion and diazinon, recoveries after storage in water–surfactant were 98 ± 6.8% and 91 ± 5.9%, respectively, comparable to recoveries obtained after storage on SPE disks, 98 ± 10.2% and 96 ± 11.6%, respectively. Chlorpyriphos was apparently less stable when stored in water–surfactant, with 77 ± 6.8% recovered, compared to acceptable recovery when stored on the SPE disk, 94 ± 11.6%.

Diazinon and malathion were detected in all blind samples that were stored and shipped on SPE disks (Table 6). For diazinon, the amounts estimated were close to those expected. For malathion, the amounts estimated were considerably greater than those expected, especially at the lower concentration. Among samples having the same expected concentrations, diazinon estimates were consistent, but malathion estimates were less consistent, especially for the higher spike.

Estimates of the amount of diazinon and malathion in samples that were stored and shipped as frozen aqueous solutions, and were subsequently solvent partitioned are shown in Table 7. Estimates of diazinon were more negatively biased than those for malathion, which was underestimated by 15–20%.

Throughout this research malathion was frequently overestimated when recovered from water–surfactant solutions with SPE disks (Tables 3 and 6), perhaps indicating that the presence of surfactant affected recovery or quantitation of malathion. Preliminary experimentation confirmed that the presence of surfactant interfered with determination of malathion. Detector responses were greater for samples containing surfactant, and these determinations were more variable than those for samples without surfactant (data not shown). Apparently, the surfactant impaired the ability to quantitate malathion. These results are consistent with a matrix effect associated with the presence of surfactant in the gas chromatograph (Schenck and Lehotay 2000).

In order to better understand how much surfactant was retained on and subsequently eluted from the SPE disks, we lyophilized the eluates from SPE disks that had filtered 300 mL

Table 1. Average recoveries of chlorpyriphos, diazinon, malathion, and acephate from water or from water–surfactant, by use of solid phase extraction disks

Pesticide	Solvent		*n*
	Water	Water–Surfactant	
	Actual recovery	(% ± SD)	
Chlorpyriphos	68 ± 12	88 ± 6.5	9
Diazinon	85 ± 4.5	89 ± 4.4	9
Malathion	78 ± 19	99 ± 16	9
Acephate	12 ± 3.5	15 ± 5.2	9

Table 2. Recovery of chlorpyriphos from water–surfactant, in the presence and absence of broccoli leaf disks, by use of solvent partitioning or by solid phase extraction (SPE) with C18 disks

Recovery Method	Spike Amount (μg)	Leaf Load (cm^2/mL)	*n*	Relative Recovery (% ± SD)[a]	Actual Recovery (% ± SD)
SPE disk	4	0	9	na	88 ± 12
SPE disk	4	4.0	9	64 ± 7.6	58 ± 3.5
SPE disk	250	0	9	na	89 ± 5.3
SPE disk	250	4.0	9	79 ± 7.0	60 ± 5.3
Solvent partition	125	4.0	12	69 ± 7.8	57 ± 6.4

[a] na, not applicable.

Table 3. Recovery of malathion from water–surfactant in the presence and absence of strawberry leaf disks by use of solvent partitioning or by solid phase extraction (SPE) with C18 disks

Recovery Method	Spike Amount	Leaf Load (cm^2/mL)	*n*	Relative Recovery (% ± SD)[a]	Actual Recovery (% ± SD)
SPE Disk	4	0	9	na	112 ± 29
SPE Disk	4	4.1	9	132 ± 23	122 ± 21
SPE Disk	250	0	9	na	98 ± 14
SPE Disk	250	4.1	9	100 ± 11	89 ± 9.5
Solvent partition	125	4.1	12	96 ± 4.1	92 ± 3.9

[a] na, not applicable.

Table 4. Recovery of diazinon from water–surfactant in the presence and absence of spinach leaf disks by use of solvent partitioning or by solid phase extraction (SPE) C18 disks

Recovery Method	Spike Amount (μg)	Leaf Load (cm^2/mL)	*n*	Relative Recovery (% ± SD)[a]	Actual Recovery (% ± SD)
SPE disk	4	0	9	na	106 ± 11
SPE disk	4	4.0	9	100 ± 14	92 ± 13
SPE disk	250	0	9	na	90 ± 5.1
SPE disk	250	4.0	9	93 ± 6.3	85 ± 6.3
Solvent partition	125	4.0	12	96 ± 4.1	92 ± 3.9

[a] na, not applicable.

Table 5. Recovery of acephate from water or water–surfactant in the presence and absence of lettuce leaf disks after lyophilization

Spike Amount (μg)	Leaf Load (cm^2/mL)	*n*	Relative Recovery (% ± SD)[a]	Actual Recovery (% ± SD)
4	0	9	na	107 ± 2.9
4	4.0	9	82 ± 8.9	88 ± 9.6
250	0	9	na	95 ± 10
250	4.0	9	125 ± 8.2	109 ± 7.2

[a] na, not applicable.

of standard water–surfactant. Comparison of the weight of this residue to that present in 300 mL of unfiltered water–surfactant provided an estimate of the proportion of surfactant that was retained on and eluted from the SPE disks. Most of the surfactant (100 ± 6.8%, $n = 3$) was retained on and eluted from the SPE disks. This conclusion was also confirmed by a lack of residue in the water–surfactant that had passed through the SPE disk. Because the mass of surfactant in 300 mL of water–surfactant solution was ~3.5 mg, the surfactant concentration in most of the blind samples that were analyzed probably exceeded 3000 ppm. This concentration likely interfered with the analysis. When water–surfactant was partitioned against ethyl acetate, 95 ± 7.4% ($n = 3$) of the surfactant remained in the water layer. Consequently, the effect of the surfactant should be considerably reduced for samples that are prepared by solvent partition with ethyl acetate compared with preparation by SPE disks.

Standard curves obtained in the presence and absence of surfactant illustrate the matrix effect (Figure 1). The presence of surfactant impaired the quantitation of malathion but not diazinon.

Discussion

Accurate determination of dislodgeable foliar residues is an important component of determining potential worker exposure to applied pesticides. SPE disks may have potential for use in sample preparation of dislodgeable foliar residues, especially for insecticides such as diazinon. The main benefits of their use include sample concentration in or near the field without the use of organic solvents and ease of storage and shipment of the disks for analysis, compared with shipping large volumes of water–surfactant, or the need for immediate field extraction with organic solvents. Storage on dry disks would be especially beneficial for analysis of pesticides such as chlorpyriphos or diazinon that may not be stable in water (Howard 1991; Racke 1992). Similar benefits of SPE disks for determination of pesticide residues in water samples were emphasized by Mueller *et al.* (2000). One drawback in the use of SPE disks is that not all pesticides, e.g., acephate, are retained on reverse phase media. A more significant drawback is that most, if not all, of the surfactant, sodium dioctyl sulfosuccinate, is retained on these SPE disks and is subsequently eluted with the analyte. The resulting high concentration of surfactant in analytical samples may interfere with the quantitation of certain pesticides such as malathion. Perhaps the use of other surfactants or eluents would lead to less analytical interference. However, the efficacy of other surfactants and eluents would need to be established.

Lyophilization of leaf wash solutions may be an alternative preparative procedure for dislodgeable residues of insecticides such as acephate that are very water soluble. However, lyophilization could not be easily used in the field. On the other hand, lyophilization avoids the cumbersome use of sodium sulfate to remove the water from these samples in preparation for analysis (California Department of Food and Agriculture, Worker Health and Safety Section, Chemical Laboratory Services, personal communication), but lyophilization would have to occur in the presence of surfactant to ensure adequate recovery. Ultimately, this might be a drawback because the analyte would remain contaminated with surfactant.

Results of testing the blind samples illustrate some of the potentials and problems in using these SPE disks for determination of dislodgeable foliar residues. Estimates of diazinon concentrations were less biased for residues determined by use of SPE disks compared to residues determined by solvent extraction (Tables 6 and 7). However, the longer storage duration of the aqueous samples, compared to the SPE samples, may have contributed to bias. Samples on SPE disks were considerably easier to prepare and ship compared to the aqueous samples. On the other hand, the biased results for the blind samples of malathion, clearly demonstrate problems associated with retention of surfactant on the SPE disks.

It may be possible to remove some or all of the surfactant from some pesticide analytes. When water–surfactant was partitioned against ethyl acetate, most of the surfactant remained in the water. Thus, it may be possible to elute analyte and surfactant from an SPE disk, remove the eluting solvent, and then partition the surfactant and analyte with a system such as water/ethyl acetate. This potential approach to surfactant removal remains untested. If required, adding this step during isolation and clean-up would be an additional drawback to use of SPE disks for determinations of dislodgeable foliar residues.

Results of this research demonstrate that SPE disks may have potential for use in determination of dislodgeable residues. However, this potential needs to be evaluated extensively before recommendation for use. The retention of surfactant on the SPE disks can lead to a matrix effect during gas chromatographic analysis, causing bias in residue estimates of pesticides such as malathion. Some pesticides, like diazinon may be unaffected by the matrix effect.

Table 6. Measured and expected concentrations of diazinon and malathion and bias of estimates for samples spiked with known concentrations of analytes, isolated by solid phase extraction

	Diazinon			Malathion		
Sample Designation	Diazinon Measured (μg/disk ± SD)	Diazinon Expected (μg/disk)	Bias (%)	Malathion Measured (μg/disk ± SD)	Malathion Expected (μg/disk)	Bias (%)
A	0.02 ± 0.002	0	–	0.07 ± 0.040	0	–
B	0.07 ± 0.004	0	–	0.31 ± 0.012	0	–
C	19 ± 1.2	17.6	+8.0	36 ± 4.8	18.9	+90
D	19 ± 2.8	17.6	+8.0	33 ± 1.6	18.9	+75
E	16 ± 1.5	17.6	−9.1	33 ± 1.8	18.9	+75
F	154 ± 6.4	176	−12.5	212 ± 9.5	189	+12
G	168 ± 15.7	176	−4.5	246 ± 46.8	189	+30
H	163 ± 13.5	176	−7.4	280 ± 35.6	189	+48

Table 7. Expected and measured concentrations of diazinon and malathion in aqueous blind spike samples, isolated by solvent partitioning

	Diazinon				Malathion			
Sample Designation	Diazinon Measured (μg/100 mL ± SD)	Diazinon Expected (μg/100 mL)	*n*	Bias	Malathion Measured (μg/100 mL ± SD)	Malathion Expected (μg/100 mL)	*n*	Bias
J	10 ± 0.2	17.6	3	−43%	15 ± 0.6	18.9	3	−21%
K	10 ± 0.6	17.6	3	−43%	15 ± 1.0	18.9	3	−21%
L	11 ± 0.1	17.6	3	−38%	17 ± 0.3	18.9	3	−10%
M	98 ± 7.3	176	6	−44%	158 ± 21.7	189	6	−16%
N	103 ± 9.1	176	6	−41%	161 ± 12.4	189	6	−15%
O	108 ± 6.9	176	6	−39%	165 ± 19.3	189	6	−13%

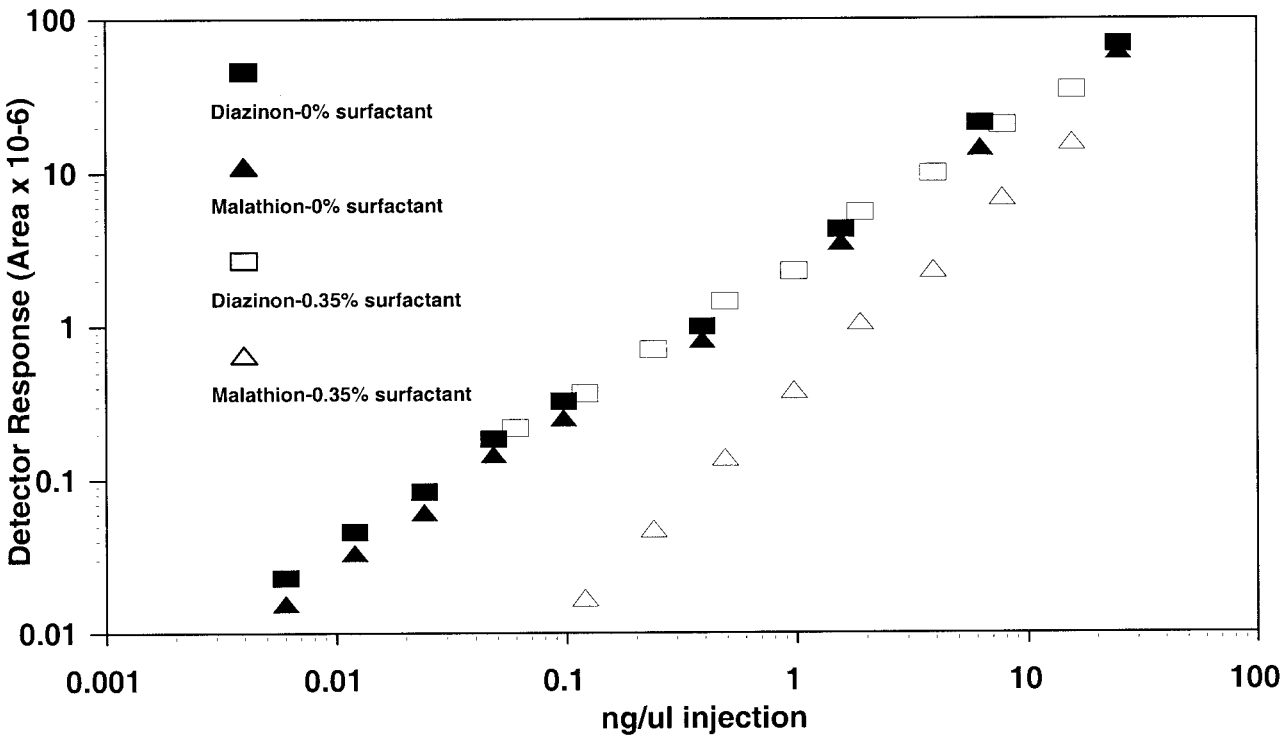

Fig. 1. Standard curves of malathion and diazinon, generated in the absence and presence of surfactant (sodium dioctyl sulfosuccinate)

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