Maintaining Sensitivity and Reproducibility with the Agilent JetClean Self-Cleaning Ion Source for Pesticides in Food and Feed

Application Note

Author

Jessica Westland
Agilent Technologies, Inc.

Abstract

Approximately 200 various pesticides were analyzed in organic honey extract on the Agilent 7010A Series Triple Quadrupole GC/MS with and without the use of the Agilent JetClean self-cleaning ion source. The chromatographic peak shape and baseline improved with the use of JetClean at 0.13 mL/min continuous H_2 flow, particularly for the later eluting, higher molecular weight (MW) analytes. The resulting R^2 values both with and without JetClean were very comparable. The MDLs were calculated from 10 replicate measurements of 2.5 ppb spiked honey extract using a 99 % confidence level. Low ppb MDLs were obtained for the majority of the analytes using JetClean, with an average of 0.170 ppb MDL without use of JetClean, and an average of 0.147 ppb with JetClean. The replicate measurements performed with and without JetClean at 2.5 ppb resulted in comparable %RSDs. All results identified that the use of a low continuous flow of H_2 into the MS source can be considered as an option for maintaining performance during pesticide analyses.

Agilent Technologies

Introduction

The global agricultural industry uses over a thousand different pesticides for food and foodstuffs cultivation. Producers are compelled to use pesticides to meet the growing demand for reasonably priced food, resulting in the need for pesticide residue monitoring in commodities worldwide. Concurrently, simple sample preparation methods, such as Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) are routinely used for the analysis of food and feed samples, often leaving a significant amount of matrix in the extracts. Analytical laboratories are challenged by these matrix residues, which negatively affect the responses of the analyzed pesticides, and eventually require source cleaning.

The use of the Agilent JetClean self-cleaning ion source (JetClean) reduces the time between manual source cleanings while still allowing for the analysis of complex samples without losing sensitivity and reproducibility [1]. The JetClean self-cleaning ion source introduces a precisely measured hydrogen gas (H_2) flow into the MS source, controlled by Agilent MassHunter Data Acquisition Software (B.07.05). The appropriate H_2 flow (µL/min) generates conditions that clean the surfaces of the source, the lenses, and other components. These actions aid in maintaining a stable detection environment and provide for response stability of the pesticides in difficult matrixes. The JetClean is equipped with two operational modes:

- Acquire and Clean (also known as On-line) mode: H_2 is running continuously during the analysis
- Clean only (also known as Off-line) mode: H_2 is introduced only post run or post sequence

Experimental

Sample preparation

Many laboratories focused on pesticide residue analysis in food commodities routinely use the QuEChERS method [2,3]. This straightforward sample preparation allows for the analysis of hundreds of pesticides at low concentrations with a single extraction. A 5-g sample of organic honey with 5 mL of water was vortexed with two ceramic homogenizers. Ten milliliters of acetonitrile (ACN) was added, and the sample was vortexed for 2 minutes. The QuEChERS EN salts (p/n 5982-5650) were added, and the capped tubes were placed on a GenoGrinder vertical shaker for 2 minutes, then centrifuged at 5,000 rpm for 5 minutes. Six milliliters of the honey extract was transferred to the QuEChERS dSPE (p/n 5982-5056) general fruit and vegetables. Then, the extract was vortexed for 2 minutes, and centrifuged at 5,000 rpm for 5 minutes [4].

Instrumentation

All analyses were run on an Agilent 7890B GC equipped with an Agilent 7693B Autosampler and the Agilent 7010A Triple Quadrupole GC/MS. Table 1 displays the GC and backflush parameters, and Table 2 shows the MS/MS method parameters. The GC was configured with a Multimode Inlet (MMI) equipped with an 4 mm ultra inert, splitless, single taper, glass wool liner (p/n 5190-2293). From the inlet, two Agilent J&W DB-5ms Ultra Inert columns (15 m × 0.25 mm, 0.25 µm; p/n 19091S-431 UI) were coupled to each other through a purged ultimate union (PUU) for the use of midcolumn/post run backflushing (Figure 1).

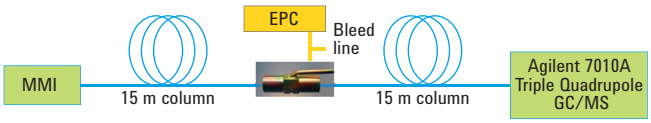

Figure 1. Column configuration for an optimal MRM application.

Table 1. Agilent 7890B GC Method Conditions

Parameter	Value
MMI Injection mode	Hot-splitless
Injection volume	1 µL
Inlet temperature	280 °C
Carrier gas	He, constant flow 1.00 mL/min (column 2 = 1.20 mL/min)
MS transfer line temperature	280 °C
Oven program (40-minute method)	60 °C for 1 minute, 40 °C/min to 120 °C, 0 minutes 5 °C/min to 310 °C, 0 minutes
PUU Backflush settings*	
Timing	1.5-minute duration during post run
Oven temperature	310 °C
Aux EPC pressure	~50 psi
Inlet pressure	~2 psi

* Backflush conditions were optimized for this application method.

MS Acquisition Method Development

The organic honey matrix-optimized transitions of the Agilent MassHunter Pesticide & Environmental Pollutant Enhanced MRM Database (Rev. A.04.00) was used to develop the MRM method for the evaluation of 195 target pesticides (Figure 2) [5]. The top three (highest responding) MRMs for each compound were selected for analysis.

Table 2. Agilent 7010A MS/MS Parameters

Parameter	Value
Electron energy	70 eV
Tune	atunes.eihs.tune.xmL
EM gain	10
MS1 and MS2 resolution	Wide
Collision cell	1.5 mL/min N_2 and 2.25 mL/min He
Quant/Qual transitions	Matrix-optimized
Dwell times	Time segment (TS) specific*
Source temperature	300 °C
Quad temperatures	150 °C
Cleaning operation	Acquire & Clean
H_2 flow (mL/min)	0.13 mL/min**

* All dwells in each TS were given the same value (no value under 10 was set) to attain a scan rate of ~5 scans/sec for the TS

** H_2 flow (mL/min) was set at the lowest achievable flow

Agilent JetClean Operation

Previously, the introduction of the H_2 flow into the MS source was introduced through an EPC module. The next stage of Agilent innovative technology, the JetClean self-cleaning ion source, moves the control of H_2 flow to the MS (Figure 3). This application used JetClean in the Acquire and Clean operation mode for continuous on-line cleaning (Figures 4–6). The Agilent MassHunter software allowed for the simple setup and operation of the process, all controlled in the MS domain.

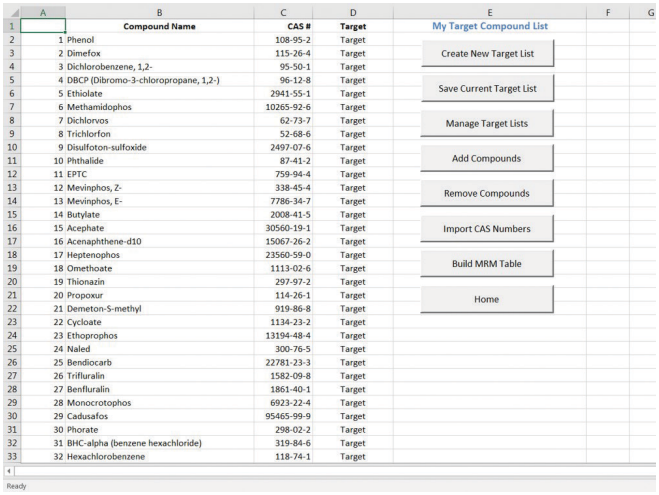

Figure 2. Screen capture of the top portion of the Target Compound List from the Agilent P&EP MRM Enhanced Database (A.04.00).

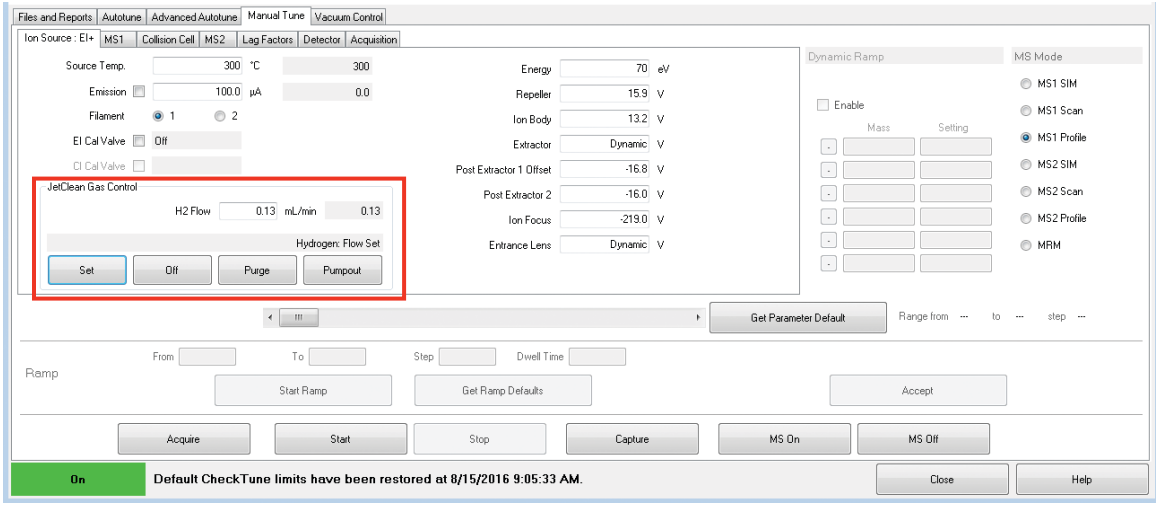

Figure 3. View of Agilent MassHunter Data Acquisition Triple Quadrupole MS Tune (B.07.05) and the Agilent JetClean Gas Control.

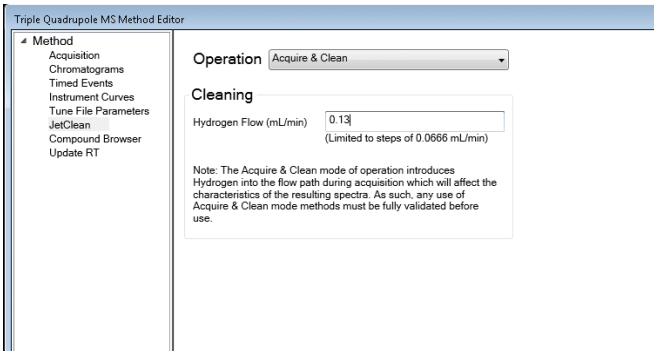

Figure 4. View of Agilent MassHunter Data Acquisition Triple Quadrupole MS Method Editor Jet Clean Settings (B.07.05).

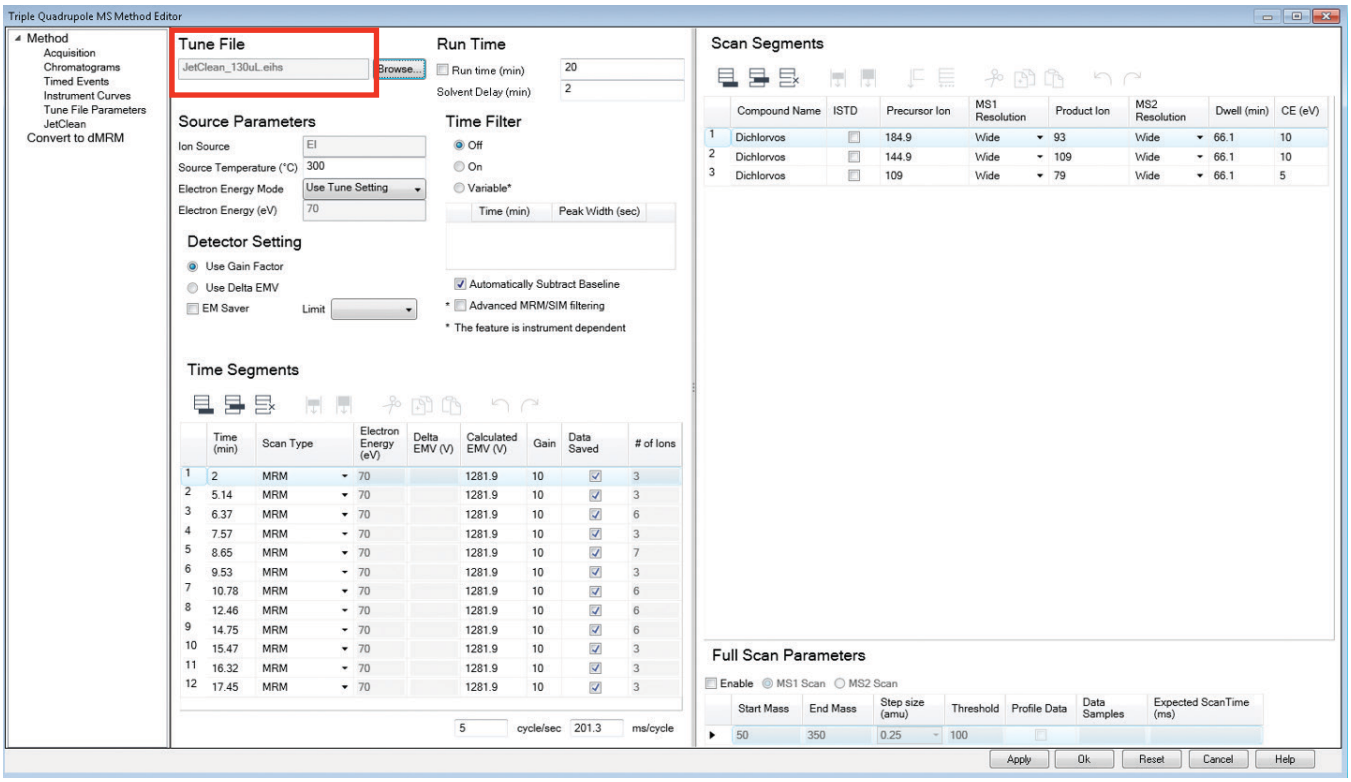

Figure 5. View of Agilent MassHunter Data Acquisition Triple Quadrupole MS Method Editor Acquisition Tab with loaded Agilent JetClean Tune File (B.07.05).

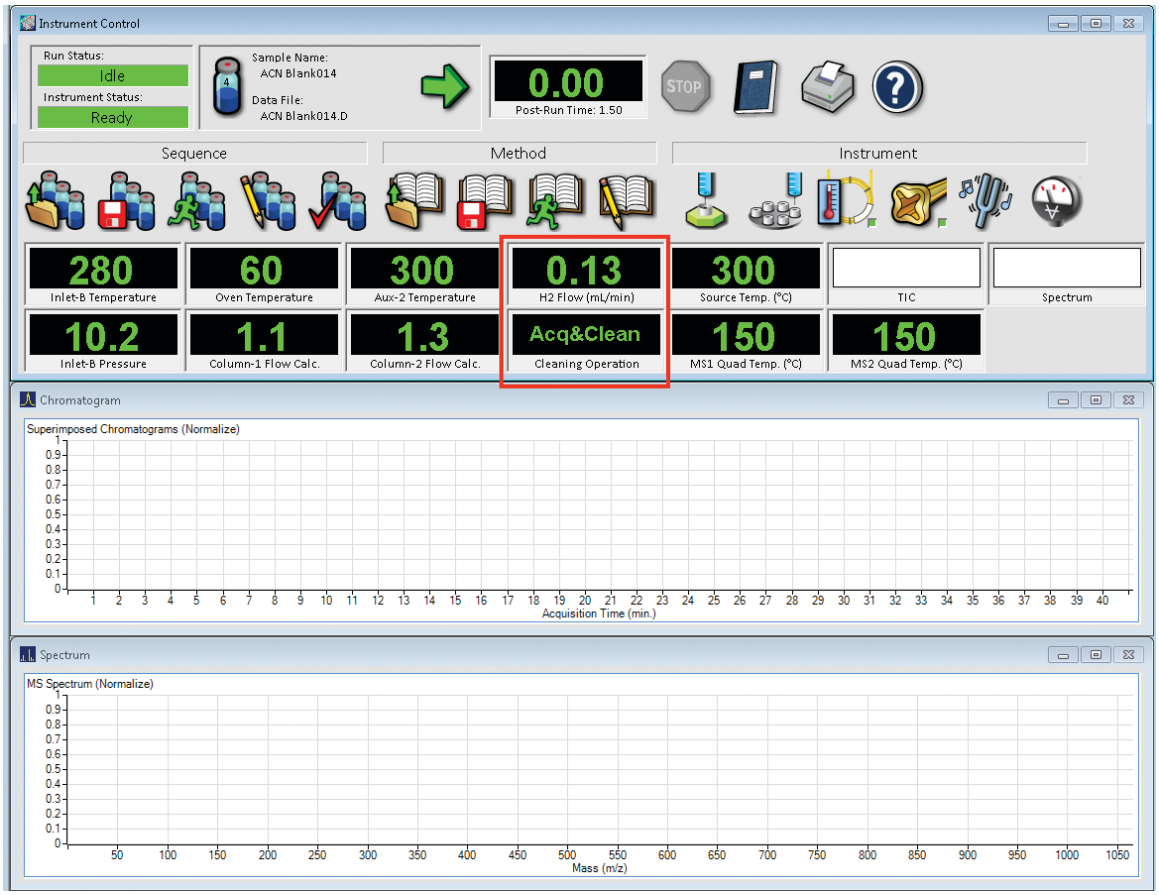

Figure 6. View of Agilent MassHunter Data Acquisition Instrument Control (B.07.05) with JetClean monitors.

Chromatographic Performance

The following chromatograms (Figures 7–13) show analytes eluting throughout the 40-minute chromatographic run at ~2.5 ppb in organic honey (concentration varies by compound). The chromatograms are of target compounds and their respective matrix-optimized MRM transitions with and without the use of JetClean. Chromatographically, the use of JetClean was seen to improve peak shape and the baseline on the later-eluting, higher molecular weight (MW) analytes.

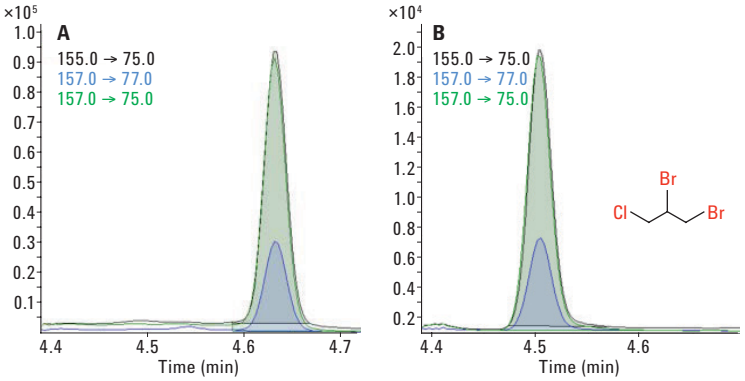

Figure 7. Example chromatograms for DBCP (in organic honey) without Agilent JetClean (A) and with Agilent JetClean Acquire and Clean at 0.13 mL/min (B).

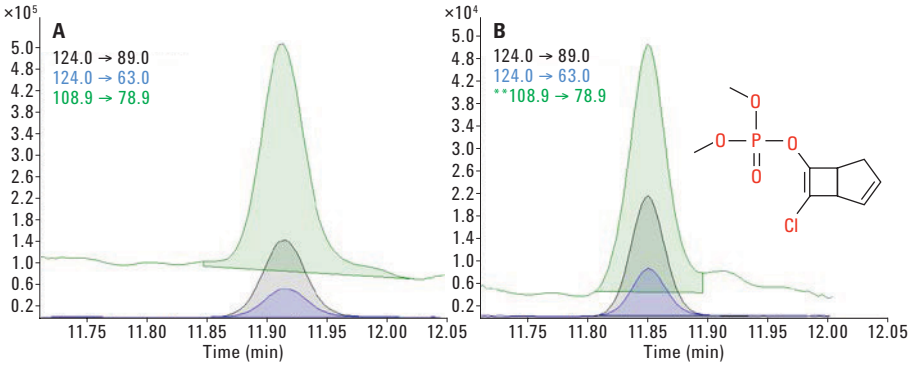

Figure 8. Example chromatograms for heptenophos (in organic honey) without Agilent JetClean (A) and with Agilent JetClean Acquire and Clean at 0.13 mL/min (B).

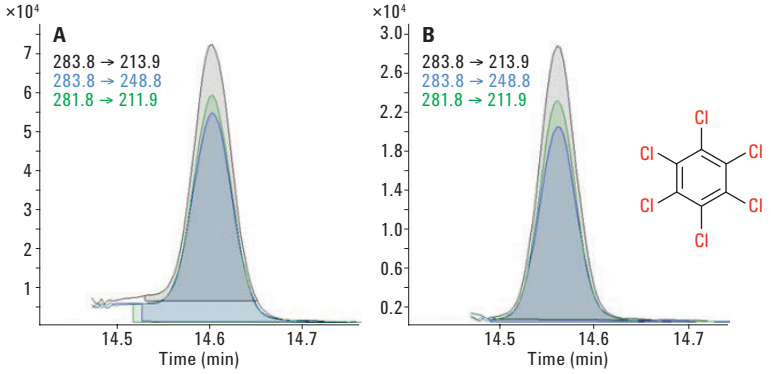

Figure 9. Example chromatograms for hexachlorobenzene (in organic honey) without Agilent JetClean (A) and with Agilent JetClean Acquire and Clean at 0.13 mL/min (B).

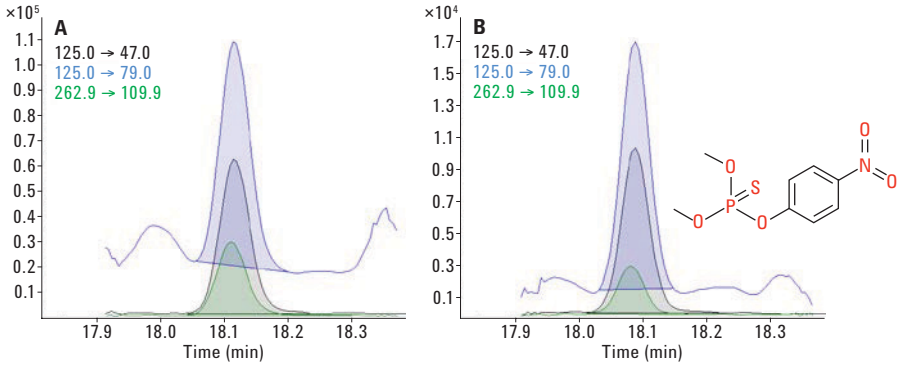

Figure 10. Example chromatograms for parathion-methyl (in organic honey) without Agilent JetClean (A) and with Agilent JetClean Acquire and Clean at 0.13 mL/min (B).

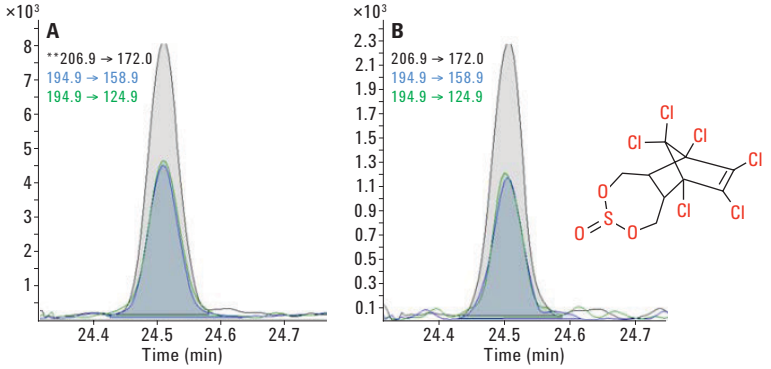

Figure 11. Example chromatograms for endosulfan-II (in organic honey) without Agilent JetClean (A) and with Agilent JetClean Acquire and Clean at 0.13 mL/min (B).

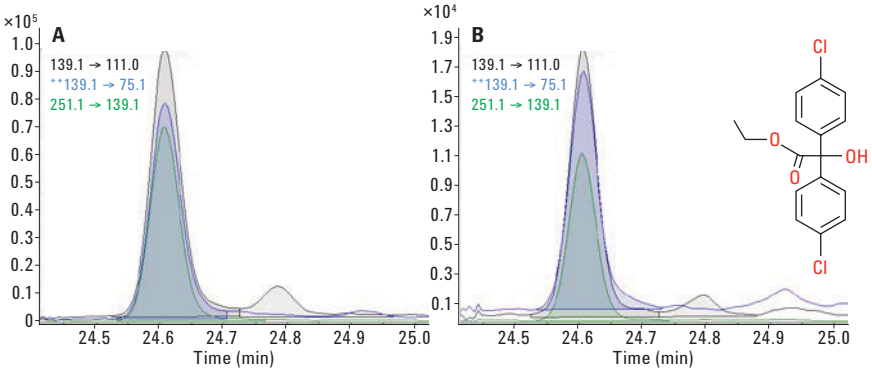

Figure 12. Example chromatograms for chlorobenzilate (in organic honey) without Agilent JetClean (A) and with Agilent JetClean Acquire and Clean at 0.13 mL/min (B).

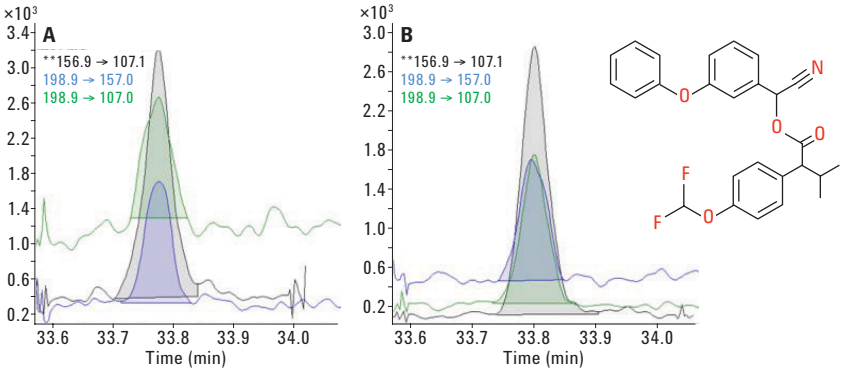

Figure 13. Example chromatograms for flucythrinate-I (in organic honey) without Agilent JetClean (A) and with Agilent JetClean Acquire and Clean at 0.13 mL/min (B).

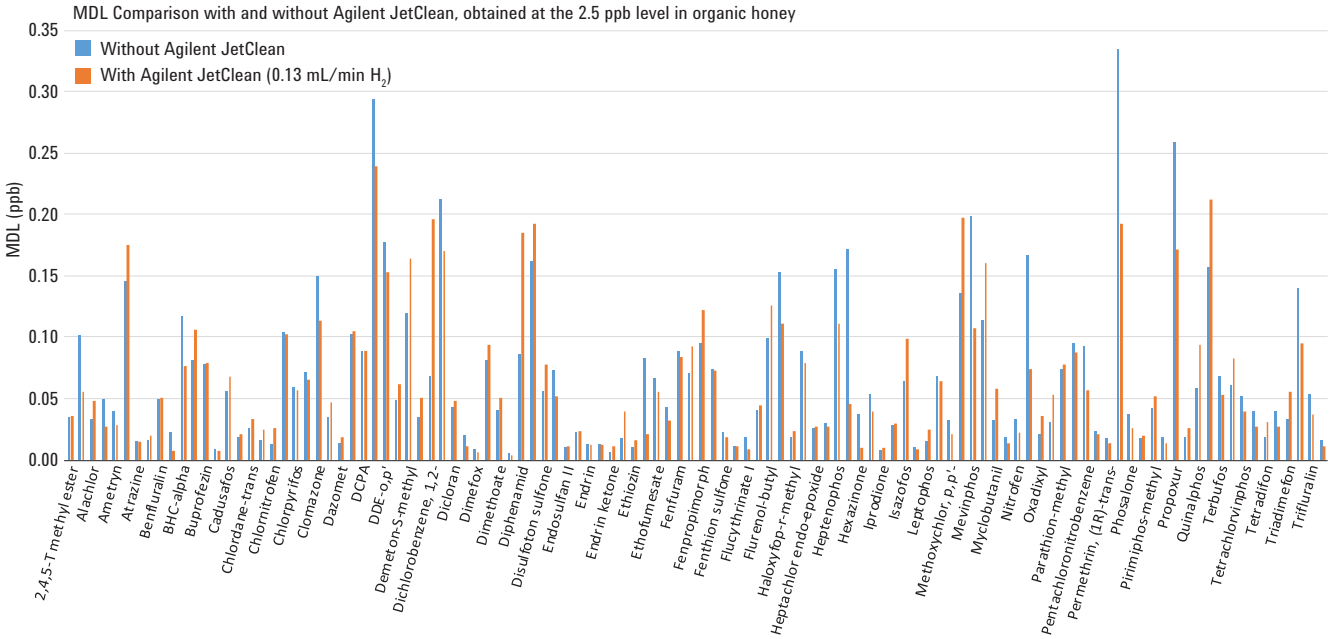

Figure 14. MDL comparison of selected target compounds with and without Agilent JetClean obtained at the 2.5 ppb level in organic honey.

Results and Discussion

Table 3 lists the R^2 values and the statistically derived method detection limits (MDLs) for representative target analytes of the various pesticides tested. The calibration ranged from 0.12 ppb–50 ppb for the majority of the analytes, although some were not included at the lowest level. The resulting R^2 values both with and without JetClean (0.13 mL/min H_2) were very comparable. The MDLs were calculated from 10 replicate measurements of 2.5 ppb spiked honey extract using 99 % confidence level. Lower MDLs were obtained for the majority of the analytes using JetClean (0.13 mL/min H_2), with an average of 0.170 ppb MDL without the use of JetClean, and an average of 0.147 ppb with JetClean.

It was observed that the use of JetClean for pesticide analysis exhibited a decrease in overall analyte response throughout the analysis (the degree of the response reduction was compound dependent). Even though this reduction in response was observed, it did not affect the ability to confidently identify the analytes and quantitate under the required limits. The replicate measurements performed with and without JetClean at 2.5 ppb resulted in comparable %RSDs.

Table 3. R^2 values and MDLs of Selected Target Analytes at the 2.5 ppb Level in Organic Honey

	R^2		%RSD			R^2		%RSD	
Analyte	**Without JetClean**	**With JetClean**	**Without JetClean**	**With JetClean**	**Analyte**	**Without JetClean**	**With JetClean**	**Without JetClean**	**With JetClean**
Aldrin	0.998	0.997	0.05	0.03	Flucythrinate I	0.998	0.992	0.02	0.01
Atrazine	0.998	0.997	0.01	0.02	Flurenol-butyl	0.997	0.997	0.10	0.13
Azinphos-ethyl	0.997	0.995	0.02	0.02	Genite	0.999	0.997	0.15	0.11
Benfluralin	0.998	0.994	0.05	0.05	Haloxyfop-r-methyl	0.998	0.994	0.02	0.02
Butralin	0.997	0.991	0.01	0.01	Heptachlor	0.998	0.996	0.09	0.08
Cadusafos	0.998	0.996	0.06	0.07	Heptachlor endo-epoxide	0.997	0.992	0.03	0.03
Carboxin	0.997	0.994	0.02	0.02	Iprobenfos	0.997	0.993	0.05	0.04
Chlordane-*trans*	0.997	0.998	0.03	0.03	Iprodione	0.998	0.999	0.01	0.01
Chlornitrofen	0.998	0.997	0.01	0.03	Irgarol	0.998	0.997	0.03	0.03
Chlorpyrifos	0.998	0.994	0.06	0.06	Isazofos	0.997	0.993	0.06	0.10
Cloquintocet-mexyl	0.998	0.993	0.03	0.05	Methidathion	0.997	0.995	0.07	0.06
DCPA	0.997	0.994	0.09	0.09	Methoxychlor, *p,p´*-	0.998	0.996	0.03	0.02
DDD-*p,p´*	0.997	0.997	0.29	0.24	Metolachlor	0.998	0.990	0.14	0.20
DDE-*o,p´*	0.997	0.995	0.18	0.15	Mirex	0.997	0.995	0.11	0.16
DDT-*p,p´*	0.998	0.996	0.05	0.06	Myclobutanil	0.998	0.998	0.03	0.06
Dicloran	0.997	0.993	0.04	0.05	Napropamide	0.997	0.996	0.02	0.01
Dieldrin	0.997	0.994	0.02	0.01	Nitrofen	0.998	0.995	0.03	0.02
Dimethenamid-P	0.998	0.993	0.08	0.09	Oxadixyl	0.998	0.994	0.02	0.04
Dimethomorph I	0.999	0.995	0.00	0.00	Oxythioquinox	0.998	0.996	0.03	0.05
Disulfoton-sulfoxide	0.997	0.992	0.07	0.05	Parathion-methyl	0.997	0.995	0.07	0.08
Endosulfan sulfate	0.997	0.996	0.02	0.02	Pentachloronitrobenzene	0.997	0.997	0.09	0.06
Endrin	0.999	0.994	0.01	0.01	Pentoxazone	0.999	0.993	0.02	0.02
Endrin	0.999	0.994	0.01	0.01	Piperonyl butoxide	0.998	0.997	0.02	0.02
Endrin ketone	0.997	0.996	0.01	0.01	Profenofos	0.997	0.996	0.02	0.01
EPN	0.997	0.996	0.02	0.04	Pyrazophos	0.998	0.996	0.02	0.03
Ethiozin	0.997	0.992	0.01	0.02	Quinalphos	0.998	0.996	0.06	0.09
Ethofenprox	0.998	0.992	0.08	0.02	Tefluthrin	0.998	0.994	0.16	0.21
Ethofumesate	0.998	0.991	0.07	0.06	Terbufos	0.997	0.996	0.07	0.05
Fenitrothion	0.997	0.991	0.07	0.09	Terbufos sulfone	0.998	0.992	0.06	0.08
Fenpropimorph	0.997	0.995	0.10	0.12	Thionazin	0.998	0.994	0.04	0.03
Fenthion	0.998	0.995	0.07	0.07	Trifluralin	0.997	0.994	0.05	0.04
Fenthion sulfone	0.997	0.994	0.02	0.02	Triphenyl phosphate	0.997	0.993	0.02	0.01

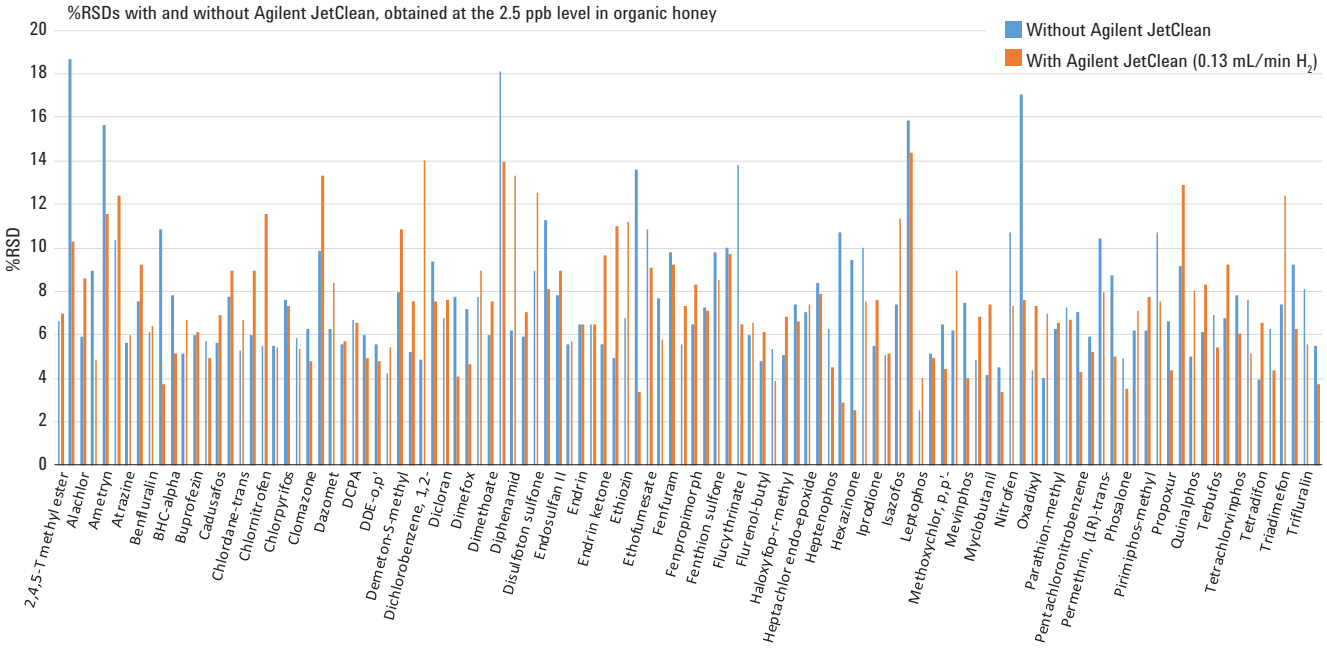

Figure 15. %RSDs of selected target compounds obtained with and without Agilent JetClean at the 2.5 ppb level in organic honey.

Conclusions

Approximately 200 pesticides were analyzed in organic honey extract on the Agilent 7010 Series Triple Quadrupole GC/MS with and without the use of the Agilent JetClean self-cleaning ion source in the Acquire and Clean mode (0.13 mL/min continuous flow). The improvements of the chromatographic peak shape and baselines (for later, higher molecular weight compounds), the comparable R^2 values, the equivalent %RSDs, as well as the low ppb MDLs; all indicate that the use of a low continuous flow of H_2 into the MS source can be considered as an option for maintaining performance during pesticide analyses.

References

1. K. A. Anderson, *et al.* "Modified ion source triple quadrupole mass spectrometer gas chromatograph for polycyclic aromatic hydrocarbon analyses" *J. Chromatogr. A* **1419**, 89-98 (2015).
2. M. Anastassiades, *et al. AOAC Int.* **86**, 412-431 (2003).
3. S. J. Lehotay, K. Mastovská, A. R. Lightfield. *J. AOAC Int.* **88**, 615-629 (2005).
4. J. Westland, J. Stevens. An Optimal Method for the Analysis of Pesticides in a Variety of Matrices, *Agilent Technologies Application Note*, publication number 5991-7303EN (**2016**).
5. Pesticides and Environmental Pollutants (P&EP) Standard MRM Database User's Manual G9250AA Rev. A.4.00, *Agilent Technologies*, publication number G3445-90040.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
September 28, 2016
5991-7342EN

Agilent Technologies