Optimized Method Development of Large Volume Injection for GC/MS/MS of Food Pesticides

Application Note

Food Testing & Agriculture

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Abstract

The development and optimization of large volume injection (LVI) techniques for trace pesticide analysis in food matrices by GC/MS/MS is discussed. Excellent inertness provided by Agilent Ultra Inert liners with wool and an Agilent J&W HP-5ms Ultra Inert GC column ensures the accurate and precise delivery of trace levels of pesticides from 5 µL food extracts in acetonitrile. Compared to hot splitless and cold splitless injections, the optimal LVI method demonstrates lower detection limits and better peak shapes for early eluting compounds.

Introduction

LVI techniques have gained wide attention for lowering system detection limits to meet newer and more stringent regulations. By introducing more sample into the system, the mass of analyte reaching the detector will be proportionately increased, resulting in larger peak area and peak height. If the baseline noise stays constant, larger peak height means greater signal-to-noise ratios and lower system detection limits. With properly optimized injection conditions, chromatography issues caused by large sample volume, such as distorted analyte peaks and long solvent tailing, can be minimized. Another advantage of LVI is the decrease in solvent that reaches the detector. In LVI, the solvent is carefully evaporated and vented from the inlet before the analytes are transferred to the analytical column. As a result, solvent impact on chromatography is greatly reduced, especially for solvents that do not wet the typical 5% phenol stationary phase well, such as acetonitrile [1].

Agilent Technologies

The Agilent Multimode Inlet (MMI) incorporates different injection modes into 1 inlet by using the same consumables and inlet liner. Its operational modes include hot split/splitless (also in pulsed mode), cold split/splitless (also in pulsed mode), and solvent vent [2]. In this application note, LVI refers to the solvent vent mode.

The Agilent Ultra Inert liner with wool provides extreme inertness for the trace analysis of labile pesticides in food matrices, as well protecting the analytical column and MS ion source [3, 4]. With the excellent selectivity and sensitivity of the Agilent GC/MS/MS system, the 5 ng/mL detection limit of analytes in matrix is easily achieved using a 1 µL hot splitless injection. Many pesticides have detection limits as low as 1 ng/mL. These limits typically meet the Maximum Residue Level (MRL) for pesticide residue requirements in most food commodities. However, recent concern regarding pesticide residues in baby food, and their potential role in disrupting the endocrine system's normal function, push pesticide detection limits to even lower levels.

This application note describes an optimized method for lowering GC/MS/MS detection limits by LVI in solvent vent mode. The completely deactivated wool in the Ultra Inert liner increases the surface area on which sample can deposit during slow sample injection in LVI, which improves solvent vaporization during solvent vent. The wool also provides better analyte delivery to the analytical column as well as being a barrier that traps the nonvolatile matrix interferences to protect the GC column and MS ion source [3, 4]. This trapping characteristic is very important for successful large volume injections of complex food extracts, because the solvent vent procedure removes the solvent but leaves a large amount of sample matrix in the liner. Without the wool in the liner, the matrix interferences can easily enter and accumulate on the column and even the MS ion source, which quickly result in column deterioration and ion source contamination.

Experimental

The standards, sample matrix preparation, and experimental conditions generally followed a previous study [4]. A representative group of 33 challenging pesticides were selected for this work. A 10 ng/mL standard solution was used for LVI method development and optimization. The optimal LVI method was then compared with hot splitless and cold splitless injection methods using Ultra Inert liners. A pepper matrix blank, prepared using an Agilent QuEChERS protocol, was used for pesticide analysis evaluation in a food matrix.

Chemicals and reagents

All reagents and solvents were HPLC or analytical grade. Acetonitrile (ACN) was from Honeywell B&J (Muskegon, MI, USA). Ultra Resi-analyzed-grade acetone was from J.T. Baker (Phillipsburg, NJ, USA). Acetic acid was from Sigma-Aldrich (St Louis, MO, USA). The pesticide standards and internal standard (triphenyl phosphate, TPP) were purchased from Sigma-Aldrich (St Louis, MO, USA), Chem Service (West Chester, PA, USA), or Ultra Scientific (North Kingstown, RI, USA).

Solutions and standards

A 1% acetic acid in ACN reagent blank solution was prepared by adding 1 mL of glacial acetic acid to 100 mL ACN. This solution was also used as the extraction solvent for the QuEChERS protocol. Pesticide standard spiking solution (20 µg/mL) and internal standard (IS) spiking solution were used [4]. A 500 ng/mL intermediate standard solution in reagent blank was made to accurately spike 10 ng/mL testing standard solution. Because this 10 ng/mL testing standard solution was for method development, IS was not added. All standard solutions were stored at 4 °C.

Pepper blank extracts were used to prepare a series of 1 to 100 ng/mL five-point calibration standards, and 10 ng/mL and 1 ng/mL QC samples were spiked in the matrix blank [4].

Instrumentation

All analyses were done on an Agilent 7890 GC equipped with an Agilent 7693B Automatic Sampler, and an Agilent 7000 Series GC/MS Triple Quadrupole system [4]. An Agilent J&W HP-5ms Ultra Inert GC column was used to provide analyte separation and a highly inert flow path to the detector. Table 1 lists the instrument parameters, except MMI conditions, and Table 2 shows the Agilent supplies. MRM transition settings were published previously [3, 4]. Backflushing was used because it significantly shortens analysis time for samples that contain high-boiling matrix residues and reduces system maintenance [5, 6].

Table 1. Instrument parameters for the Agilent GC/MS/MS system.

GC	Agilent 7890 Series
Autosampler	Agilent 7693 Automatic Sampler and sample tray 10 µL syringe (p/n 5181-3360) Pre injection solvent A (acetone) washes: 3 Post injection solvent B (acetonitrile) washes: 3 Sample pumps: 3
Carrier gas	Helium, constant pressure
Inlet	Multimode Inlet (MMI)
Oven profile	75 °C for 2.57 min, to 150 °C at 50 °C/min, to 200 °C at 6 °C/min, to 300 °C at 16 °C/min, hold for 1 min
Post run	3 min at 300 °C
Capillary Flow Technology	Purged Ultimate Union used for backflushing the analytical column and inlet Aux EPC gas: Helium plumbed to Purged Ultimate Union
Bleed line	0.0625 in od x 0.010 in id x 100 cm, 316 SS tubing, on top of the oven (p/n 0100-2354)
Aux pressure	4 psi during run, 75 psi during backflushing
Analytical column	Agilent J&W HP-5ms Ultra Inert, 0.25 mm x 15 m, 0.25 µm (p/n 19091-431UI)
Column connections	Between inlet and Purged Ultimate Union
Restrictor	Inert fused silica tubing, 0.15 mm x 650 mm (p/n 160-7625-5)
Restrictor connections	Between Purged Ultimate Union and the MS
MS	Agilent 7000 Series GC/MS Triple Quadrupole
Mode	MRM
Transfer line temperature	300 °C
Source temperature	300 °C
Quad temperature	Q1 and Q2 = 150 °C
Solvent delay	2.57 min
Collision gas flows	Helium quench gas at 2.35 mL/min, N_2 collision as at 1.5 mL/min
MS resolution	MS1 and MS2 = 1.2 amu (low resolution or wide setting)

Table 2. Agilent supplies.

Vials	Amber, write-on spot, 100/pk (p/n 5182-0716)
Vial caps	Blue, screw cap, 100/pk (p/n 5182-0717))
Vial inserts	150 µL glass with polymer feet, 100/pk (p/n 5183-2088)
Septa	Advanced Green Non-Stick 11 mm, 50/pk (p/n 5183-4759)
Column ferrules	0.4 mm id, 85/15 Vespel/graphite, 10/pk (p/n 5181-3323)
Liner O-rings	Non-stick liner O-ring, 10/pk (p/n 5188-5365)
Capillary flow technology	Ultimate Union (p/n G3182-61580) Internal nut (p/n G2855-20530) SilTite metal ferrules, for 0.10 to 0.25 mm id columns, 10/pk (p/n 5188-5361)
Inlet liners	Ultra Inert deactivated single taper splitless liner with wool (p/n 5190-2293), 5/pk (p/n 5190-3163)

The versatile temperature programmability of the MMI performs hot/cold split/splitless and solvent vent injections. The optimized LVI settings, together with the hot splitless injection and cold splitless injection settings for comparison, are listed in Table 3.

Table 3. Agilent MMI parameters for different injection modes.

Parameter	Hot splitless	Cold splitless	Solvent vent (LVI)
Initial temperature (°C)	250	75	75
Initial time (min)	–	0.02	0.085
Rate (°C/min)	–	750	750
Final temperature (°C)	–	350	350
Vent flow (mL/min)	–	–	100
Vent pressure (psig)	–	–	2.5
Vent time (min)	–	–	0.085
Purge flow (mL/min)	60	60	60
Purge time (min)	1	1	2.57
Injection volume (µL)	1	1	5
Injection speed	Fast	Fast	69 µL/min
Cryo	Off	On (Air)	On (Air)
Cryo fault detection	Off	On	On
Cryo temperature (°C)	–	75	75

Results and Discussion

LVI method development and optimization

As a solvent elimination technique, LVI is a function of the solvent type, inlet temperature, vent flow of evaporation gas, and analyte boiling point. Furthermore, inlet pressure during evaporation, vent time, and inlet liner also have an impact on the rate of solvent removal and entire system performance. The optimization process of these parameters is discussed in detail.

LVI method development and optimization on MMI were initially based on the solvent elimination calculator integrated in the instrument control software. This calculator was designed to determine reasonable starting conditions for an LVI method. When the MMI is put into the programmed

temperature vaporizer (PTV) solvent vent mode, an additional button appears on the inlet screen, as shown in Figure 3 of the LVI tutorial [1]. On the first screen of the solvent elimination calculator (Figure 4 in LVI tutorial [1]), sample solvent, desired injection volume, and boiling point of the earliest eluting analyte need to be entered. The calculator uses these parameters to calculate the starting LVI conditions.

The QuEChERS sample preparation protocol has gained wide attention for multiresidue pesticide analysis in food in recent years. Because acetonitrile is the most common solvent for QuEChERS extraction, the method was developed and optimized based on acetonitrile. Although LVI can analyze up to 50 µL of sample in an MMI [1], 5 µL injection volume was used in this study due to the concern of excess sample matrix. The boiling point of the first eluting analyte was left at 150 °C, as suggested by the calculator. The next screen (Figure 5 in LVI tutorial [1]) showed calculated results and the five parameters that can be adjusted, including inlet temperature, vent flow, injected volume, vent pressure, and outlet pressure.

During the optimization process, it was noticed that early eluting analytes were more sensitive to the parameter settings, while the middle-to-late eluters did not show much difference. The early eluting pesticides usually have low boiling points, and so they tend to be more sensitive to the solvent evaporation conditions. Acetonitrile is not a suitable solvent for a nonpolar GC column such as the HP-5ms Ultra Inert. Due to the polarity difference, acetonitrile could not wet the stationary phase very well. This caused analyte peak splitting when using the oven program for solvent focusing, especially with the early eluters. As a result, the LVI optimization process was centered to achieve better recovery and peak shape of early eluting pesticides.

Vent flow

The calculator recommended 30 °C for inlet temperature. It was difficult to reach this temperature with air cooling, and so 70 °C was used during vent flow optimization. The calculated vent flow was 100 mL/min. However, vent flows of 50, 100, 150, and 300 mL/min were investigated.

Vent flow has a linear effect on solvent elimination, that is, higher vent flow provides faster solvent evaporation. However, fast solvent elimination can result in the loss of analytes, especially the more volatile compounds. The "suggested injection rate" is designed to leave a small amount of solvent in the liner at the end of the venting period to trap the more volatile analytes. Therefore, a faster injection rate is accompanied by higher vent flow. Figure 1 shows the chromatograms from four different vent flows. Higher vent flow of 100 and 150 mL/min showed more compact peak shape than lower vent flow of 50 mL/min, which indicated that faster solvent elimination (up to 150 mL/min) was helpful to prevent solvent-caused peak splitting. When vent flow goes too high, 300 mL/min, lower responses indicate loss of analytes. As 100 and 150 mL/min vent flow gave similar results, 100 mL/min was selected due to less risk of analyte loss.

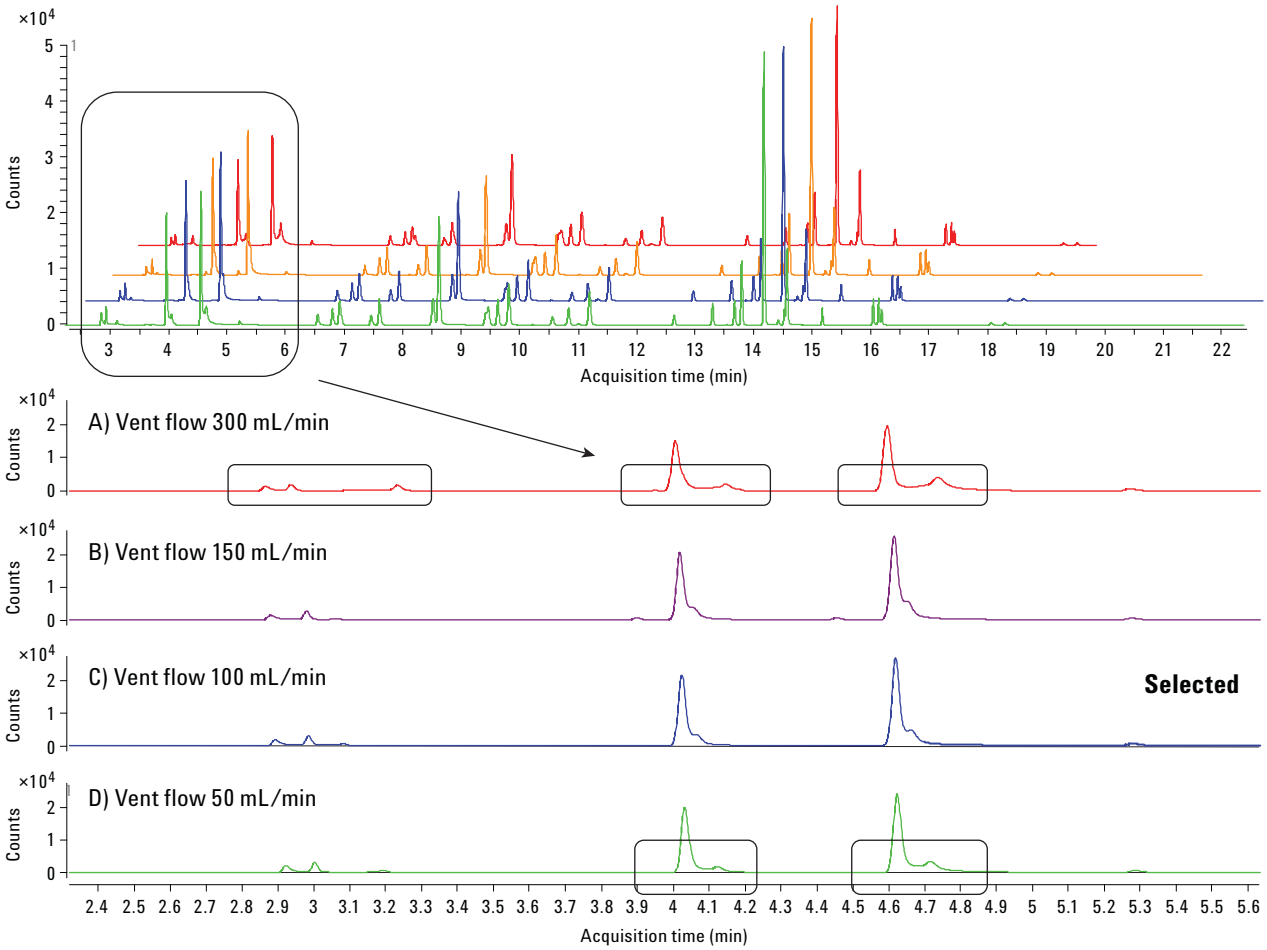

Figure 1. Vent flow optimization study using 5 µL of 10 ng/mL pesticide standard solution. Vent flow of 100 mL/min was selected.

Vent pressure

Vent pressure affects how much solvent reaches the column during venting. Theoretically, the lower the vent pressure, the higher the elimination rate, and the faster the solvent evaporates. As the vent pressure is increased, more solvent can be loaded onto the column before the analytes are transferred. Vent pressures of 1, 2.5, and 5 psig were investigated, and the corresponding chromatograms are shown in Figure 2. Peaks with 2.5 and 5 psig vent pressure show more compact peak shape and slightly higher responses than peaks with 1 psig. As 2.5 and 5 psig generated similar results, 2.5 psig vent pressure was finally selected because lower vent pressure loads less solvent onto the column before analytes were loaded.

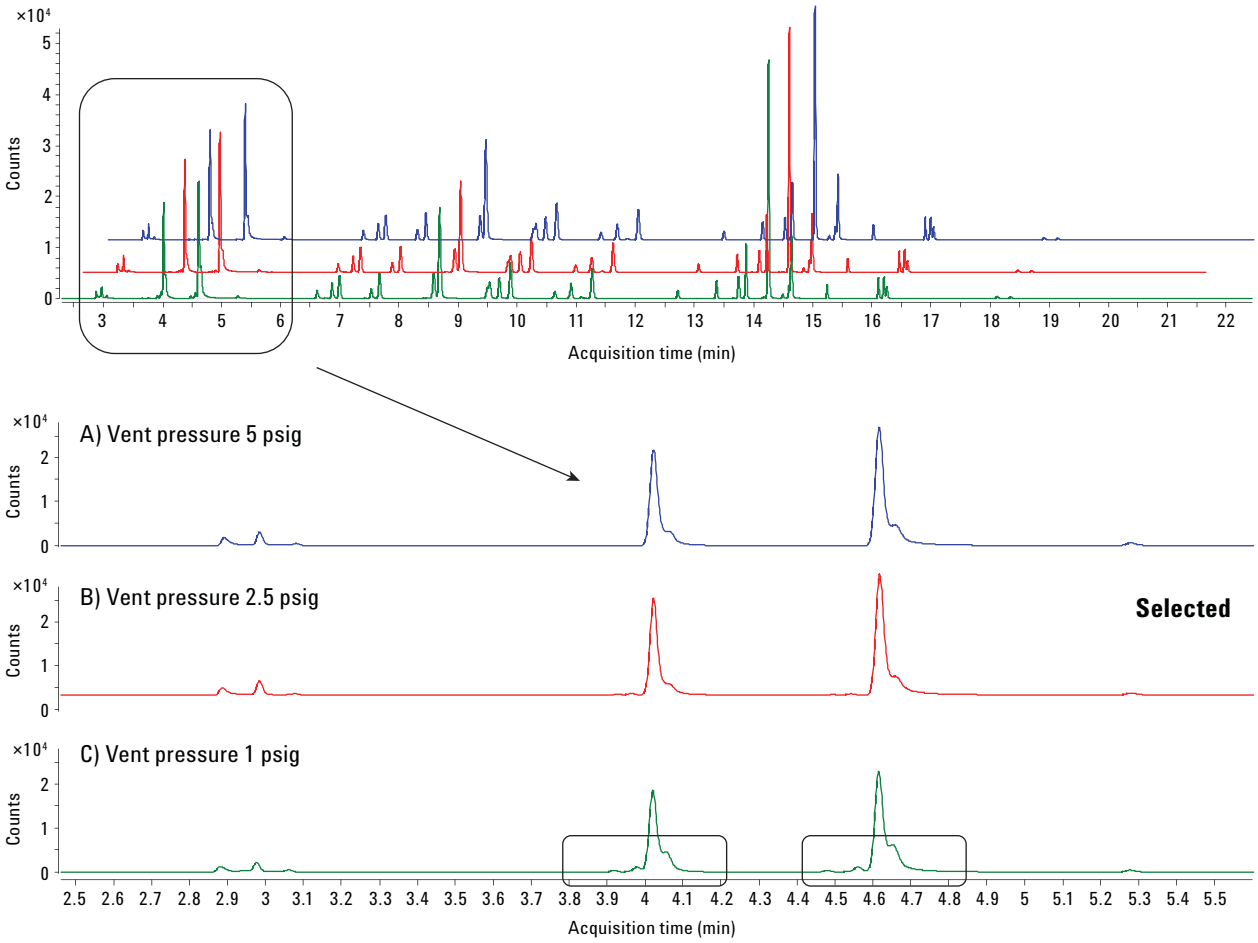

Figure 2. Vent pressure optimization study using 5 µL of 10 ng/mL pesticide standard solution. A vent pressure of 2.5 psig was selected.

Inlet temperature

The MMI used in this study can be cooled by liquid nitrogen or air. For simplicity, air was used as the coolant, and so a reasonable initial inlet temperature was 60 °C. Because the boiling point of acetonitrile is 82 °C, the initial inlet temperature cannot be higher or even close to the boiling point in solvent vent mode. Therefore, inlet temperatures of 60, 70, and 75°C were tested. Figure 3 shows the chromatograms acquired under different inlet temperatures.

Inlet temperature has a significant impact on elimination rate. A small change in inlet temperature can result in a big difference in the elimination rate. The higher the inlet temperature, the higher the elimination rate, and the faster the solvent evaporates. Relatively fast solvent evaporation can reduce the acetonitrile solvent effect on peak shape, but too fast evaporation will cause sample loss of early eluting analytes. Typically, the inlet temperature should not exceed 5 °C below solvent boiling point to achieve satisfactory recovery. Figure 3 shows peak splitting improved significantly as the inlet temperature increased. Setting the inlet temperature at 75 °C almost removed peak splitting or peak shoulder, and the early eluting peaks showed the best peak shape so far without losing response. As a result, an inlet temperature of 75 °C was used subsequently.

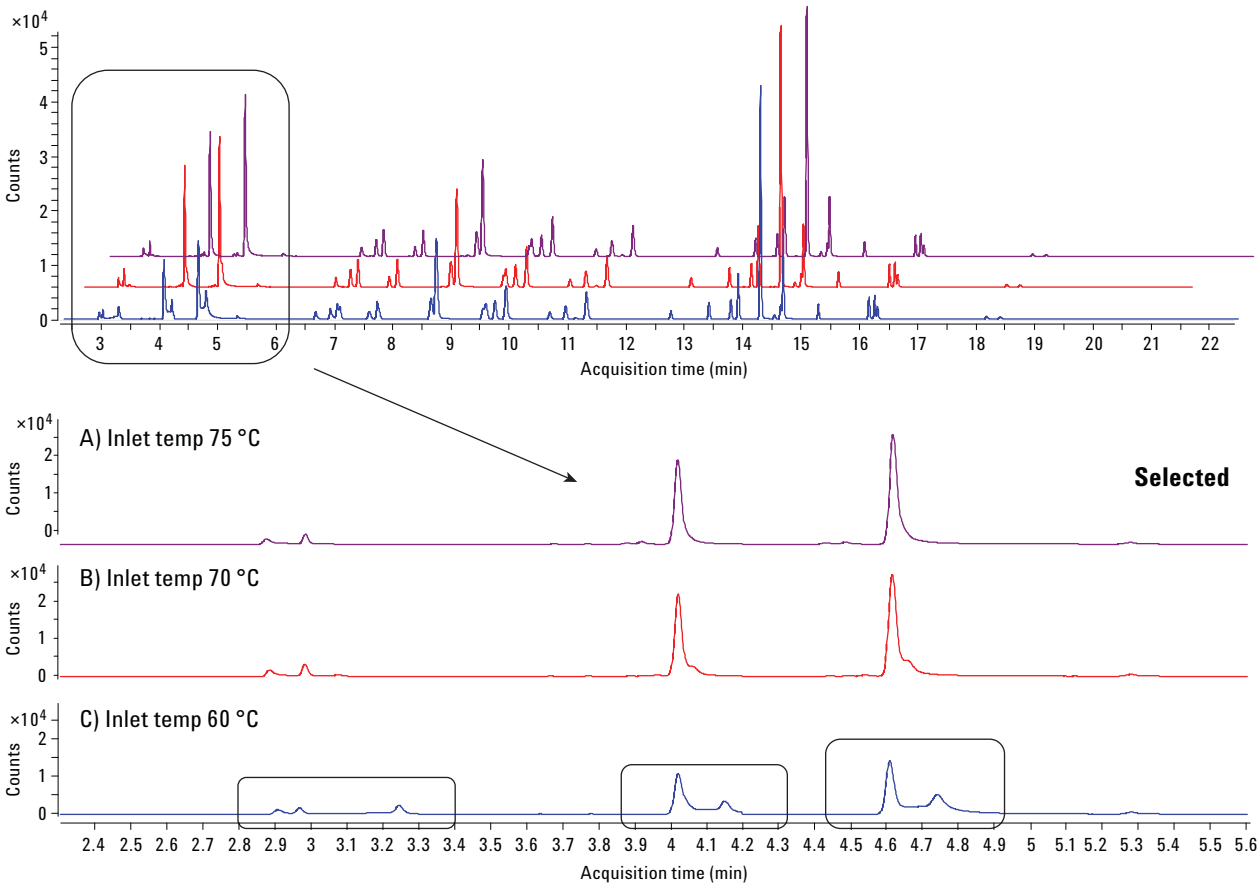

Figure 3. Inlet temperature optimization study using 5 µL of 10 ng/mL pesticide standard solution. The inlet temperature starting point was set to 75 °C.

Vent time

The selected settings (100 mL/min vent flow, 75 °C inlet temperature, and 2.5 psig vent pressure) were entered into the calculator. The elimination rate (µL/min), injection rate (µL/min), and vent time (min) were calculated correspondingly. A calculated injection rate of 69 µL/min was, therefore, used. The calculated vent time of 0.07 min was adjusted further. As recommended in the LVI tutorial [1], the peak shape could be improved by extending the vent time to reduce the amount of solvent reaching the column. The trade-off for a longer vent time is the potential response loss of early eluters.

After optimizing the above parameters, the recovery and peak shape of early eluting peaks were greatly improved. However, a small amount of peak splitting was still evident before the real peak on the chromatogram. Therefore, the vent time was extended to 0.08 and 0.09 min. Figure 4 shows the chromatograms obtained under different vent time settings. A slightly longer vent time was helpful in smoothing out peak shape and baseline, but the use of longer vent time also carries the risk of losing analytes, as shown in the 0.09 min chromatogram. A final compromise of 0.085 min vent time was used to achieve better peak shape as well as good recoveries.

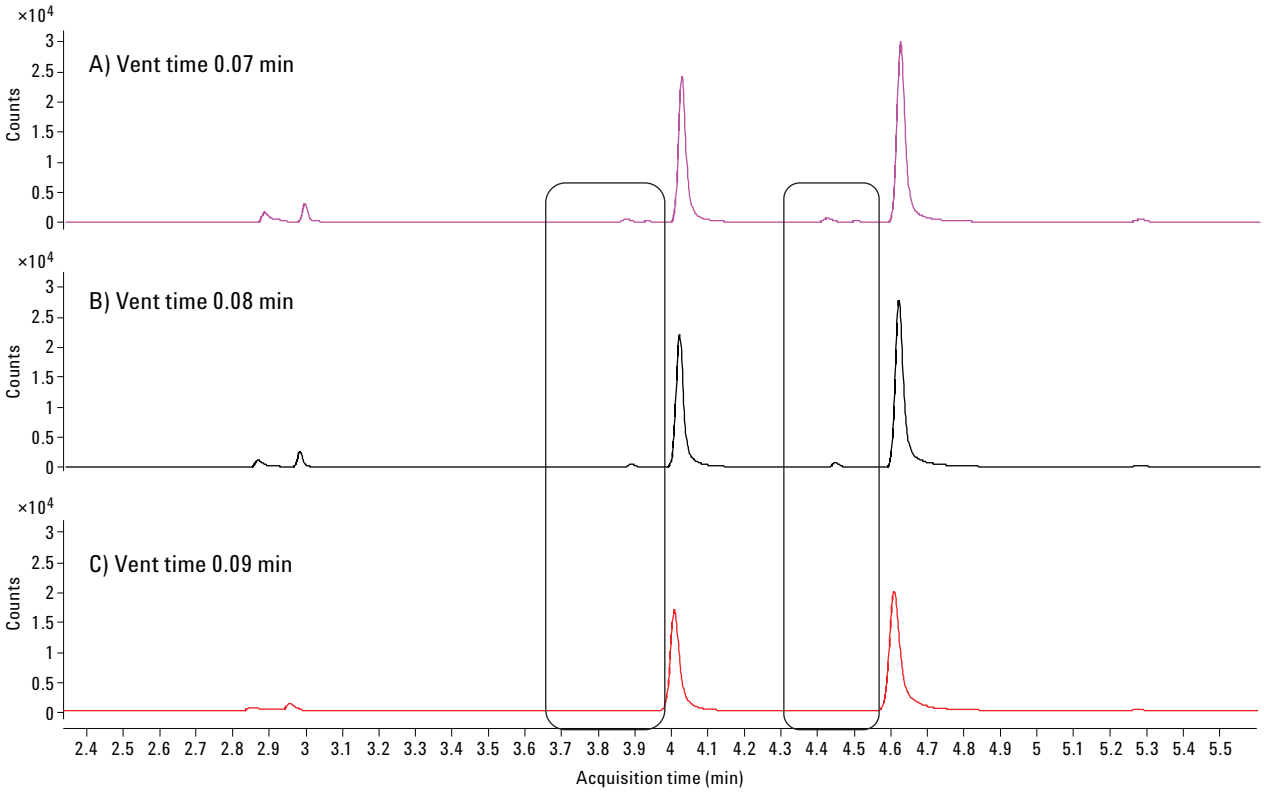

Figure 4. Vent time optimization study using 5 µL of 10 ng/mL pesticide standard solution. A vent time of 0.085 min was chosen as a compromise.

Oven temperature profile

As this work followed previous studies, the published oven temperature profile was initially used for the LVI method development [3, 4]. With the LVI optimal inlet and injection conditions, it was noticed that the early eluting analytes, especially the first and second peaks, were still tailing significantly with poor resolution. In addition, the late eluting peaks always had low responses. Although the low responses are typically compound related, we tried to improve the low responses of late eluters. For late eluting compounds, higher oven temperature, in general, might increase their responses. The final oven temperature was increased from 280 to 300 °C, the final inlet temperature was raised from 300 to 350 °C, and the transfer line temperature was also increased from 280 °C to 300 °C. As seen in Figure 5, the higher temperature settings showed higher responses of late eluting compounds as well as early eluting compounds than the lower temperature settings. As the result, higher temperature settings were used.

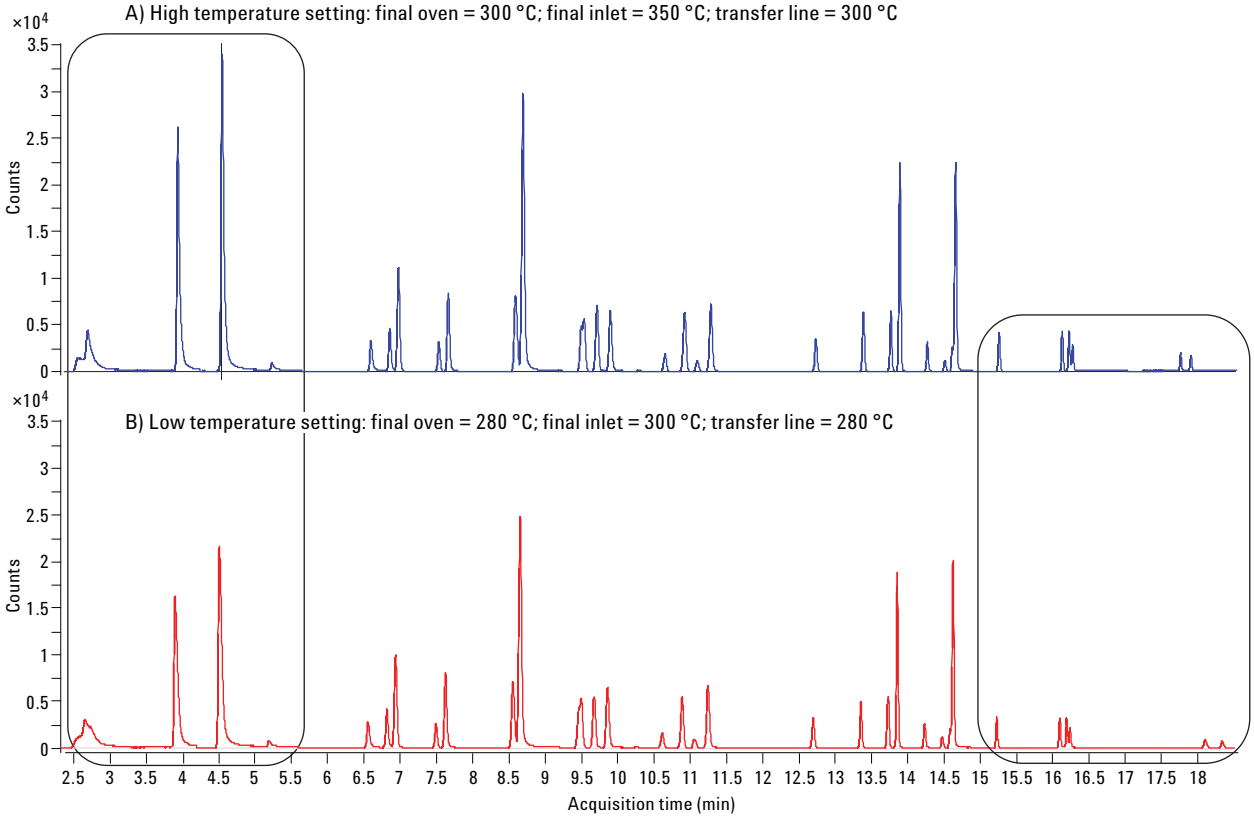

Figure 5. Oven and inlet temperature setting optimization study using 5 µL of 10 ng/mL pesticide standard solution. A higher temperature program was selected.

Previous work used an oven program starting at 100 °C to minimize peak splitting caused by acetonitrile under hot splitless mode [3, 4]. Using the new LVI conditions, the oven program was lowered to evaluate its impact on the chromatogram. Figure 6 shows the early eluters' peak shape, responses, and resolution were significantly improved by lowering the initial temperature. Because the inlet temperature was optimized to start at 75 °C, oven temperatures less than 75 °C were not investigated. The starting point for the oven program was 75 °C, held for 2.57 min to match the calculated purge time. The final oven temperature profile was 75 °C for 2.57 min, to 150 °C at 50 °C/min, to 200 °C at 6 °C/min, to 300 °C at 16 °C/min, and hold for 1 min. Post run for backflushing was 3 min at 300 °C.

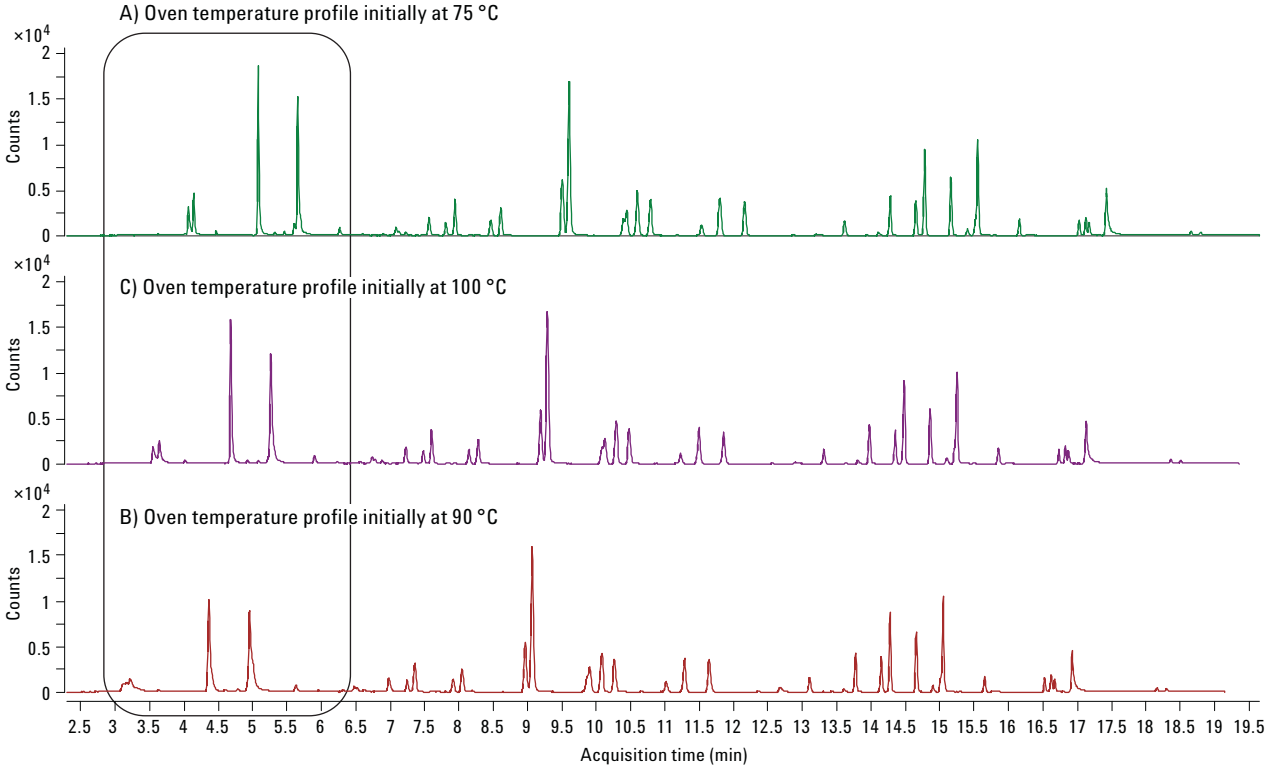

Figure 6. Oven temperature program optimization study using 5 µL of 10 ng/mL pesticide standard solution. The initial temperature was set to 75 °C.

Inlet liner

Peak shape could be improved by using liners with wool [1]. Wool in the liner holds the analytes during solvent venting and allows more solvents to be vented. The LVI tutorial also warns of the loss of analytes due to irreversible adsorption. This concern can be minimized by using Agilent Ultra Inert liners with wool due to the optimal deactivation of the liner and wool. This LVI study used an Ultra Inert liner with wool, but another liner targeted for cold splitless and LVI injections, the 2 mm dimple liner (p/n 5190-2296), was assessed for comparison. Figure 7 shows the comparison results.

The optimized LVI method based on the Ultra Inert liner with wool was used for the dimpled liner experiment. As shown in Figure 7 B, minor peak splitting was observed when using the dimpled liner. Obviously, wool inside the liner was helpful in removing the acetonitrile solvent, thus reducing its impact on the chromatography. With further optimization of the vent time (extended to 0.1 min), the peak splitting from the dimpled liner was minimized while maintaining comparable recoveries, which is demonstrated in Figure 7 C.

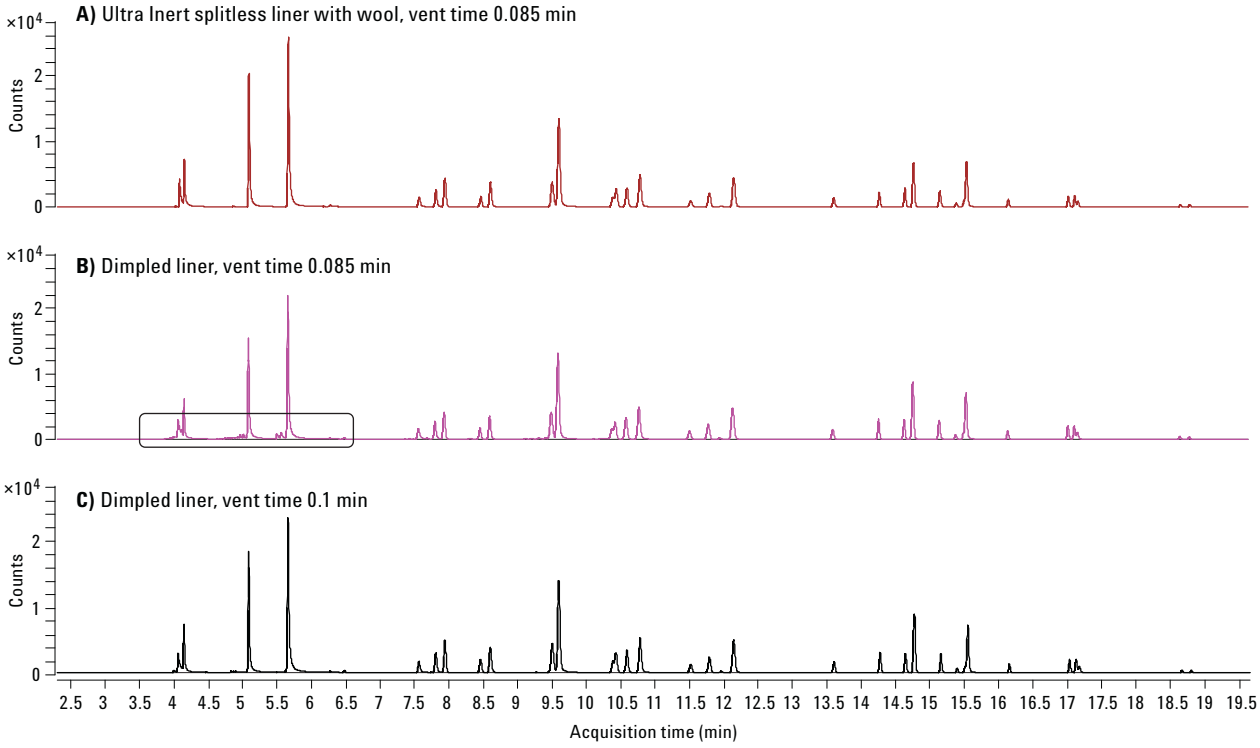

Figure 7. Comparison of the Agilent Ultra Inert liner with wool to a dimpled liner. A) and B) are chromatograms obtained by 5 µL injection of 10 ng/L pesticide standard using the optimized LVI method based on the Agilent Ultra Inert liner with wool. A) used the Ultra Inert splitless liner with wool, and B) used the dimpled liner. C) is the chromatogram achieved with the optimized dimpled liner based LVI method. Equivalent performance was achieved by the Ultra Inert liner with wool and dimpled liner with the corresponding optimal LVI method.

A list of optimal method parameters was chosen for the Ultra Inert splitless liner with wool after this study. The parameters are listed in Table 3. An example chromatogram of 5 µL injection of 1 ng/L pesticide standard solution is shown in Figure 8.

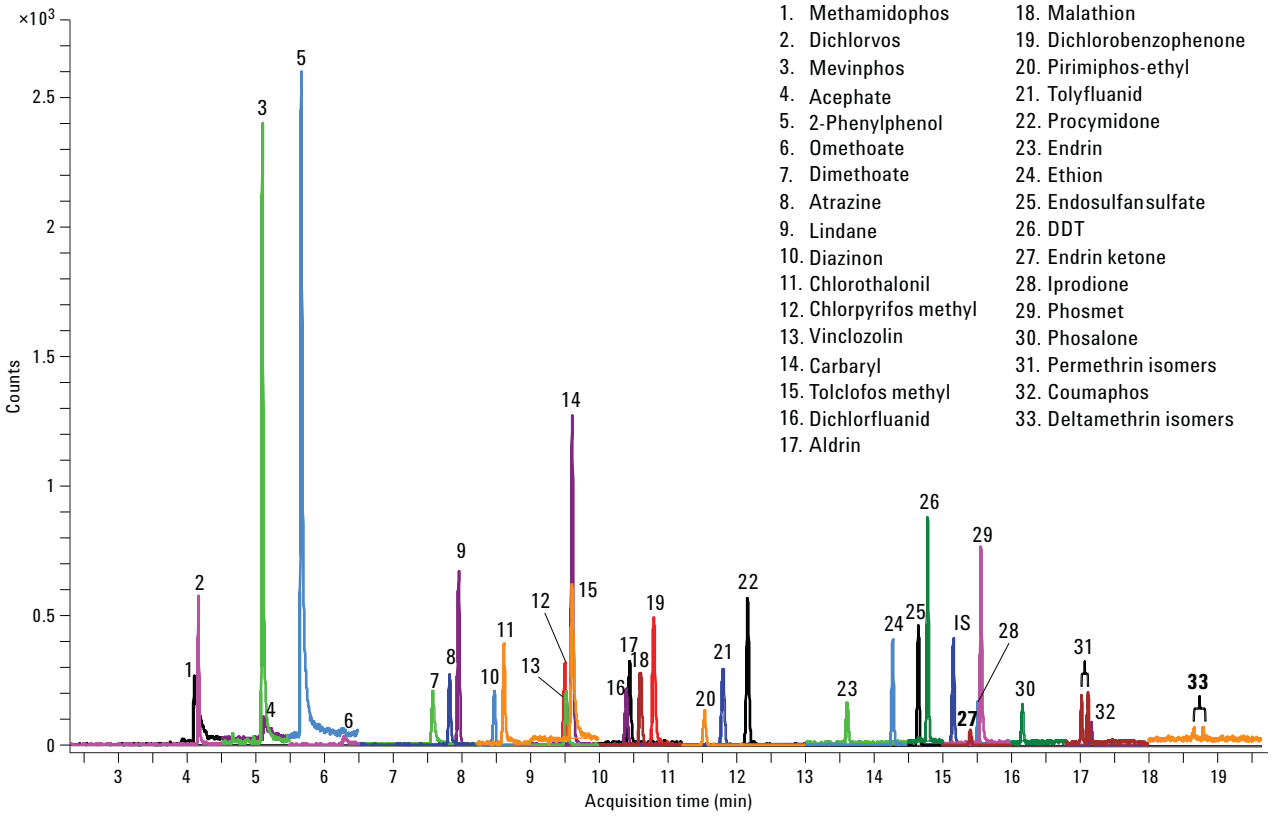

Figure 8. GC/MS/MS MRM chromatogram of 1 ng/mL pesticide standard using an Agilent Ultra Inert splitless liner with wool and optimized LVI method. 5 µL injection volume.

Comparison of LVI to other injection modes

Ultra Inert splitless liners with wool can be used for different injection modes with the MMI, from hot splitless to cold splitless to LVI. The optimized LVI method was, therefore, compared with hot splitless and cold splitless injection modes. Apart from differences in the inlet mode and conditions, the other components of the hot and cold splitless methods were kept the same as the LVI method. Figure 9 shows that with the optimal LVI GC/MS/MS method, the system sensitivity can be improved significantly, thus meeting trace level detection requirements. Another benefit of using the LVI method is the improved peak shape of early eluting compounds due to the removal of solvent.

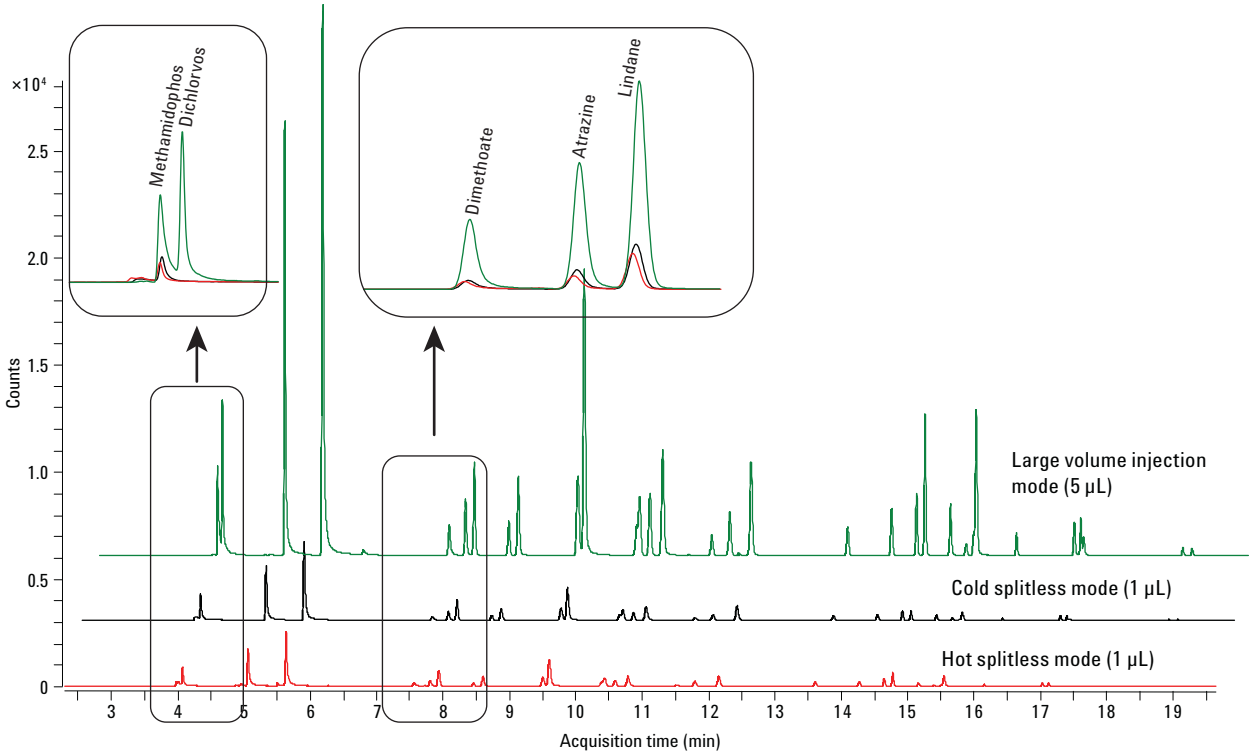

Figure 9. Comparison of hot splitless, cold splitless, and LVI injection methods using Agilent Ultra Inert liners with wool on an Agilent MMI. 10 ng/mL pesticide standard.

Multiresidue pesticide analysis in a pepper matrix

To demonstrate a practical application, the optimized LVI method was used for multiresidue pesticide analysis in a pepper matrix extracted using the QuEChERS sample preparation protocol. Figure 10 A shows the GC/MS/MS MRM chromatogram of 1 ng/mL pesticides spiked in a pepper matrix blank using the LVI method with a 5 µL injection. For comparison, the corresponding chromatogram using cold splitless with a 1 µL injection is shown in Figure 10 B. Clearly, all pesticides showed higher responses with the LVI 5 µL injection than with the cold splitless 1 µL injection, which demonstrates the lower detection limits. Methamidophos, omethoate, and permethrin were not detectable under the cold splitless mode. However, they were clearly quantifiable under the LVI mode at 1 ng/mL. The early eluting pesticides gave better peak shapes in the LVI mode than in the cold splitless mode. 2-Phenylphenol (5) was found in the pepper blank matrix [4] and explains why it showed almost identical response in the two chromatograms.

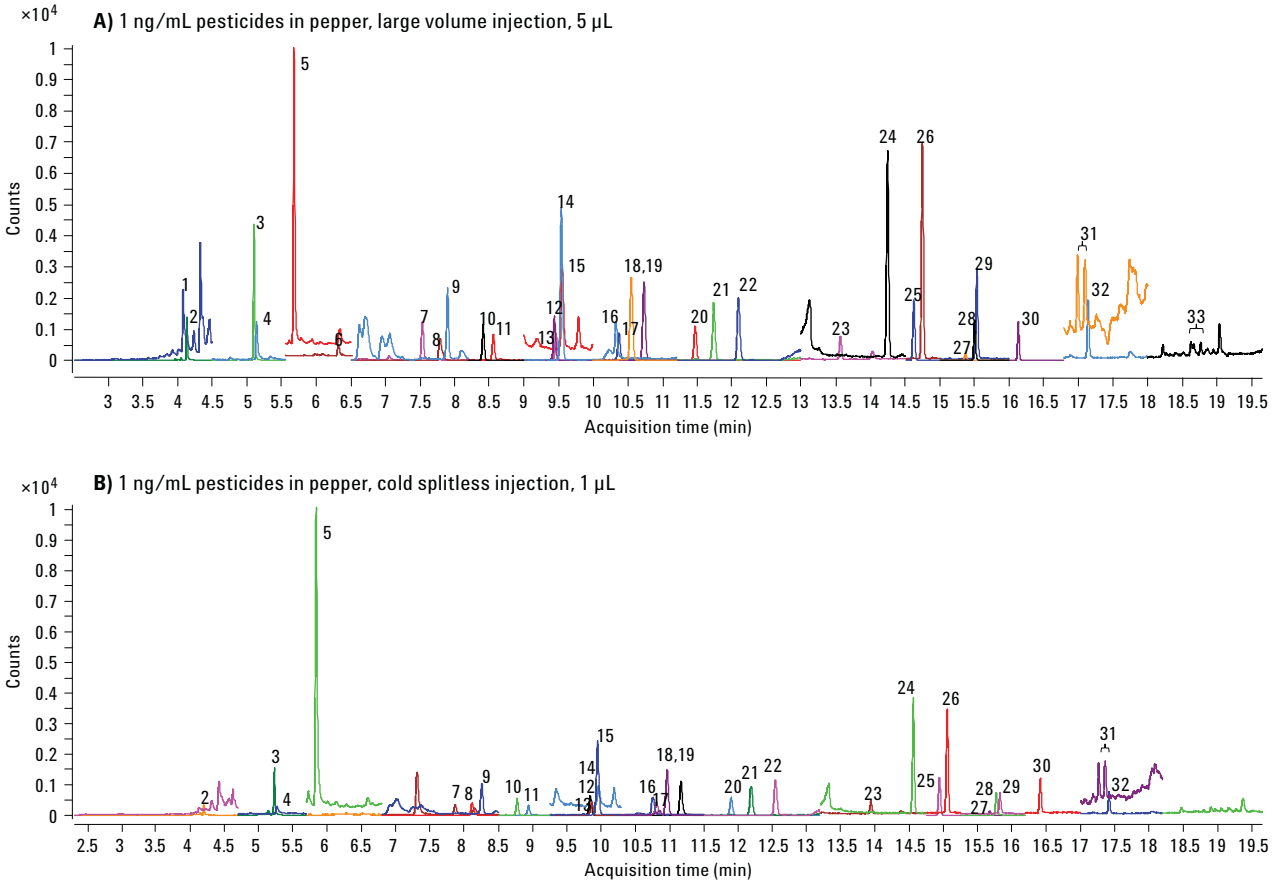

Figure 10. GC/MS/MS MRM chromatogram of 1 ng/mL pesticides spiked in a pepper matrix blank using the Agilent Ultra Inert splitless liner with wool with A) LVI method (5 µL injection), and B) cold splitless method (1 µL injection). Refer to Figure 8 for peak identifications. Pesticide methamidophos (1), omethoate (6), and permethrin (33) were not detected under cold splitless mode with the 1 µL injection.

The repeatability of multiple injections using the 5 µL method was evaluated with 6 injections of 1 and 10 ng/mL pepper sample, respectively. In addition, 10 injections of 10 ng/mL pepper sample using the cold splitless method were analyzed for comparison. The results were quantified against the corresponding calibration curve of 1 to 100 ng/mL in the pepper matrix. The calculated concentrations were used for % RSD calculation as shown in Table 4. In general, the LVI method showed comparable repeatability to that of the cold splitless method. Improved repeatability was achieved by the LVI method for compounds that have either poor peak shape, such as methamidophos and dichlorvos, or low responses, such as endrin ketone, permethrin, and deltamethrin, under 1 µL cold splitless injection. However, for very sensitive pesticides, such as acephate and omethoate, higher RSDs were obtained in the LVI mode. This can be attributed to much more matrix being introduced to the system. With 6 injections on the LVI method, the total matrix introduced to the system was already equivalent to 30 injections on the cold splitless method. Therefore, we recommend putting more effort into sample cleanup when using LVI methods. Additionally, frequent liner replacement is also recommended to maintain system performance and to protect the column and MS ion source.

Table 4. Method repeatability (% RSD of calculated concentrations)

	LVI Method (5 µL)		Cold Splitless Method (1 µL)	
Method and Sample	**10 ng/mL in pepper (n = 6)**	**1 ng/mL in pepper (n = 6)**	**10 ng/mL in pepper (n = 10)**	**1 ng/mL in pepper (n = 6)**
Methamidophos	9.2	6.6	14.8	NA[1]
Dichlorvos	3.8	5.2	10.4	8.9
Mevinphos	4.4	8.1	4.3	3.0
Acephate	23.7	45.1	8.6	NA[1]
2-Phenylphenol	5.8	NA[2]	8.1	NA[2]
Omethoate	34.3	41.7	13.9	NA[1]
Dimethoate	8.8	20.9	4.6	8.2
Atrazine	1.7	10.8	1.2	3.1
Lindane	1.2	7.7	1.4	1.7
Diazinon	2.8	5.3	1.3	1.9
Chlorothalonil	8.9	8.0	4.8	8.4
Chlorpyrifos methyl	2.5	7.0	1.8	4.4
Vinclozolin	1.5	8.6	1.3	3.5
Tolclofos-methyl	2.3	6.0	1.2	2.1
Carbaryl	12.4	15.3	9.2	16.7
Dichlofluanid	4.4	14.3	2.2	7.2
Aldrin	4.4	4.7	1.9	6.4
Malathion	1.5	5.5	1.6	3.1
Dichlorobenzophenone	1.7	9.8	1.3	1.8
Pirimiphos-ethyl	1.9	5.4	1.1	4.6
Tolylfluanid	2.0	3.0	1.8	2.5
Procymidone	1.1	7.3	1.4	2.5
Endrin	1.3	7.5	0.9	5.2
Ethion	3.4	3.5	1.9	2.8
Endosulfan sulfate	4.1	2.8	3.0	2.7
DDT	4.2	5.1	8.0	8.0
Endrin ketone	2.4	5.5	2.2	11.6
Iprodione	13.4	13.0	4.7	6.5
Phosmet	12.6	23.6	17.0	22.4
Phosalone	3.2	6.8	5.8	7.1
Permethrin	2.3	2.6	2.7	14.7
Coumaphos	4.6	7.4	7.7	9.7
Deltamethrin	3.7	9.4	3.5	NA[1]

NA[1] - data is not available due to undetected responses

NA[2] - data is not useable due to incurred compound in matrix blank

Conclusions

This application note shows the development and optimization of an LVI GC/MS/MS method using the Agilent Ultra Inert splitless liner with wool and the Agilent J&W HP-5ms Ultra Inert GC column for multiresidue pesticide analysis. Based on the solvent elimination calculator imbedded in the instrument control software, the method optimization was conducted according to the evaluation of critical parameters, including vent flow, vent pressure, inlet temperature, vent time, oven temperature program, and inlet liner. The optimized LVI method provided lower detection limits for all compounds and better peak shape for early eluting compounds when compared to cold splitless and hot splitless methods. A pepper matrix, extracted with the QuEChERS sample preparation protocol, was used to evaluate detection limits and method repeatability. The lower detection limits and better repeatability for low response compounds were demonstrated. When using an LVI method, sample matrix had more impact on liner durability, especially for active pesticides, due to the larger amount of sample matrix being introduced to the system. Frequent liner replacement is, therefore, recommended to maintain system performance and to protect the column and MS ion source. In addition, investing in sample cleanup is very helpful in achieving better results when using LVI methods.

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