Analytical Method Development for 18 Pesticides in House Dust and Settled Residues Using SEC, SPE, TMS Methylation, and GC–MS

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Abstract

An analytical method is developed to analyze eighteen pesticides in carpet dust and also dust that has settled on surfaces in order to determine the potential exposure of children to pesticide residues. For nonacid pesticides, the extract after centrifugation and filtration is cleaned up using size-exclusion chromatography (SEC) and then analyzed by gas chromatography (GC) coupled with a mass spectrometer (MS). The best solvent for extraction is ethyl acetate–cyclohexane (3:1). The recoveries of spiked nonacid pesticides from 2 g of dust are between 72% and 110% with a variation between 4.2% and 25.6%, and the detection limit is 10 to 50 ng/g dust, depending on the pesticide. For acid pesticides, the dust is extracted with a saturated $Ca(OH)_2$ solution, centrifuged, cleaned up by polyvinylbenzene/polystyrene-type solid-phase extraction cartridges, and methylated with trimethylsilyldiazomethane (TMS). Acid pesticides on filter paper samples are extracted with acidified acetone (3mM H_3PO_4) and methylated with TMS. Methylation with TMS is fast and easy to perform. Methyl esters of the pesticides are completely separated and detected at low levels by GC–MS in the selective ion monitoring mode. The average recoveries of pesticides from 2 g of dust are between 81% and 104%. The average recoveries of pesticides spiked on filter paper are between 88% and 113%. A capillary column with a stationary phase of trifluoropropylmethyl polysiloxane gives the best separation and sensitivity for most pesticides on the GC–MS.

Introduction

Pesticide residues in residential homes originate from indoor pesticide application or are brought in by humans, animal pets, or wind from outdoor soil and lawns that have been treated with pesticides. These residues degrade more slowly than those outdoors because they are more protected from sunlight, moisture, temperature extremes, wind and rain dispersal, and microbial activity (1,2). Many pesticides have been found in house dust (3,4) resulting in health risk to humans, especially children. Pesticide residues that are dislodgable present greater exposure hazards than other pesticide residues.

A set of eighteen pesticides that have a high potential for being present in residential houses was selected for study as part of our ongoing research on pesticide residues that can result in exposure to children in the home environment. We targeted our investigation on developing an analytical method to simultaneously measure the occurrence in house dust of the following pesticides: chlorpyrifos, methamidophos, malathion, methyl parathion, atrazine, diazinon, carbaryl, pendamethalin, resmethrin, tetramethrin, alachlor, trifluralin, metolachlor, 2,4-D-butyl ester, picloram, 2,4-D-acid, dicamba, and mecoprop. These pesticides belong to the chemical groups of organophosphates (chlorpyrifos, methamidophos, malathion, methyl parathion, and diazinon), acetanilides (alachlor and metolachlor), triazines (atrazine), phenoxyacetic ester (2,4-D-butyl ester), carbamates (carbaryl), pyrethoids (resmethrin and tetramethrin), nitroanilines (pendamethalin and trifluralin), and carboxylic acids (picloram, 2,4-D-acid, dicamba, and mecoprop). This large amount of physical–chemical properties (including acid and nonacid compounds) that can combine with unknown compounds found in common house dust poses the biggest challenge to this analysis.

Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are the methods most commonly used to purify analytes from interfering substances in environmental sample matrices. Such purification is based on the differences of polarity between components. When simultaneously analyzing a group of pesticides with a broad range of polarities in a combined mixture with interfering sample substances that also have similar polarities, it is very difficult or even impossible to isolate the pesticides. High-performance size-exclusion chromatographic techniques (SEC) can be used to separate compounds based on differences in their molecular weights without regard for polarity. Using this methodology, one can separate pesticides having molecular weights less than 400 carbon units (cu) from larger-size matrix substances such as lipids (> 600 cu) (5). However, it cannot sepa-

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rate pesticides from interfering substances in the environmental matrix that are of similar size. Thus, techniques based on the polarity differences of compounds may need to be employed in addition to SEC, or the extraction method must be optimized to eliminate as many interfering substances as possible.

If the matrix substances are volatile, the optimization of gas chromatography (GC)–mass spectrometry (MS) may separate them from pesticides or allow for the selective detection of pesticides. The U.S. Environmental Protection Agency (EPA) has a general gel-permeation chromatographic (GPC) cleanup method that is used to analyze pesticides and other environmental organic pollutants (6). In addition, there are reports using SEC to clean up acetone (7,8) or methanol (9) extracts of pesticides from plants or soil, respectively. When we tried these methods on the dust samples in this work, the inferences from dust were unsatisfactory for GC–MS analysis. Therefore, in addition to selecting and optimizing the GC–MS methods, we had to test extraction solvents and optimize the SEC methodology for the purpose of cleaning up the dust extract.

Carboxylic acid herbicides are an important second set of pesticides in this study. They are widely used to control broadleaf weeds in agriculture and the turf-grass industry (10). They are found frequently not only in water and soil, but also in house dust (4,10). However, methods developed for nonacid pesticides cannot be used for this group. Therefore, a second analytical method was developed to study the occurrence of the four carboxylic acid pesticides picloram, 2,4-D-acid, dicamba, and mecoprop in house dust.

The carboxylic acid pesticide method development also presented challenges. GC is one of the most common methods used for the investigation of carboxylic acid herbicides in the environment because of its high sensitivity, accuracy, and reliability. Generally, carboxylic acid herbicides in the free acid form are not volatile enough for GC analysis. Methylation is one of the most common techniques used to transform them into volatile methyl esters for GC analysis, especially GC–MS (7,8). Diazomethane is commonly used as the reagent for the methylation of organic acids in GC analysis. However, diazomethane is unstable, explosive, and carcinogenic. It has to be prepared from other reagents in a special apparatus right before usage, and diazomethane methylation requires water-free conditions. Therefore, such methylation is both a labor- and time-intensive process. Hashimoto et al. (11) have reported that the methylation of carboxylic acids with trimethylsilyldiazomethane (TMS) is rapid and quantitative under mild conditions (room temperature and neutral medium) in benzene–methanol (4:1) for GC analysis. Rimmer and others (7,8) have used TMS methylation with the same solvent system for the GC–MS analysis of phenoxyalkanoic herbicides (7,8). We have found that the complete evaporation of the solvent after methylation (which is necessary in order to eliminate the excess TMS in the previously mentioned method) is prone to cause a loss of methyl esters in acid pesticides.

Others have extracted carboxylic acid herbicides with alkaline water (12), neutral aqueous methanol (13), acetone (10), acidified aqueous organic solvents (4,10), or acidified organic solvents (10). These extracts have been cleaned up by LLE (10,14), SPE (4), or SEC techniques (7,8). We evaluated the use of several of the published methods for our dust samples; however, the results either had too much interference for GC–MS analysis or the recoveries of the carboxylic acid pesticides were too low.

The first goal of this study was to develop a method that allowed for the analysis of common nonacid pesticides found in house dust using GC–MS and SEC for the removal of interfering compounds in the dust extract. Both the extraction procedures and the SEC cleanup were optimized in order to attain high sensitivity, reproducibility, and accuracy for environmental matrix specimens that contain multiple residues. We needed a fast sensitive method to analyze the residues of fourteen nonacid pesticides carried by house dust or dislodgable from household surfaces or both. The methods currently available in the literature for the analysis of pesticides in house dust, soil, and other samples cannot be successfully applied to our analysis because their accuracy and sensitivity seriously suffer from interfering substances in the dust samples (3). Also, some methods are too complicated and time-consuming for a large number of samples or deal with a different combination of pesticides (4,15).

The second goal of this study was to develop extraction, cleanup, and TMS methylation methods for the simultaneous analysis of the four carboxylic acid pesticides from dust and to confirm the analysis of the four acid pesticides on filter paper that is used as a wipe for household surfaces or a collecting surface for settled particulates.

Experimental

Chemicals and accessories

All of the analyte standards were purchased from ChemService (West Chester, PA). Dichloromethane (pesticide-residue-grade) and other solvents (analytical-grade) were purchased from Fisher Scientific (Fair Lawn, NJ). Benzophenone (the internal standard candidate) was purchased from Aldrich (Milwaukee, WI). Calcium hydroxide and sodium hydroxide were also purchased from Fisher Scientific. Methyl *tert*-butyl ether (MTBE), methanol, and other solvents were of high-performance liquid chromatographic (HPLC)-grade or ACS-certified-grade (Aldrich). TMS (2M in hexane) was also purchased from Aldrich. The helium used for GC–MS was 99.9995% pure.

Stock solutions (1000–2000 mg/L) for each nonacid pesticide and the internal standard candidate were prepared by dissolving each particular pesticide standard in acetone. Nonmatrix-matched calibration solutions that did not include substances other than pesticides were prepared by the mixing and serial dilution of the stock solution with acetone for concentrations of 0.02, 0.05, 0.1, 0.5, 1, and 5 mg/L for each pesticide. Matrix-matched calibration solutions (which include interfering substances from dust) were prepared in the same way except for the substitution of acetone with a 10-mL ethyl acetate–cyclohexane (3:1) extract from 10 g of dust not spiked with pesticides that had been cleaned by SEC. The extraction procedures will be described. The units for the concentrations of the matrix-matched calibration solutions mentioned were milligrams of pesticide per kilogram of dust. The matrix-matched calibration solutions were used for the recovery tests of pesticides in dust.

Stock solutions (1000–2000 mg/L) for each carboxylic acid pes-

ticide were prepared by dissolving each particular pesticide standard in acetone. Calibration solutions were prepared by the mixing and serial dilution of the stock solution with acetone at concentrations of 0.05, 0.1, 0.5, 1, and 5 mg/L for each pesticide. A standard solution for each pesticide used for spiking the filter paper had aqueous acetonitrile (1%) as the solvent. Filter paper was No. 1 type from Whatman (Maidstone, England).

Dust sampling and extraction for nonacid pesticides

House dust was collected by a vacuum cleaner. Two grams of vacuum cleaner dust was extracted three times in a 20-mL vial with 5 to 10 mL of the solvent that was to be screened—acetone, methanol, acetonitrile, dichloromethane, ethyl acetate, cyclohexane, ethyl acetate–cyclohexane (3:1), or dichloromethane–cyclohexane (3:1)—by shaking it in a mixer (Model 16715, Barnstead, Dubuque, IA) for 10 min each time. In order to extract 5–20 g of dust, a 100-mL Erlenmeyer flask was used as a substitute for the 20-mL vial and shaken at 120 rpm on a shaking waterbath (Model 224, Fisher Scientific). The solvent volume had to be large enough to submerge the dust specimen. The supernatant was decanted into 50-mL polypropylene centrifuge tubes (Fisher Scientific). Caution was taken to retain all dust particles in the vial. The extract mixture was then centrifuged for 10 min. The supernatant was transferred to a weighed 50-mL flask (200 mL for large volumes of extract) of a rotary evaporator. Then, it was condensed to approximately 1 mL at 35°C. A 10-mL aliquot of dichloromethane was added to the flask, then the solution was condensed to 1 mL; such procedures were repeated two more times in order to replace the extraction solvent with dichloromethane. This solvent exchange was done in order to match the injection solvent with the mobile phase in the SEC procedure about to be performed. Because large volumes of solution are going to be injected into the HPLC, the swelling of the beads might be affected if the injection solvent did not match the mobile phase. The flask was weighed again in order to obtain the weight (approximately 1 g) of the condensed extract, which was then filtered through a 25-mm syringe filter (0.45-µm nylon membrane with glass fiber prefiltration) (Alltech Associates, Deerfield, IL). The filtrate was collected in a 1.5-mL amber vial for further cleanup with SEC or direct GC–MS analysis.

SEC cleanup of dust extract

Cleanup was conducted using a high-resolution SEC polyvinylbenzene/polystyrene column (EnvirosepABC column, 300- × 7.8-mm i.d.) protected by an EnvirosepABC guard column (60- × 7.8-mm i.d.) (Phenomenex, Torrance, CA) on an HP1090 HPLC (Agilent Technologies, Sunnyvale, CA) equipped with a diode-array detector (DAD) and autosampler. The detection wavelength was set at 254 nm with the reference wavelength at 450 nm. The injection volume was between 10 and 250 µL with a drawing speed of 100 µL/min. All the tubing used was stainless steel in order to avoid the swelling of plastic tubing when using dichloromethane. The column was set at room temperature (21°C to 22°C). SEC effluent was collected manually at selected time intervals during the run and condensed to approximately 0.2 mL for GC–MS analysis. The exact volume was determined by the weight of the condensed effluent and its density. The density of the solvent mixture was determined by measuring the weight of 1-mL of the solvent mixture.

GC–MS conditions and analysis for nonacid pesticides

Pesticides in the dust were analyzed on an HP5890 Series II GC coupled to an HP 5971A MS (Agilent Technologies). Operating conditions were as follows: electron impact ionization with an ionization voltage of 70 eV, an interface temperature of 310°C, an ion source temperature of 185°C, and an electronic multiplier at 200 V above the autotune for scan mode and 400 V above the manual tune for selective ion monitoring (SIM). The MS was tuned daily with perfluorotetrabutylamine. Autotune was used for the scan mode and manual tune was used for the SIM mode in order to increase the MS response on ion fragments with a mass-to-charge ratio (*m/z*) of more than 200. The three ions used in the manual tune were *m/z* 219, 264, and 314. The dwell time for SIM was 60 ms.

Other GC–MS conditions were as follows unless stated elsewhere. The analytical column was an RTX-200MS (Restek, Bellefonte, PA) (30-m × 0.25-mm i.d.) with a 0.5-µm film of trifluoropropylmethyl polysiloxane, and the guard column had intermediate polarity with dimensions of 5- × 0.25-mm i.d. (Supelco, Bellefonte, PA). A double-taper splitless injection-port liner (Supelco) without fillings was used. The injection temperature was 220°C. A 2-µL aliquot of the sample solution was injected by hand or an HP7673A autosampler (Agilent Technologies) in splitless mode at 0.5 min before purging the injection port.

Pesticides were identified by matching both the characteristic MS fragment ions and the chromatographic retention times. For quantitation, one injection of the standard solution with a concentration of 0.5 mg/L for each pesticide was performed between every four injections of the samples. A response factor was obtained by dividing the pesticide peak area from a sample chromatogram by the peak area of the same pesticide in the chromatogram from the most recently injected standard solution. Each pesticide concentration was calculated by inserting such a response factor into the linear equation for the response factor versus each pesticide concentration, which was obtained by analyzing the calibration solutions using the same GC–MS conditions.

Glassware silanization

The silanization of glassware reduces the absorption of polar compounds such as carboxylic acid pesticides onto glassware surfaces and protects delicate samples against the possible reactive effects of OH sites present on glassware. Silanization was done by coating and rinsing the glassware with 5% (v/v) dimethyldichlorosilane in toluene for 10 to 15 s, then rinsing two times with toluene and three times with methanol. The glassware was dried in the oven.

GC–MS conditions and analysis for carboxylic acid pesticides

The optimized GC–MS conditions were the same as those for nonacid pesticides except for the following: the column head pressure was 72 kPa, and the oven temperature began at 100°C (0 min), was raised to 210°C (0 min) at 10°C/min, and then raised to 305°C (2 min) at 30°C/min. The conditions for the MS tuning, scan, and SIM were the same as detailed for the analyses of the

nonacid pesticides. The second oven-temperature programming that was used began at 80°C (0 min) and was then raised to 300°C (5 min) at 30°C/min when the column head pressure was 103 kPa.

Dust extraction for carboxylic acid pesticides

The following protocols were tested to extract carboxylic acid pesticides from dust.

Protocol I (1)

Two grams of dust with acetonitrile–phosphate buffer (7:3, v/v) (pH 3, 0.1M sodium acid phosphate) was shaken for 10 min. The extraction was repeated two more times, and the extracts were combined, centrifuged, and filtered through a 25-mm syringe filter (0.45-µm nylon membrane with glass fiber prefiltration) (Alltech Associates). The pH of the effluent was adjusted to 12 by adding 1M NaOH. Rotary evaporation at 48°C was used to remove the acetonitrile. The remaining liquid in the flask was partitioned two times with 20 mL of petroleum ether. The aqueous layer was acidified to a pH of 1 by adding 5M HCl. The effluent was subjected to SPE in order to remove interfering molecules from the house dust.

Protocol II (2)

Two grams of dust with 0.2M NaOH was shaken for 5 min. The extraction was repeated two times, and the extracts were combined, centrifuged, and filtered through a similar filter as that of Protocol I. The pH of the effluent was decreased to between 1 and 2 by adding 5M HCl, and the effluent was cleaned by SPE.

Protocol III (6)

An amount of 2 to 20 g of dust was shaken with distilled water and 0.2 to 2 g $Ca(OH)_2$ (weight ratio of dust and $Ca(OH)_2$ adjusted to 10:1) for 30 min. The extraction was repeated two times, and the extracts were combined, centrifuged, and filtered through the same type of syringe filter as previously mentioned. The pH of the effluent was adjusted to between 1 and 2 by adding 5M HCl. The effluent was subjected to SPE for cleanup.

SPE cleanup of dust extract followed by TMS methylation

A polyvinylbenzene/polystyrene SPE cartridge (Oasis HLB, Waters Co., Milford, MA) was conditioned with 6 mL of 10% methanol in MTBE, 6 mL methanol, and then 4 mL distilled water at pH 2. The filter effluent previously described was passed through the SPE cartridge at approximately 5 mL/min. The cartridge was washed with 2 mL distilled water at pH 2, dried under vacuum for 20 min, and then eluted with 8 mL of 10% methanol in MTBE. The top layer (mainly MTBE) of the effluent was transferred to a 20-mL vial, the bottom layer (aqueous) was extracted twice with diethyl ether, and the extracts were combined with the MTBE layer.

The combined solution was condensed carefully to dryness with a gentle flow of N_2. Then, 0.5 mL methanol and 50 µL TMS (2M in hexane) were added in order to methylate the carboxylic acid pesticides. The mixture was sonicated for 0.5 h and injected into the GC–MS after 1 h.

Extraction and methylation of filter paper sample for carboxylic acid pesticides

Each spiked filter paper sample was submerged under acidified acetone (3mM H_3PO_4) in a 250-mL Erlenmeyer flask and shaken for 5 min at 120 rpm in order to extract the pesticides. The combined extract was condensed, methylated, and injected into the GC in the same way as the dust extract, except that SPE cleanup was not used.

Determination of recoveries and detection limits

The recovery and detection limits were determined under two conditions: the vacuum cleaner dust was spiked with known amounts of pesticides and the filter paper spiked with known amounts of pesticides. Two grams of dust were spiked with 0.1 mL of an acetone solution containing 2, 5, or 10 µg of each nonacid pesticide. Samples were mixed and kept for 1 h at room temperature in order to allow for the adsorption of pesticides. Samples were then extracted, cleaned up with SEC, and analyzed by GC–MS as previously described. The matrix-matched standard solutions were used to determine the amount recovered for each pesticide in the spiked dust. The percentage of the recovery was calculated. Also, dust (2–20 g) was spiked with 0.1 mL of the acetone solution containing each acid pesticide in the amount of 0.5 or 5 µg. The spiked samples went through extraction, SPE cleanup, methylation, and GC–MS analysis as previously described. Calibration solutions were used to quantitate the amount of each acid pesticide recovered by extraction, and the recovery was calculated.

Filter paper (Type 1, Whatman) was spiked with 0.1 mL acetone solution containing each nonacid pesticide in the amount of 0.025, 0.25, or 2.5 µg. The spiked filter paper was extracted with acetone by submerging it in a 250-mL Erlenmeyer flask and shaking it for 5 min at 120 rpm. After two repetitions of the extraction, the extract was condensed to 0.5 mL and analyzed by GC–MS, and the recovery for each pesticide was calculated. In order to determine the recovery of the carboxylic acid pesticides from filter paper, each filter-paper specimen was spiked similarly with a 0.1-mL acetone solution containing each acid pesticide in the

Table I. Retention Time of Nonacid Pesticides Using SEC Under Different Conditions*

Mobile Phase	Flow rate (mL/min) 0.5	1	1.5	2
Chloroform, $CHCl_3$	14.6 to 17.15	7.20 to 9.04	5.01 to 6.18	–
Chloroform–dichloromethane (1:3)	14.35 to 17.33	–	5.00 to 6.16	–
Dichloromethane, CH_2Cl_2	14.31 to 17.42	7.22 to 9.04	4.95 to 6.16	3.70 to 4.92
Chloroform–methanol (3:1)	15.0 to 18.50	–	5.05 to 6.24	–
Dichloromethane–cyclohexane (1:3)	15.23 to 18.67	7.51 to 9.27	5.13 to 6.37	–
Dichloromethane–hexane (1:1)	–	7.63 to 9.51	5.30 to 6.59	–

* The injection volume for SEC was 100 µL, and the concentration of each pesticide was 50 mg/L.

amount of 0.5 or 5 µg. The four acid pesticides spiked on the filter paper were recovered and analyzed as detailed previously. The recovery of each pesticide was then calculated.

The detection limit for each nonacid pesticide (milligrams of pesticide per kilogram of dust) was taken as the minimum detection limit for GC–MS in the SIM mode on the matrix-matched solutions of the pesticide standards following the standard convention. The minimum detection limit was the minimum concentration needed to generate a signal-to-noise ratio of 5:1. The detection limit for each carboxylic acid pesticide (milligrams of pesticide per kilogram of dust) was determined using a method similar to that used by Roinestad et al. (16). Twenty grams of blank dust (which was considered as a matrix) were extracted as per protocol III. The acid pesticide standards (0.05 µg each) were spiked right before methylation in order to make matrix-matched standards. The detection limit was calculated from the minimum detection limit for GC–MS in the SIM mode on the matrix-matched solution of four acid pesticide standards. Again, the minimum detection limit was the minimum concentration needed to generate a signal-to-noise ratio of 5:1.

Results and Discussion

Nonacid pesticides

An analytical method used to analyze the dichloromethane–cyclohexane (3:1) extract of dust for nonacid pesticides by GC–MS was developed first without preliminary cleanup procedures. It was simple and easy to perform. However, we found that the injection-port liner needed to be changed and the front 10 to 20 cm of the guard column connected to the injection port had to be cut off after approximately every 20 samples in order to eliminate the residual deposits from compounds present in the sample extract for the purpose of maintaining the quality of the analyses. If this was not done, the GC–MS responses would have been significantly decreased. Clearly, a cleanup method was required.

Table II. Retention Time of Each Pesticide* Using SEC†

Pesticide	Retention time (min)	MW (cu)
Methamidophos	6.12	141
Benzophenone‡	5.21	180
Carbaryl	5.82	201
Atrazine	5.91	215
Methyl parathion	5.25	263
Alachlor	5.21	270
2,4-D-Butyl ester	5.44	276
Pendamethalin	5.34	281
Metolachlor	5.16	284
Diazinon	5.17	304
Malathion	4.85	330
Tetramethrin	4.92	331
Trifluralin	5.14	335
Resmethrin	5.02	338
Chlorpyrifos	5.35	351

* Presented in order of MW. Injection volume for SEC was 100 mL, and concentration of each pesticide was 100 mg/L.
† Mobile phase: dichloromethane at 1.5 mL/min.
‡ Also assigned to be the internal standard.

SEC cleanup of extract

Because the dust extract was difficult to analyze directly by GC–MS as a result of various interfering substances, we tried SEC to remove larger competing molecules. Several conditions were necessary in order to satisfactorily clean up the extracts. We found that the cross section of the HPLC outlet tubing was large enough so that the SEC effluent accumulated on it; therefore, the substances separated by SEC were remixed. This was resolved by connecting a 26-gauge stainless steel needle to the outlet in order to force the SEC effluent into a very thin stream instead of drops, which we then collected at more accurate time intervals. We also found that because most of the condensed dust extracts were viscous, the autosampler could not determine an accurate volume when using a drawing speed of 400 µL/min. This was resolved by reducing the drawing speed to 100 µL/min.

Five to ten micrograms of each nonacid pesticide was injected for each run during the SEC optimization because the DAD detector could easily detect all fourteen pesticides at these amounts. Different mobile phases and flow rates were tested in order to optimize the separation of nonacid pesticides from the matrix substances of the dust samples. The retention times of the pesticides decreased slightly with the increase of solvent polarity, which meant that the adsorption of pesticides onto the column stationary phase was not significant (Table I). Also, the retention times decreased significantly when the flow rates increased (Table I). The effluent was collected in a time range of 1 min longer than the pesticide retention time range that was obtained under the SEC conditions. The collected effluent was condensed to 0.2 mL and injected to the GC–MS in order to determine if there were peaks resulting from dust substances that fused or overlapped with the pesticide peaks or if the chromatographic baseline was acceptable for the analysis. The GC–MS analysis indicated that the cleanup of the interfering dust substances was acceptable when the SEC had a flow rate of 1.5 mL/min. However, a further decrease of the SEC flow rate to 1 or 0.5 mL/min did not make a difference in the cleanup.

In evaluating different solvent systems for the mobile phase of the SEC cleanup, we found that dichloromethane with its lower boiling point was more easily condensed than chloroform or methanol. Using dichloromethane without methanol also avoided the possibility of the transesterification of some of the ester pesticides such as the organophosphates, 2,4-D-butyl ester, and the pyrethroid pesticides. The separation between the pesticides and matrix substances did not improve when dichloromethane–cyclohexane (1:3) or dichloromethane–hexane (1:1) was used as the mobile phase.

Using a mobile phase of dichloromethane and a flow rate of 1.5 mL/min, we observed that the selected nonacid pesticides had only one SEC peak with a retention time between 4.8 to 6.2 min (Tables I and II). When the molecular weight of a pesticide was more than approximately 258 cu, the SEC retention time was less than 5.5 min. When the molecular weight of a pesticide was less than approximately 258 cu, the SEC retention time was more than 5.5 min. These results obeyed the general rule that larger-

size molecules move faster on the SEC column. Therefore, the optimized conditions for SEC were that the mobile phase was dichloromethane, the flow rate 1.5 mL/min, and the effluent collection interval from 4.3 to 8 min. The injection volume was set at a maximum of 100 µL because the dust samples contained substances that exceeded the SEC capacity if larger amounts were used.

GC optimization

Eight different GC columns were tested in order to find the optimum one based on the separation and abundance of the detection responses of the analytes. The optimized conditions are listed in Table III, and corresponding chromatograms are presented in Figures 1A to 1H. The best column was RTX-200MS (30-m × 0.25-mm i.d., 0.5-µm film thickness) with a stationary phase of trifluoropropylmethyl polysiloxane. There was still one overlapping pair of compounds (pendamethalin and 2,4-D-butyl ester), which had to be identified and quantitated by their characteristic MS fragment ions (Table IV). Three characteristic MS fragment ions of each pesticide were used for the SIM mode in order to achieve a higher GC–MS response to the pesticide (Table IV).

Many dust extracts had GC–MS peaks with the same retention time and MS fragment ions as benzophenone. The peak areas, however, varied from sample to sample (data not presented). Thus benzophenone is not recommended for use as an internal standard, so we used external standards in the final methodology.

The matrix substances in the dust were not completely separated from pesticides by SEC or running GC–MS in the scan mode. The SIM mode in GC–MS or the "extract ion chromatogram" function in Chemstation software (Agilent Technologies) had to be used in order to avoid interference from the dust substances. The latter was also used to quantitate pendamethalin and 2,4-D-butyl ester because of their GC–MS peaks being fused together.

Splitless injection was chosen because split injection and on-column injection are generally much less tolerant of interfering substances in samples (17,18). Responses doubled when the injection volume increased from 1 to 2 µL and increased only slightly when the injection volume was increased to 4 µL. The injection volume was finally set at 2 µL in order to obtain a high response and avoid loading too much matrix substance onto the GC. Filling the double- or single-taper glass injection liner with deactivated glass wool (Supelco) or Carbofrit (Restek) more-efficiently retained the matrix substances inside the liner; however, the GC–MS response decreased rapidly after several injections.

Table III. GC Columns and Their Optimized Conditions

	Column	Optimized column head-pressure and temperature program	Undetectable	Peaks overlapped
Figure 1A	SPB-608 (Supelco), 30-m × 0.25-mm i.d., 0.25-µm film, 35% diphenyl–65% dimethyl polysiloxane	172 kPa, 40°C (1 min) to 280°C (6 min) at 10°C /min	methamidophos	atrazine and diazinon, malathion and carbaryl and alachlor
Figure 1B	DB-5 (J&W), 30-m × 0.25-mm i.d., 0.25-µm film, 5% phenyl–95% dimethyl polysiloxane	124 kPa, 50°C (1 min) to 100°C at 25°C/min, then to 260°C at 5°C/min	chlorpyrifos, methamidophos, metolachlor	malathion and metolachlor
Figure 1C	HP-5 (Agilent), 30-m × 0.20-mm i.d., 0.33-µm film, 5% phenyl–95% dimethyl polysiloxane	241 kPa, 40°C (1 min) to 180°C (21 min) at 30°C/min, then to 280°C (2 min) at 20°C/min	methamidophos, carbaryl, methyl parathion, 2,4-D-butyl ester	none
Figure 1D	PTA-5 (Supelco), 30-m × 0.25-mm i.d., 0.1-µm film, 5% phenyl–95% dimethyl polysiloxane	172 kPa, 40°C (1 min) to 180°C (7 min) at 30°C/min, then to 300°C (10 min) at 20°C/min	diazinon	carbaryl and alachlor, metolachlor and chlorpyrifos, benzophenone and 2,4-D-methyl ester
Figure 1E	HP-1 (Agilent), 12-m × 0.2-mm i.d., 0.33-µm film, dimethyl polysiloxane	138 kPa, 40°C (1 min) to 180°C (10 min) at 30°C/min, then to 200°C (5 min) at 30°C/min	pendamethalin, metolachlor	methylparathion and carbaryl and alachlor, benzophenone and 2,4-D-butyl ester
Figure 1F	RTX-200 (Restek), 60-m × 0.25-mm i.d., 1-µm film, trifluoropropylmethyl polysiloxane	345 kPa, 40°C (1 min) to 195°C (6 min) at 30°C/min, then to 210°C (28 min) at 30°C/min, then to 300°C (26 min) at 35°C/min	none	malathion and metolachlor (not completely separated)
Figure 1G	RTX-200 (Restek), 30-m × 0.25-mm i.d., 1-µm film, trifluoropropylmethyl polysiloxane	172 kPa, 80°C (0 min) to 300°C (5 min) at 30°C/min	none	carbaryl and metolachlor
Figure 1H	RTX-200MS (Restek), 30-m × 0.25-mm i.d., 0.5-µm film, trifluoropropylmethyl polysiloxane	103 kPa, 80°C (0 min) to 300°C (5 min) at 30°C/min	none	carbaryl and metolachlor

The retained matrix substances acted as catalysts for the pyrolysis of analytes in the injection port. Therefore, the fillings were not used.

The injection temperature was tested at 200°C, 220°C, and 260°C in order to optimize GC–MS sensitivity and reproducibility for nonacid pesticides in the dust extract with dichloromethane–cyclohexane (3:1) as the solvent. Although the GC–MS responses were slightly higher at 260°C than other injection temperatures, the variation between injections at 260°C was higher than those observed at other temperatures and the GC–MS response decreased gradually when repeating the injection at the same conditions. A brown deposit of substances from the extract became visible inside the glass injection liner after approximately 10 injections, which could cause the degradation of pesticides and a possible decrease in the GC–MS responses. The injection temperature was set at 220°C in order to ensure the proper vaporization of analytes and minimize the degradation of analytes in the injection port.

Extraction procedures

Acetone, methanol, acetonitrile, dichloromethane, and ethyl acetate were evaluated for extraction by shaking. The GC–MS response decreased significantly after 1 or 2 injections of the dust extract using acetone, methanol, acetonitrile, or dichloromethane as the extraction solvent. These extracts contained too many interfering matrix substances. Using these extraction solvents, the compounds that were interfering with the GC–MS analyses could not be removed with the SEC cleanup procedures

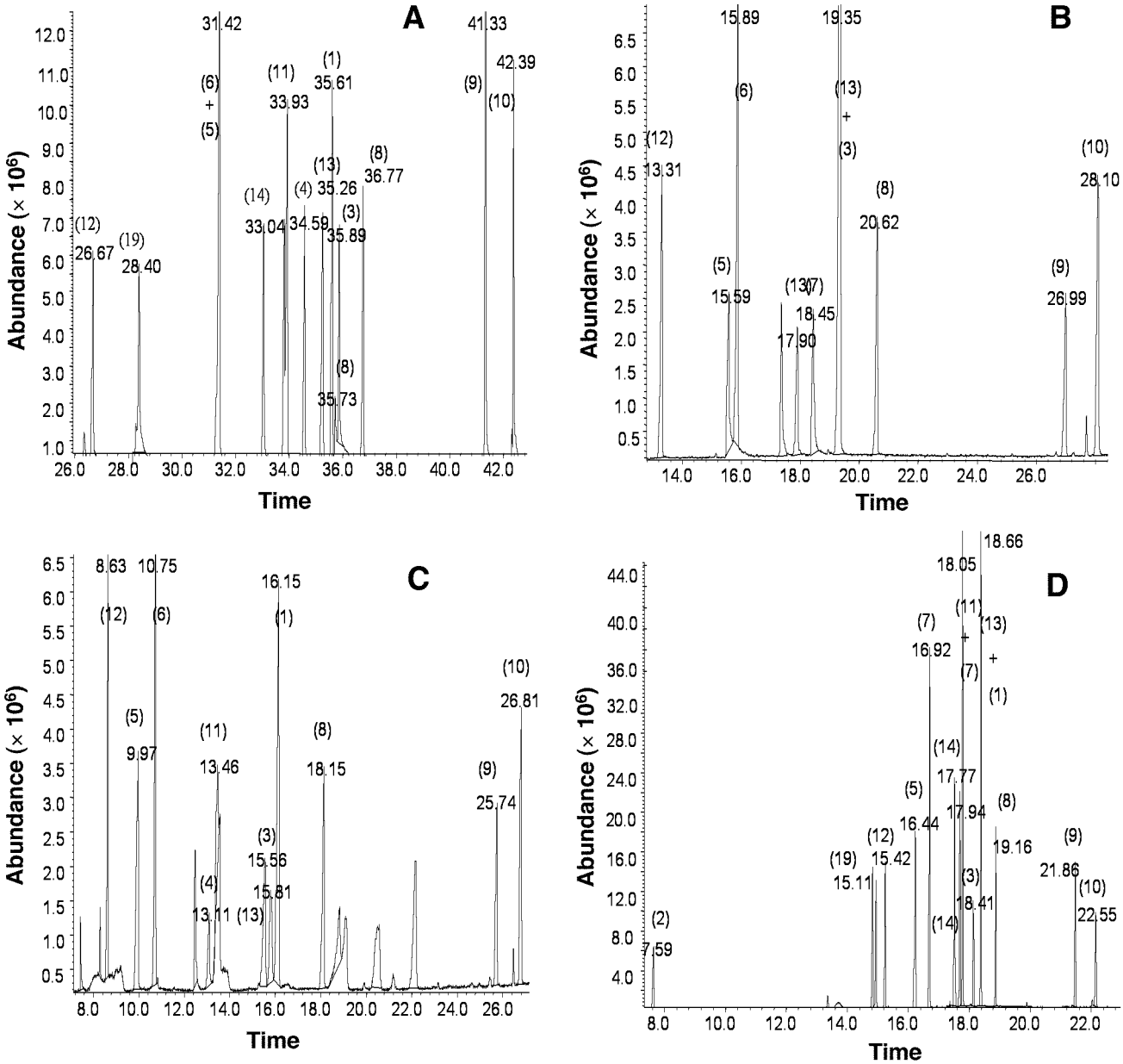

Figure 1. GC–MS chromatograms of pesticides on different columns that are listed in Table III. The concentrations of the pesticides in acetone are 5 mg/L for chromatogram G, 1 mg/L for chromatogram H, and 100 mg/L for all other chromatograms. The pesticides detected in each chromatogram are represented by the numbers assigned to them in Tables IV and VIII.

developed (Table I). Furthermore, extracts with acetone, methanol, or dichloromethane could only be filtered through a 0.2-µm nylon filter when the pressure was more than 400 kPa or a 0.45-µm nylon filter with glass-fiber prefiltration when the pressure was more than 150 kPa. In general, this was difficult to perform. However, acetonitrile extract passed easily through the latter filter. The cyclohexane extract did not have the interfering substances and passed through the filters easily, but the extraction efficiency for many pesticides was poor (data not shown).

Based on these results, the weaker solvent (cyclohexane) was added to ethyl acetate in order to decrease the solvent strength of the shaking extraction solvent and allow for easy filtering. When the ratio of ethyl acetate to cyclohexane was decreased to 3:1, we found that SEC with a mobile phase of dichloromethane and a flow rate of 1.5 mL/min was successful in cleaning up the interfering compounds in the unspiked/blank extract in which we found atrazine, methyl parathion, and resmethrin at 0.44, 0.078, and 0.051 µg/g dust, respectively (Figure 2). Using the matrix-matched calibration solutions, we compensated for the pesticide residues in the blank dust for the recovery tests. These conditions also were found to clean up the ethyl acetate–cyclohexane (3:1) extract from the dust specimen spiked with the 14 pesticides (Figure 1H).

GC–MS results on matrix samples after SEC cleanup

When ethyl acetate–cyclohexane (3:1) was used as the extracting solvent under the optimized conditions of extraction and SEC cleanup, recoveries of most pesticides were between 72% and 110% with a variation between 4.2% and 25.6% (Table VI) without the interference of other substances. The detection limit for this method was between 10 and 50 ng for each pesticide per gram of dust, depending on the pesticide. Concentrations of matrix-matched standard solutions were linear to the GC–MS peak areas for all nonacid pesticides (Table V).

Acetone efficiently extracted the pesticides spiked onto the filter paper (Table VII). These results are important for analyzing filter

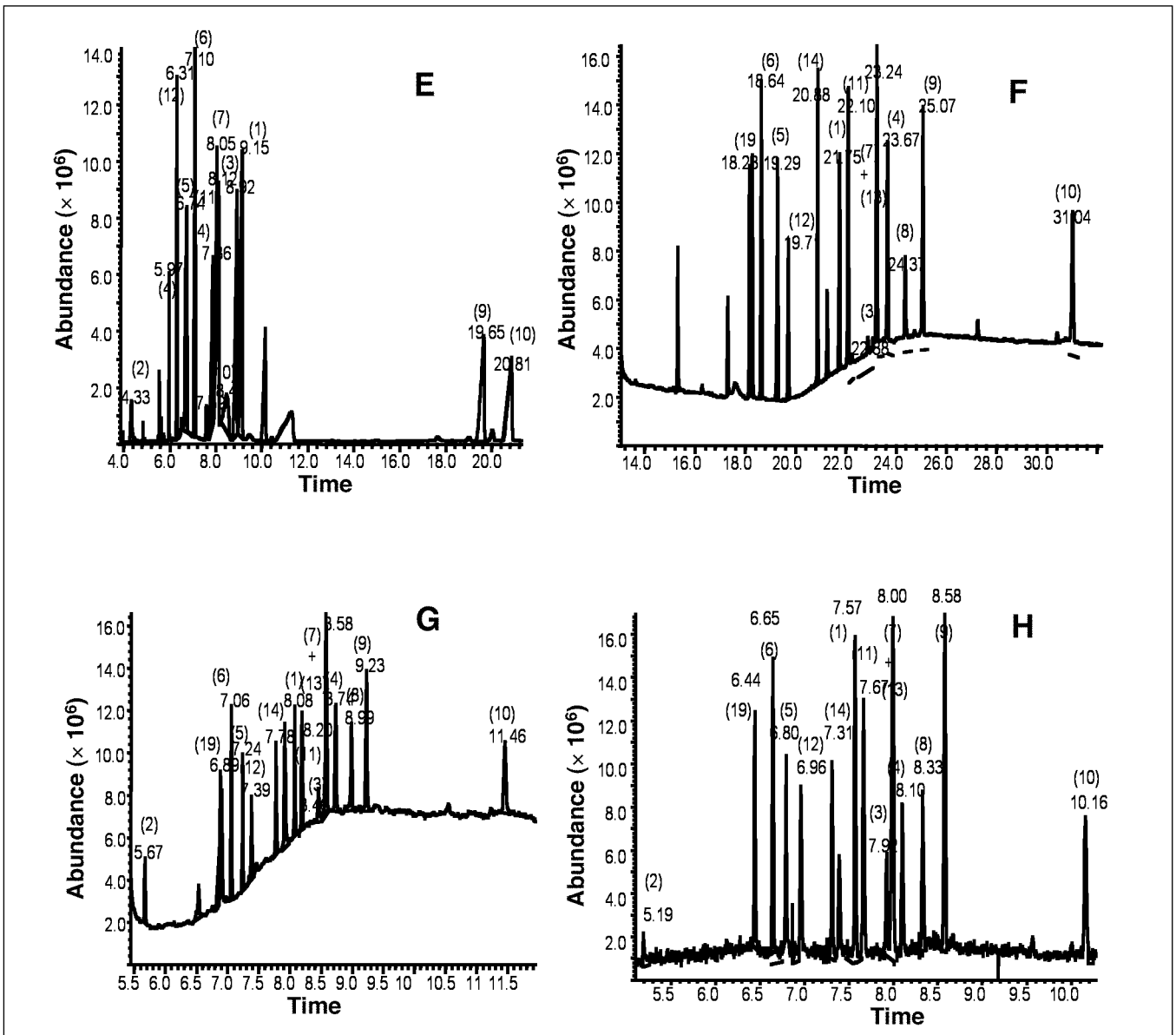

Figure 1. *(Continued)*

papers that have been used to sample settled particulates containing pesticides and for those filter papers that have been used to wipe household surfaces.

Carboxylic acid pesticides

The published method of methylating carboxylic acids with TMS for GC analysis was carried out in benzene–methanol in a 4:1 ratio with excess TMS (7,8,11). The TMS residue in the solution generated a strong background on GC–MS, which decreased the signal-to-noise ratio and caused the column to bleed. In order to eliminate the excess TMS, the solution was completely dried after methylation (7,8,11). However, a significant loss in 2,4-D-methyl ester (approximately 35%) was observed after a complete drying with nitrogen. Therefore, the complete evaporation of the solution after methylation with TMS was avoided. When benzene was replaced by methanol, the yellow color of TMS disappeared in 0.5–1 h during the methylation, and the background of the GC–MS chromatogram was well-defined. In addition, when benzene–methanol was used as the solvent, there was an unknown peak generated from TMS methylation that could only be partially separated from the peak of 2,4-D-methyl ester on the RTX-200MS column. Therefore, only methanol was used as the solvent for methylation for the remainder of the experiments.

Using the capillary column with the trifluoropropylmethyl stationary phase (RTX 200MS) and optimized GC conditions, methyl esters of the four acid pesticides were completely separated in 15 min. Sensitivity for each pesticide was better than 50 pg under

Table IV. Characteristic Fragments on GC–MS with Electron-Impact Ionization of Pesticides and Benzophenone

Pesticide	Base peak (*m/z*)	Ions for SIM*
Chlorpyrifos (1)	197	197, 199, 97
Methamidophos (2)	94	94, 141, 111
Malathion (3)	125	125, 173, 93
Methylparathion (4)	125	125, 109, 263
Atrazine (5)	200	200, 173, 215
Diazinon (6)	137	137, 179, 199
Carbaryl (7)	144	114, 115, 127
Pendamethalin (8)	252	252, 192, 162
Resmethrin (9)	123	123, 143, 171
Tetramethrin (10)	164	164, 123, 107
Alachlor (11)	160	160, 188, 146
Trifluralin (12)	306	306, 264, 290
Metolachlor (13)	162	162, 238, 146
2,4-D-Butyl ester (14)	185	185,175, 162
Benzophenone† (19)	77	77, 105, 182

* The order for listing is the order of the fragment ion abundance.
† Also assigned to be the internal standard.

Table V. Calibration Equations Obtained from Matrix-Matched Standard Solutions*

Pesticide	Equation	Range (mg/L)	R^2
Chlorpyrifos	$y = 3.2432x + 0.0202$	0.05–5	0.9932
Methamidophos	$y = 1.0234x + 0.0432$	0.1–5	0.9593
Malathion	$y = 0.4542x + 0.0342$	0.05–5	0.9766
Methylparathion	$y = 2.965x + 0.0576$	0.05–5	0.9887
Atrazine	$y = 1.145x + 0.1215$	0.05–5	0.9901
Diazinon	$y = 3.6521x + 0.0364$	0.05–5	0.9962
Carbaryl	$y = 1.5326x + 0.0854$	0.05–5	0.9679
Pendamethalin	$y = 3.5428x + 0.0765$	0.05–5	0.9691
Resmethrin	$y = 3.2634x + 0.0764$	0.05–5	0.9801
Tetramethrin	$y = 2.164x + 0.0236$	0.05–5	0.9726
Alachlor	$y = 5.3421x + 0.0542$	0.05–5	0.9894
Trifluralin	$y = 3.124x + 0.0512$	0.05–5	0.9620
Metolachlor	$y = 3.298x + 0.0197$	0.05–5	0.9843
2,4-D-butyl ester	$y = 3.012x + 0.0653$	0.05–5	0.9652

* Each equation was obtained by regressing concentrations (*y*) versus GC–MS SIM responses (*x*) for the four matrix-matched standard solutions that had different concentrations.

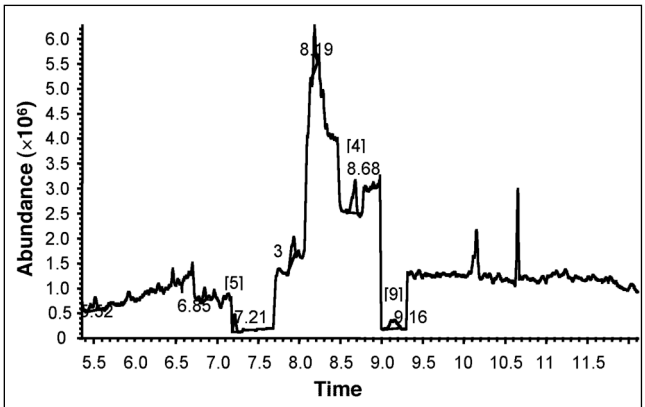

Figure 2. GC–MS chromatogram in SIM mode for a blank/unspiked dust sample extract cleaned by SEC using optimized conditions for both SEC and extraction. The pesticides detected in the chromatogram are represented by the numbers assigned to them in Tables IV and VIII.

Table VI. Recoveries Of Nonacid Pesticides from Dust Extracts Cleaned Up By SEC*,†

Pesticide	Detection limit (ng/g of dust)	Recovery from 10 µg/2g of dust	Recovery from 5 µg/2g of dust	Recovery from 2 µg/2g of dust
Chlorpyrifos	10	85.9 ± 10.0	85.0 ± 6.3	82.5 ± 10.2
Methamidophos	25	88.2 ± 9.3	96.2 ± 17.6	90.2 ± 10.6
Malathion	50	81.2 ± 4.3	109.1 ± 15.1	84.8 ± 11.4
Methylparathion	25	72.6 ± 6.5	81.1 ± 9.9	86.2 ± 17.4
Atrazine	10	80.3 ± 6.6	85.5 ± 11.9	98.5 ± 16.5
Diazinon	10	83.4 ± 7.1	89.9 ± 14.3	77.9 ± 3.3
Carbaryl	10	87.4 ± 9.3	78.4 ± 5.1	90.1 ± 16.1
Pendamethalin	50	81.3 ± 9.2	91.9 ± 14.2	83.6 ± 12.9
Resmethrin	25	82.8 ± 5.9	79.2 ± 7.7	85.8 ± 8.9
Tetramethrin	25	81.5 ± 6.6	85.6 ± 5.9	83.6 ± 5.2
Alachlor	25	78.8 ± 5.1	94.5 ± 24.2	81.8 ± 6.7
Trifluralin	50	77.5 ± 4.0	73.2 ± 17.4	78.6 ± 11.4
Metolachlor	52	80.7 ± 11.9	88.1 ± 12.7	99.5 ± 9.1
2,4-D-butyl ester	25	88.2 ± 14.6	81.3 ± 12.4	96.6 ± 16.4

* The conditions for SEC were mobile phase as dichloromethane, flow rate at 1.5 mL/min, and effluent collection time of 4.3 to 8 min.
† Mean and standard deviations.

SIM mode. The GC–MS electron-ionization mass spectra were obtained for methyl esters of the four acid pesticides after methylation with TMS. The three most significant MS fragment ions for each pesticide were used to program the SIM mode for GC–MS (Table VIII). The GC–MS response in SIM mode was linear with the concentration of each of the four acid pesticides after methylation and were in the concentration range of 0.05 to 5 mg/L (Table IX).

The recovery of the four acid pesticides from dust was less than 30% when using protocol I (data not included). The removal of acetonitrile from the extract by rotary evaporation was time-consuming and hard to control, because acetonitrile distilled azeotropically with water. If a significant amount of acetonitrile was still in the extract, recoveries of the pesticides by SPE decreased. When using protocol II for the dust extraction, the pH of the extraction system had to be monitored and adjusted with the addition of acid or base in order to keep the pH near 12, because different dust samples have different acid–base properties and NaOH does not have the buffering capacity to control the pH. However, with protocol III, $Ca(OH)_2$ had the buffering capacity to

Table VII. Recovery of Each Pesticide Spiked on Filter Paper*

Pesticides	Each pesticide spiked (µg) 0.025	0.25	2.5
Chlorpyrifos	89.2 ± 9.9	103 ± 3.5	95.3 ± 5.4
Methamidophos	75.1 ± 10.1	80.2 ± 7.1	90.0 ± 14.2
Malathion	69.4 ± 12.2	89.2 ± 9.0	108 ± 17.5
Methylparathion	85.5 ± 8.8	87.3 ± 8.2	79.2 ± 8.6
Atrazine	108 ± 5.6	117 ± 3.2	87.5 ± 3.1
Diazinon	96.2 ± 9.1	99.1 ± 4.2	89.3 ± 8.2
Carbaryl	97.0 ± 8.6	81.0 ± 7.1	88.0 ± 12.3
Pendamethalin	112 ± 36.3	84.0 ± 6.5	95.0 ± 4.2
Resmethrin	80.2 ± 7.1	89.1 ± 9.7	75.0 ± 3.1
Tetramethrin	94.2 ± 8.2	91.0 ± 3.2	82.7 ± 5.4
Alachlor	91.6 ± 4.2	99.0 ± 5.1	112 ± 5.3
Trifluralin	68.0 ± 17.3	80.0 ± 1.1	77.2 ± 7.5
Metolachlor	85.0 ± 2.0	74.5 ± 2.2	98.4 ± 12.1
2,4-D-Butyl ester	80.6 ± 10.2	78.4 ± 3.2	92.1 ± 5.6

* Mean and standard deviations

Table VIII. Characteristic Fragments on GC–MS with Electron-Impact Ionization of the Methyl Esters of Carboxylic Pesticides

Pesticide	Base Peak (*m/z*)	Ions for SIM*
Picloram (15)	196	196, 198, 254
2,4-D-acid (16)	199	199, 175, 177
Dicamba (17)	203	203, 205, 188
Mecoprop (18)	169	169, 142, 228

* Presented in the order of the fragment ion abundance.

Table IX. Calibration Equations Obtained from Standard Solutions

Pesticide	Equation*	Range (mg/L)	R^2
Picloram	$y = 0.5542x + 0.0230$	0.05–5	0.9931
2,4-D-Acid	$y = 0.4869x + 0.0034$	0.05–5	09923
Dicamba	$y = 0.4753x + 0.0375$	0.05–5	0.9961
Mecoprop	$y = 0.5287x - 0.0065$	0.05–5	0.9908

* Each equation was obtained by linear regression using concentrations (y) versus the GC–MS SIM peak areas (x) for the five standard solutions with different concentrations.

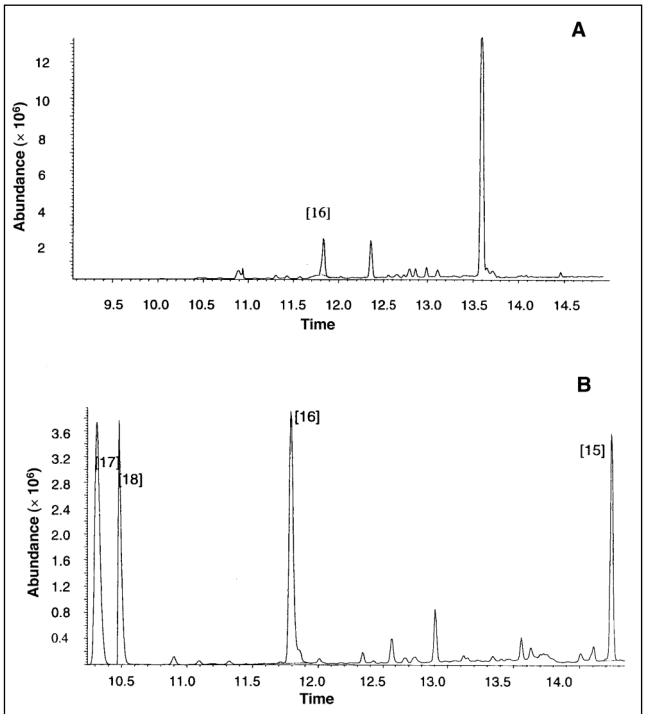

Figure 3. (A) GC–MS chromatogram in SIM mode for 2 g of the blank dust extracted with a saturated aqueous $Ca(OH)_2$ solution. The extract was cleaned up by SEC (Oasis HLB, 6 mL) and methylated with TMS. (B) GC–MS chromatogram in SIM mode for 2 g of dust spiked with 5 µg of each of the four acid pesticides extracted with a saturated aqueous $Ca(OH)_2$ solution. The extract was cleaned up by SEC (Oasis HLB, 6 mL) and methylated with TMS. The pesticides detected in each chromatogram are represented by the numbers assigned to them in Tables IV and VIII.

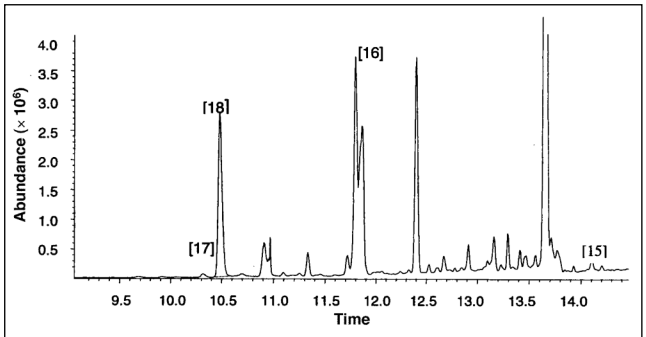

Figure 4. A typical GC–MS chromatogram in SIM mode for 2 g of an unknown dust sample extracted with a saturated aqueous $Ca(OH)_2$ solution. The extract was cleaned up by SEC (Oasis HLB, 6 mL) and methylated with TMS. The pesticides detected in the chromatogram are represented by the numbers assigned to them in Tables IV and VIII.

maintain the pH near 12 for the extraction. Chromatograms obtained from protocol III had low background and no interference from the blank dust or the spiked dust for the methyl esters of the four acids (Figure 3). Table X presents the recoveries of the pesticides from spiked dust when using protocol III for the extraction. Generally, the recoveries decreased and the variation of the recoveries increased as the amount of dust increased. The detection limit was higher for picloram than for the other pesticides (Table X). Figure 4 is a typical chromatogram for actual house dust samples. We found 2,4-D-acid, dicamba, and mecoprop in this sample.

Acid pesticides were efficiently extracted from filter paper using acidified acetone as the solvent (Table XI). This enabled the sensitive analysis of deposition from the air samples and wipes of household furnishings.

Conclusion

A capillary column with a stationary phase of trifluoropropylmethyl polysiloxane was the best for the simultaneous analysis of the nonacid pesticides targeted in this research. Several extracting solvents were tested in order to completely recover the pesticides and avoid interference from substances in the dust samples when analyzing by GC–MS. Both the extraction solvent and SEC parameters had to be optimized in order to achieve efficient recoveries of pesticides and avoid interference of matrix substances. The optimum extraction solvent of those evaluated was ethyl acetate–cyclohexane (3:1). The conditions for SEC were using dichloromethane as the mobile phase, 1.5 mL/min as the flow rate, an effluent collection interval from 4.3 to 8.0 min, and an injection volume of no larger than 100 µL. This method is relatively easy and fast to conduct. A variation of the pesticide recoveries might be decreased if sonication as described in EPA method 3350B (19) were to be substituted for shaking in future research. The four acid pesticides in household dust were efficiently extracted without interference from the TMS methylation when using a saturated aqueous $Ca(OH)_2$ solution. The methylation of carboxylic acid pesticides with TMS was quantitative and easy to perform.

Table X. Recoveries of Carboxylic Acid Pesticides from Dust*

		Detection limits (µg/g of dust)							
		0.004		0.002		0.002		0.002	
		Picloram		2,4-D-acid		Dicamba		Mecoprop	
Dust (g)	Pesticide (µg)	%Recovery	%CV	%Recovery	%CV	%Recovery	%CV	%Recovery	%CV
2	0.5	95.5	14.0	88.0	10.2	95.3	10.6	81.6	8.7
	5.0	100.7	6.3	105.8	11.8	100.9	9.6	103.9	14.1
10	0.5	70.5	11.2	80.4	18.3	63.6	13.5	64.4	15.8
	5.0	82.3	13.4	73.1	6.9	73.2	14.1	75.7	16.3
20	0.5	22.1	32.6	28.6	10.5	37.6	7.3	46.5	21.4
	5.0	41.2	25.8	43.3	25.6	53.8	17.3	37.8	31.6

* Average recoveries and coefficient of variance (CV) were obtained from triplicate samples. Recovery CV was the standard error divided by average recovery.

Table XI. Recoveries of Carboxylic Acid Pesticides Spiked to Filter Paper*

	Picloram		2,4-D-acid		Dicamba		Mecoprop	
Pesticide (µg)	%Recovery	%CV	%Recovery	%CV	%Recovery	%CV	%Recovery	%CV
0.5	103.4	10.1	113.4	12.0	87.8	13.4	97.2	8.9
5.0	95.4	5.4	90.8	7.4	97.4	4.5	110.3	10.5

* Average recoveries and coefficient of variance (CV) were obtained from triplicate samples.

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