ENVIRONMENTAL ANALYSIS

# Size Exclusion Chromatographic Cleanup for GC/MS Determination of Organophosphorus Pesticide Residues in Household and Vehicle Dust

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**Size exclusion chromatography (SEC) was used as a cleanup method for the analysis of organophosphorus pesticides in household and vehicle dusts. The pesticides investigated were diazinon, methyl parathion, chlorpyrifos, malathion, phosmet, and azinphosmethyl. These compounds are of interest due to their use in agricultural tree fruit production and/or urban pest control. Pesticides were determined via gas chromatography/mass spectrometry with selected-ion monitoring and cool on-column injection. The lower limit of method validation was 0.20 μg/g. Method limits of detection in dust ranged from 0.012–0.055 μg/g. Dust samples were collected with vacuums from the homes and vehicles of people living and working in a rural agricultural region in the central part of Washington State. The analytes were extracted from the dust by sonication in acetone. The extracts were solvent-exchanged to cyclohexane, frozen, thawed, and centrifuged prior to SEC injection. Following SEC, the eluent was split into 2 fractions, concentrated, and injected on-column into the gas chromatograph. This method represents the first complete publication describing the SEC cleanup of organophosphorus pesticides in dusts. Recoveries of pesticides in dusts ranged from 63.5–110.8 ± 4.9–19.6% over a fortification range of 0.20–10.00 μg/g. This optimized, automated, and reproducible SEC method does not require further treatment or cleanup for trace determination of these organophosphorus pesticides.**

Size exclusion chromatography (SEC), also called gel permeation chromatography, has been used as a cleanup method for determination of pesticides in different matrixes. SEC achieves the separation of components by molecular size. Separation occurs by repeated exchange of the solute molecules between the bulk solvent of the mobile phase and the stationary liquid within the pores of the column packing material (1). Molecular size selectivity is determined by the pore size of the column stationary phase. Pore size and solute interactions are also influenced by the composition of the mobile phase. Larger molecules are excluded from the pores of the stationary phase, which facilitates their rapid travel through the column. Conversely, the inclusion of smaller molecules within the pores of the stationary phase impedes their progress through the column, leading to longer retention times.

SEC cleanup has been applied to the removal of fats found in foods for pesticide analysis (2). AOAC INTERNATIONAL has adopted a method incorporating SEC cleanup for organochlorine pesticide residues in animal fats (3). More recently, SEC has been used in multiresidue analysis of pesticides in fruits and vegetables (4). Efforts have also been made for using SEC in environmental research. Adaptation of a multiresidue method was described by Johnson et al. to determine pesticide application spray drift on grass (5). Durand and Barcelo have compared SEC with Florisil solid-phase extraction (SPE) cleanup in soil for the determination of pesticides including carbamates, triazines, and 2 organophosphorus (OP) insecticides (6).

Ribick et al. has summarized some of the advantages of using SEC gels for cleanup of environmental samples for trace residue analysis (7). These advantages include compatibility with a wide range of organic solvents, a long column life, and the ability to achieve separation under isocratic conditions. SEC is also amenable to automation, with run times of 40–60 min at a flow rate of 5 mL/min.

With the publication of the 1993 National Research Council report "Pesticides in the Diets of Infants and Children" (8) and with the passage of the Food Quality Protection Act of 1996, concern about children's exposure to pesticides has grown. Of particular concern are children's exposure to pesticides in the home, because contact with treated surfaces can result in dermal absorption through skin or ingestion exposures due to hand-to-mouth behavior (9). Residues found indoors may also persist longer than those found outdoors (10). Household and vehicle dusts, as well as residential yard soils, may represent potentially significant sources for children's exposure to pesticides, especially if they live near pesticide-treated farmland or if their parents come into contact with pesticides in the workplace (10–13). If parents or other family

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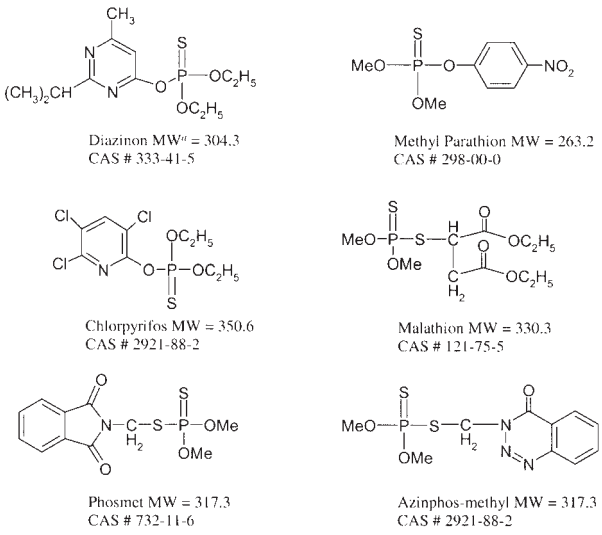


**Figure 1. Chemical structures and chemical abstract service (CAS) numbers for the analytes (MW = molecular weight, g/mol).**

members are occupationally exposed to pesticides, these contaminants may be brought into the home or vehicle on work boots or clothing or on the skin, and vehicles used for work may be used to transport the family. Additional cumulative exposure to OP insecticides may also be derived from the use of over-the-counter home use products and from professional applications made in and around the home.

Analyzing solvent-extracted household and vehicle dust samples is much more difficult than analyzing soil or vegetable surface residue samples due to the complicated nature of the dust matrix (10, 14). Household and vehicle dust contains natural products like waxes, fatty acids, and a spectrum of synthetic organic compounds such as cleaning products and phthalate plasticizers (15). Dusts can also contain a variety of biocontaminants as a result of fungi growth in certain environments (16). These and other dust constituents interfere with the analytical specificity required to determine trace amounts of OP pesticides within the matrix. Common preparative column chromatographic techniques, such as SPE, often cannot achieve the level of cleanup required for subsequent gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) analysis due to the wide variation in chemical and physical properties of dust contaminants.

A limited amount of published research on the application of SEC cleanup for pesticide residues in dusts exists, particularly for OP pesticides. Lewis et. al. published an evaluation of pesticide monitoring methods for small children (11). Analytes included the OP pesticides chlorpyrifos, diazinon, dichlorvos (DDVP), and malathion. Sampling methods used for dust collection were compared, and the paper referenced the analytical methodology of Hsu et al. (1988; 17). The Hsu method describes thorough Soxhlet extraction of air samples on polyurethane foam (PUF) plugs and dermal contact samples on gloves. The method does not mention dust. Following Soxhlet extraction, the PUFs and gloves were concentrated via Kuderna-Danish (K-D) and nitrogen evaporation to a final volume of 0.5 mL for GC/MS analysis. Roberts and Camann also report a method for the determination of chlorpyrifos in household dust with a limit of quantitation (LOQ) of 1–5 g/g (15). The Hsu method is also referenced here and the method of analysis is GC/MS with no cleanup. The differences between the Hsu method for PUFs and gloves compared with the procedures of Lewis and Roberts are apparent after Soxhlet extraction. Sample extracts were diluted to 20 mL prior to injection, which explains the high LOQs. The K-D and nitrogen concentration steps used by Hsu are possible in relatively clean matrixes such as precleaned PUFs and gloves. However, concentration of dust extracts without extensive cleanup would yield interferences during GC/MS analysis.

An SEC cleanup method for OP pesticides in household dust is reported by Simcox et al. (10) and uses a gravity-fed column. However, SEC is amenable to low pressure liquid chromatography (LC) and automation (7). Automated, low pressure LC systems have the advantages of higher sample throughput, reproducibility, and recovery. The goals for the development of this SEC cleanup method for OP pesticide residue analysis in household and vehicle dust include adaptation of the gravity column chromatography method to a low pressure LC system and improvement of the column separation efficiency between dust co-extractants and the OP pesticides.

The analytical methodology presented here specifies the determination of 6 OP pesticides: azinphosmethyl, methyl

**Table 1. Quantitation and confirmation ions for GC/MS determinations for OP pesticides in dust**

| Mass/charge | Azinphosmethyl | Phosmet | Malathion | m-Parathion | Chlorpyrifos | Diazinon |
|---|---|---|---|---|---|---|
| *m/z*[a] | 160 | 160 | 125 | 263 | 314 | 304 |
| *m/z*[b] | 132, 104 | 133, 317 | 174, 285 | 109, 233 | 199, 258 | 137, 179 |
| Ion ratios,[c] % | 24, 76 | 7, 7 | 9, 8 | 109, 6 | 126, 52 | 116, 120 |

[a] Quantitation ion.
[b] Confirmation ions.
[c] Confirmation ion response expressed as a percentage of the quantitation ion.

**Table 2. Method validation for fortified control household and vehicle dust sample recoveries**

| Parameter | Azinphosmethyl | Phosmet | Malathion | m-Parathion | Chlorpyrifos | Diazinon |
|---|---|---|---|---|---|---|
| | | | Household dust | | | |
| Mean[a] | 99.8 | 91.4 | 63.5 | 97.0 | 65.7 | 71.2 |
| CV[b] | 19.1 | 11.0 | 7.5 | 14.1 | 8.0 | 4.9 |
| *N*[c] | 6 | 6 | 6 | 6 | 6 | 6 |
| | | | Vehicle dust | | | |
| Mean | 103.6 | 110.8 | 84.9 | 104.9 | 86.3 | 73.1 |
| CV | 15.8 | 18.5 | 19.6 | 14.1 | 15.1 | 15.8 |
| *N* | 9 | 9 | 9 | 9 | 9 | 9 |

[a] Mean percent recovery (%).
[b] Coefficient of variation (%).
[c] Number of replicates.

parathion, phosmet, malathion, chlorpyrifos, and diazinon. The first 3 pesticides listed are products used primarily to control codling moth in Washington State tree fruit production. The latter 3 OP pesticides may be used in agriculture and also have registrations for urban or residential pest control. Chemical structures, molecular weights, and CAS numbers for the analytes appear in Figure 1. Tributyl phosphate (TBP; CAS No. 126-73-8) was used as an internal standard (ISTD).

## Experimental

### *Origin of Samples*

Two methods of household dust collection were used. The first method has been described by Simcox et al. (10). An HVS-3 (Cascade Stamp Sampling Systems, Bend, OR) high-volume, small-surface sampler was used to collect dust from carpeted or rug-covered areas in each home. Sample weight was targeted at 10 g, with particles >150 m. Some problems were encountered using the HVS-3. Obtaining sufficient sample mass was often problematic because the force of the vacuum suction was difficult to regulate. The HVS-3 is also cumbersome to clean in between samples to insure minimal sample cross-contamination. In addition, HVS-3 vacuums are relatively expensive to purchase when multiple units are required for extensive sampling. Therefore, our research group's more recent studies have used GS-80 (Nilfisk of America, Malvern, PA) vacuums equipped with HEPA exhaust cartridges. All vehicle dust was collected using the Nilfisk unit. Both front and back footwells were vacuumed, and mats were removed prior to vacuuming. Samples were transported to the laboratory on dry ice and stored at –10 C until analysis. Analysis of freezer-stored samples was completed within 4 months.

### *Chemicals*

(**a**) *Primary analytical standards of azinphosmethyl (Guthion).*—High purity; Bayer Agrochemicals Division (Kansas City, MO).

(**b**) *Reference material for the remaining OP pesticides.*—Chem Service (West Chester, PA); high purity.

(**c**) *TBP.*—Aldrich (Milwaukee, WI); 99% purity.

(**d**) *Stock solutions.*—Prepared individually from each pesticide standard at 1.00 mg/mL in acetone.

(**e**) *Mixed standards used for fortified control samples and for external calibrations.*—Prepared from the stock solutions and diluted in hexane.

(**f**) *Cyclohexane and dichloromethane.*—High purity; Burdick & Jackson (Muskegon, MI).

(**g**) *Acetone.*—Optima grade; Fisher Scientific (Fair Lawn, NJ).

Solvent pretreatment was not required.

### *Extraction*

House dust sample preparation and extraction procedures were modified from Nigg et al. (18) and Simcox et al. (10). Briefly, samples were sieved either manually or with a mechanical shaker through a 150 m stainless steel sieve to remove large particles and nondust debris. Subsamples containing 1.0 g sieved dust were transferred to a 50 mL polypropylene centrifuge tube. Ten milliliters acetone were added to the tubes containing the dust and then extracted via sonication for 1 min at 20 kHz. Acetone extracts were then centrifuged at 2500 rpm for 5 min. An 8 mL aliquot of clear supernatant liquid was decanted into a glass 15 mL screw-top test tube and evaporated under nitrogen at 39 C to <1 mL using an N-Evap (Organomation Associates, Berlin MA). Sample recovery was adjusted by 8/10 for the acetone fraction decanted. The remaining acetone was thoroughly mixed on a Vortex mixer and solvent-exchanged with 5 mL cyclohexane and concentrated to <3 mL at 50 C. Following resuspension to exactly 3 mL with cyclohexane, the extract was then mixed again and frozen solid at –10 C to facilitate removal of suspended particles in the next step. The frozen sample was then thawed and centrifuged for 10 min at 3000 rpm. The supernatant liquid was then transferred to a glass 15 mL gradu-

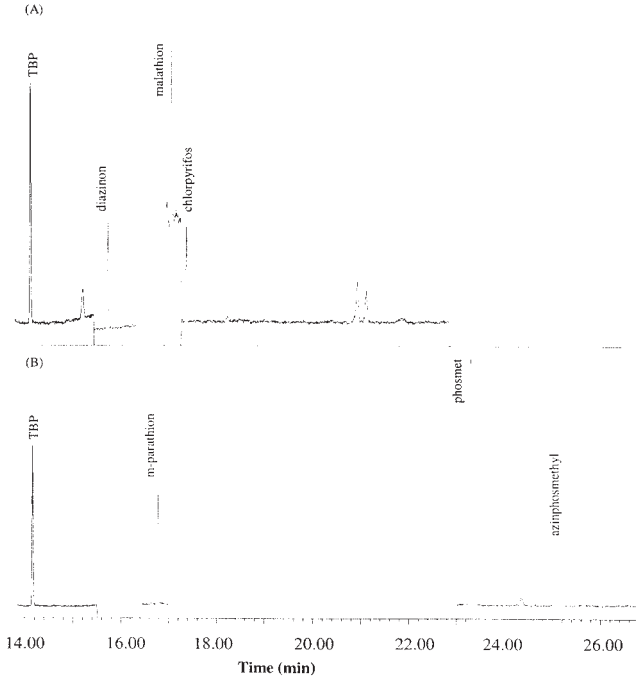


**Figure 2. GC/MS selective ion chromatograms of a fortified control household dust sample. Fractions (A) and (B) were injected separately. All OP compounds were fortified at 0.40 μg/g. TBP concentration is 0.50 μg/mL. TBP, diazinon, m-parathion, malathion, chlorpyrifos, phosmet, and azinphosmethyl were eluted at $t_R$ = 14.17, 15.81, 16.79, 17.16, 17.47, 23.34, and 25.12 min, respectively.**

ated centrifuge tube. At this point, the extracts could be stored at –10 C until the SEC cleanup. Preparing the extracts for SEC cleanup involved thawing the sample and adding 0.5 mL dichloromethane.

Vehicle dust sample preparation was identical to household dust preparation, but minor differences exist between the methods for extraction. Following the sonication and first centrifugation at 2500 rpm for 5 min, the sample was decanted into a glass 15 mL screw-top test tube and an additional 5 mL of acetone was added to the dust. The sonication and centrifugation steps were repeated, and the resulting supernatants were decanted and added to the first extract. The supernatant liquid was evaporated to <1 mL on the N-Evap at 45 C, followed by the addition of 5 mL cyclohexane. Then the sample was mixed on a Vortex mixer, concentrated to <3 mL on the N-Evap at 45 C, and mixed again. Vehicle dust samples were analyzed after the household dust samples were completed. The extraction methodology was modified because of the different characteristics of the dust. Vehicle dust samples contained more sand and larger-grained particles which necessitated a second extraction. Also, the second dust extraction was added in an effort to increase malathion and chlorpyrifos recoveries. Following freezing the sample a second time, the procedure continued according to the method described for household dust.

### *SEC Cleanup*

The SEC used for this analysis was a laboratory-built instrument. The SEC was operated under the following equipment and operating conditions:

(**a**) *Injector*.—Valco E60 (VICI, Houston, TX); loop size, 3.0 mL.

(**b**) *Pump*.—Perkin-Elmer Series 400 (Norwalk, CT) single piston pump; quaternary solvent programming capability; mobile phase, cyclohexane–dichloromethane (85 + 15, v/v); flow rate, 5 mL/min.

(**c**) *Column*.—25 mm 54 cm Bio Beads S-X3 (Bio-Rad Laboratories, Hercules, CA).

(**d**) *Detector*.—V4 absorbence detector (ISCO, Lincoln, NE); wavelength, 225 nm; sensitivity, 1.0 mAUFS; rise time, 0.05/0.02.

(**e**) *Fraction collector*.—Rainin Dynamax Model-FA (Varian Assoc., Walnut Creek, CA) equipped with collection rack designed for Turbo Vap flasks; collection time, 2 fractions: (A) 22–42 min: diazinon, malathion, chlorpyrifos; (B) 43–62 min: m-parathion, phosmet, azinphosmethyl.

(**f**) *Integrator*.—3396 Series II (Hewlett-Packard, Palo Alto, CA); chart speed, 0.5 cm/min; attenuation, 4.

SEC columns were prepared by the slurry method described in the Bio-Beads S-X instruction manual (Bio-Rad Laboratories). Beads were swollen overnight in mobile phase prior to column packing. Borosilicate glass columns suitable for low pressure LC (<2000 kPa) were obtained from Omni-Fit (Toms River, NJ). Mobile phase was pumped through the column for a few hours for conditioning. Care was taken to insure that all air bubbles were dislodged from the column packing. Flow rate and back pressure were stabilized when the column was ready for use. One adjustable end-fitting was used on each column to accommodate minor changes in bed volume.

A 5 mL Luer-tip glass syringe was used to transfer 3 mL sample into the injector loop. The SEC system was equipped with a series of contact closures that initiated data and fraction collection programs upon injector actuation. The injector loop was continually rinsed with mobile phase between injections. Approximately 230 mL mobile phase was collected for each sample injected. The fractions were collected in 200 mL Turbo Vap flasks having 0.1 to 1.0 mL graduation marks.

Sample fractions A and B were kept separate and concentrated to <1 mL using the Turbo Vap. The concentrated sample fractions were solvent-exchanged with 3–5 mL isooctane concentrated to < 1 mL. After resuspending to 1.0 mL with isooctane, each sample fraction was transferred to a 1.5 mL GC vial. The ISTD (TBP) was added to the GC vials at this point. Samples were stored at –15 C prior to analysis.

### *Gas Chromatography*

Analyses were completed using a Hewlett-Packard 5890 Series II GC equipped with a 7673 series autosampler, electronic pressure control, cool on-column (COC) injection port,

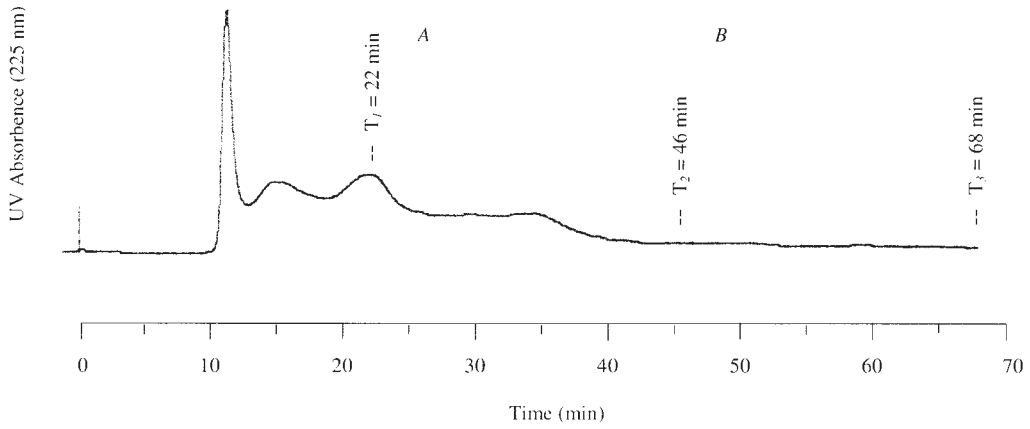


**Figure 3. Size exclusion chromatogram of fortified control household dust. Fractions A and B shown at 5.0 μg/g for 6 OP pesticides.**

and 5971 mass selective detector (MSD). Instrument control and data acquisition were performed with Chemstation software (Hewlett-Packard). A guard column, consisting of a 1 m length 0.53 mm id deactivated fused silica, was installed between the COC inlet and the analytical column. The analytical column used was a DB-5 MS, 30 m 0.25 mm id, with a 1.0 m film thickness (J&W Scientific, Folsom, CA). The guard column was attached to the analytical column with a glass capillary press-fit column union. Prepurified helium was used as carrier gas.

Chromatographic conditions used in this analysis were based on modifications of the method described by Moate and Jenkins (19). The COC injection volume was 2 L. The COC inlet was used in constant flow mode with helium carrier gas linear velocity equivalent to 32.2 cm/s at 275 C and 99.3 kPa head pressure. The injection port programming included an initial temperature of 75 C held for 0.10 min, then ramped to 260 C at 70 C/min and held for 4 min before returning to 75 C. Initial oven temperature was 75 C held for 2.5 min and ramped to 225 C at 15 C/min and held for 1.5 min. The second stage of the oven program ramped the temperature to 275 C at 25 C/min and then immediately ramped to 280 C at 35 C/min and held for 10.2 min. MSD transfer line temperature was set to 280 C. The MSD was operated in selected-ion monitoring (SIM) mode.

### *Determination*

Quantitation on the mass spectrometer was achieved from the absolute response of a single ion for each analyte. Primary identification of the analytes was determined from their retention time. Two additional ions were monitored for each analyte for qualitative confirmation. Quantitation ions selected were usually the base peak, having the strongest reponse with an $m/z > 150$. One exception was malathion, which had an interference in the base peak in dust matrix. An alternate ion with a lower $m/z$ was selected. Confirmation ions were primarily selected that had an approximate response of at least 5% of the quantitation ion and little matrix interference. Ions monitored are shown in Table 1. Peak areas determined from the quantitation ions on the GC/MS were integrated and compared with an external standard (ESTD) calibration curve. ESTDs ranged from 0.10–10.0 g/mL. The ESTD calibration curve consisted of 5 points and correlation coefficients typically exceeded $R^2 = 0.995$. ESTDs were regularly reinjected as check standards throughout the GC/MS analysis. The check standards verified uniform instrument sensitivity through the entire sequence. Check standard performance was typically within 20% of known value.

TBP was used as an ISTD for 2 purposes. First, TBP response for each injection was normalized to reduce any variation associated with the GC. Second, a systematic and uniform increase in response was noted in the dust samples compared with the clean ESTDs. This increase in response is characteristic of matrix enhancement sometimes experienced with on-column injections. To account for this discrepancy, the median TBP response for the dust extracts was normalized to the median TBP response in the ESTDs. Coefficients of variation (CVs) for TBP response were typically 7–16%.

### *Method Validation*

This analytical method offers a lower limit of method validation (LLMV) of 0.20 g/g for all 6 OP pesticides, based on a sample size of 1.00 g. The LLMV is the lowest concentration of the fortified sample determination trials (20). Limits of quantitation or detection (LOQ/LOD) can be considerably lower depending upon the definition and statistics applied to the LLMV. Extrapolation from the LLMV to a response factor of 3:1 signal-to-noise in dust yields effective LODs of 0.012 g/g for phosmet; 0.027 g/g for diazinon, methyl parathion, malathion, and chlorpyrifos; and 0.055 g/g for azinphosmethyl. Table 2 shows fortified control household and vehicle dust recovery efficiencies for the 6 OP pesticides.

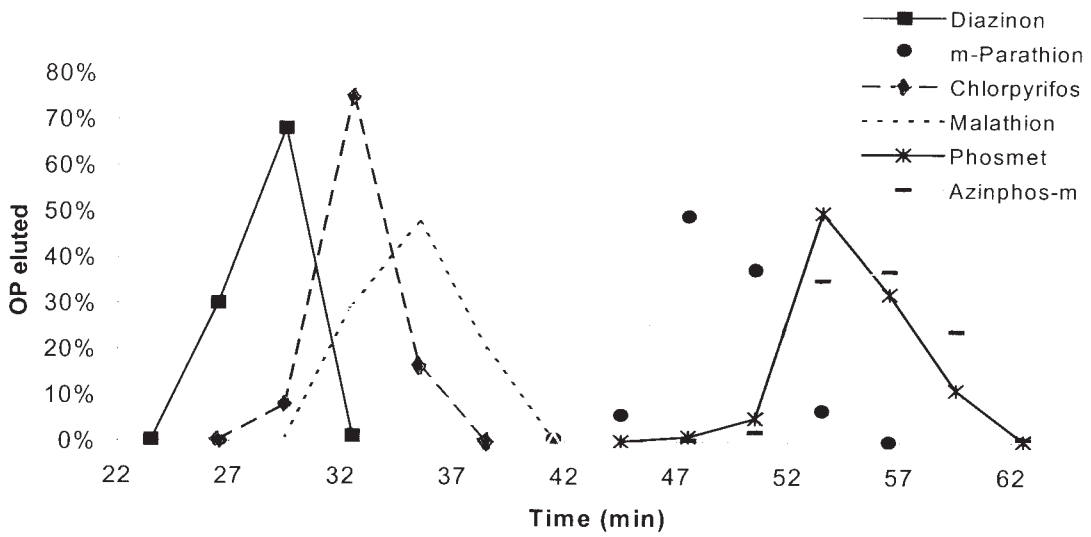


**Figure 4. SEC elution profiles of organophosphorus pesticides. Fractions were collected and analyzed at 3 min intervals.**

Method validation for household dust consisted of 2 sets of 3 replicates of fortified control samples. The household dust replicate samples were run at 2 fortification levels: 5.00 and 0.20 g/g. Nine vehicle dust fortified control replicate samples were run between 0.40 and 10.00 g/g.

Additional fortified control samples were evaluated with field sample analyses for quality control (QC) purposes for both household and vehicle dust. Compilation of the fortified control samples with the method validation trials yielded a total sample set of $N = 21$ for household dust and $N = 33$ for vehicle dust. Fortification levels ranged from 0.40–10.00 g/g. Recoveries for this fortified control sample set ranged from 62–81% for household dust and 81.4–106.0% for vehicle dust. These continuing QC data show the consistency of the method over a 3-month period. The relatively high CVs (>15%) for interday analyses are likely due to thermal lability of the OP pesticides in the inlet of the GC (19).

Figure 2 shows extracted ion chromatograms for 2 fractions of control household dust extracts fortified at 2 times the LLMV (0.40 g/g). Fraction A contains TBP (ISTD), diazinon, malathion, and chlorpyrifos. Fraction B contains TBP (ISTD), m-parathion, phosmet, and azinphosmethyl. The equivalent chromatograms for control vehicle dust extract fortifications are similar. The GC method was optimized for all 6 OP pesticides and TBP. The first 13 min of the run was not collected, as is common practice in GC/MS, so as to extend filament lifetime in the ionization source. Breaks and variations in the baseline signal intensity depict changes in SIM. Injections of ESTDs contained all 6 analytes, as it was not necessary to separate the OP pesticides into 2 groups for the GC run.

## Results and Discussion

### *Optimization of the SEC Conditions*

Preliminary research focused on the quantitation of 2 pesticides, phosmet and azinphosmethyl. A 2-column SEC approach showed promise for these OP pesticides. Two short, 20 cm columns were connected in sequence. The first column contained Bio-Beads S-X3 followed by S-X12. S-X3 has a molecular weight exclusion limit of 2000 daltons and S-X12 has a working range up to 400 daltons. When the dust extract was first pumped through the S-X3 column, fractions with a molecular weight lower than 2000 daltons were separated roughly and then pumped onto the S-X12 column. The fraction with a molecular weight lower than 400 daltons which included the OP pesticide was subject to further separation. This dual, short-column configuration offered better separation efficiency and cleaner extracts than can be obtained using an S-X3 column alone with a cyclohexane–dichloromethane (1 + 1) mobile phase.

Further experimentation with 4 additional OP pesticides showed that mobile phase optimization had a greater effect on selectivity than the combination of 2 stationary phases. S-X3 was chosen for optimization because fewer column back pressure problems were encountered when changing mobile phase ratios. The goal was to optimize the pore size, and thus the affinity, of the S-X3 beads for the analytes. The pore size of the S-X3 beads decreased by increasing the cyclohexane fraction of the mobile phase. A series of experiments were run increasing the cyclohexane fraction from 50 to 95% in dichloromethane. The optimum composition was determined to be 85% cyclohexane in dichloromethane. Further increases in the cyclohexane fraction yielded little change in separation efficiency and produced unpredictable changes in the column bed volume and back pressure at flow rates of 5 mL/min.

Optimizing the affinity of the stationary phase for the pesticides resulted in long residence times in the SEC column. Considerable effort was made to keep the run time near 60 min, which was accomplished by maintaining a flow rate of 5 mL/min. Because of the large volume of solvent eluted from the column, 2 fractions were collected. The first fraction con-

tained diazinon, malathion, and chlorpyrifos while the second fraction contained m-parathion, phosmet, and azinphosmethyl. Fractions were injected separately on the GC due to increased interferences encountered with the mass spectrometer when analyzing combined fractions. Fraction A contains matrix interferences for the analytes collected in fraction B.

Figure 3 depicts the $UV^{225}$, trace of a fortified household dust extract eluted from the SEC column. One gram of control household dust was fortified with 5.00 g of the 6 OP pesticides and extracted prior to SEC. Figure 3 shows that much of the $UV^{225}$-absorbing constituents in the injected sample elutes prior to collection of fraction A. Some absorbance from the matrix is also apparent in fraction A, starting at 22 min. However, little matrix interference is observed on the GC/MS for the OP pesticides collected in this fraction. No appreciable matrix interferences are collected in fraction B, as indicated in Figures 2 and 3.

Figure 4 shows the distribution of OP pesticides within the 2 collected fractions from the SEC column. Complete elution of diazinon, malathion, and chlorpyrifos is attained from 22–42 min. Elution of m-parathion, phosmet, and azinphosmethyl is completed from 42–62 min. The figure illustrates a convenient point of fractionation between malathion and m-parathion. The clean break between compounds simplifies data analysis of the 2 fractions. It is interesting to note the degree of separation achievable between OP pesticides with similar molecular size and shape. SEC theory would indicate little separation between compounds with relatively similar molecular size. For SEC of large molecules (>1000 daltons), it is commonly assumed that molecular weight is often analogous to molecular size. The same assumption cannot be applied to small molecules. The resolution attained in this assay is credited to the optimization of the pore size of the SEC stationary phase for the OP pesticides. Clearly, some additional solvent–sorbent interactions are occuring within the SEC column to produce these results.

### *Additional Developments*

Freezing the dust extracts in cyclohexane assisted in sample cleanup. Cyclohexane freezes solid in a –15 C freezer. The highly ordered structure of solid cyclohexane crystal lattice excludes much of the small particulate impurities still present in the extract after centrifuging. Upon thawing the sample extract, much of the coextracted particulate material will clump and is easily removed with an additional centrifuge step. This method has the added benefit of removing the need for filtering the extracts prior to injection on the SEC. Usually, sample extracts are passed through a syringe filter (0.45 m) prior to any type of LC injection. The dust extracts contain so much fine particulate matter that several large (25 mm id) filters are required to pass the entire sample. Plugging of the filter is commonly experienced, which can lead to sample loss.

Use of a thick-film GC column stationary phase proved to be advantageous for the determination of the OP pesticides. The 1.0 m film used in the DB-5 MS column allowed for greater injection capacity. Frequent peak splitting occurred for some of the pesticides, particularly malathion, with a 0.25 m film column of the same stationary phase. Injection capacity was not compromised by the analytes, but by matrix constituents coeluted with the OP pesticides in the SEC fractions. Peak splitting was not observed with ESTDs, but would become a problem in fortified control samples at the same analyte concentration. The 1.0 m film column was used successfully for injections up to 2 L. Regular cutting or replacement of the guard column was necessary for injection volumes of 1–2 L.

## Conclusions

Household and vehicle dusts are very complicated matrixes. It often presents a challenge for the analytical chemist to extract the necessary constituents without introducing too much interference in later identification and quantitation steps. It is remarkable that more methodology for the determinations of OP pesticides in dusts has not been published. The SEC method presented here provides a very efficient cleanup method for the analysis of OP pesticides in household and vehicle dust. Reproducible recoveries have been routinely achieved with multiple OP pesticides in one sample. Currently this assay has been used to analyze approximately 150 household and 190 vehicle dust samples in support of ongoing field research projects. This method is also versatile and is currently being adapted to include the analysis of other pesticides and metabolites.

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