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Maintaining Sensitivity and Reproducibility with the JetClean Self-Cleaning IonSource for Pesticides in Food and Feed

Authors
Jessica Westland[1]; Vivian Chen[2] and Elizabeth Almasi[3]; [1]Agilent Technologies, Wilmington

Introduction

The global agricultural industry uses over a thousand 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 practices, such as QuEChERS are routinely used for the preparation of food and feed samples, often leaving significant amount of matrix in the extracts. Analytical laboratories are challenged by these matrix residues, which with time negatively affects the response of the analyzed pesticides, and eventually requires source cleaning. Agilent's JetClean self-cleaning ion source (JetClean) reduces the need for manual source cleaning while still allowing for the analysis of complex samples without losing sensitivity and reproducibility.

The Agilent JetClean utilizes carefully monitored hydrogen gas (H_2) introduction to the source, controlled by Agilent's MassHunter Data Acquisition Software. The appropriate H_2 flow (in the µL/min range) 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 matrices.

JetClean has two operational modes:

1. Acquire and Clean (or on-line) mode, when H_2 is running during the analysis
2. Clean only (or off-line) mode when H_2 is introduced only post run or post sequence

Experimental

Methodology: The analysis was conducted on an Agilent 7890B GC and 7010 Series Triple Quadrupole GC/MS. See Tables 1 – 3 for method parameters. The system was configured with a Multimode Inlet, equipped with an ultra-inert liner (p/n: 5190-2293). The inlet was then connected to two HP-5ms UI columns (15 m × 0.25 mm × 0.25 µm; p/n: 19091S-431 UI) coupled to each other through a purged ultimate union (PUU) for the use of backflushing (see Figure 1).

The H_2 cleaning was operated in the "Acquire & Clean" mode which allowed constant H_2 flow during the analytical runs.

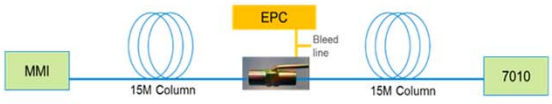


Figure 1. Column Configuration for Optimal MRM Application.

Table 1. 7890B GC Method Conditions

Injection port liner	4-mm Ultra Inert liner with wool		
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)		
Oven program		60 °C	1 min
	40 °C/min	120 °C	0 min
	5 °C/min	310 °C	0 min
MS transfer line temperature	280 °C		

Table 2. PUU Backflush Settings*

Timing	1.5 min during post-run
Oven temperature	310 °C
Aux EPC pressure	~50 psi
Inlet pressure	~2 psi

*Backflush conditions were optimized for the application. A 1.5 min backflush duration may be too short for other methods. It can be extended up to 5 min duration.

Table 3. 7010 MS/MS Parameters

Electron Energy	70 eV
Tune	atunes.eihs.tune.xml
EM gain	10
MS1 & MS2 resolution	Wide
Collision Cell	1.5 mL/min N_2 & 2.25 mL/min He
Quant/Qual transitions	Matrix Optimized
Dwell times	Time Segment (TS) specific*
Source temperature	300 °C
Quad temperatures	150 °C
JetClean:	Acquire & Clean mode

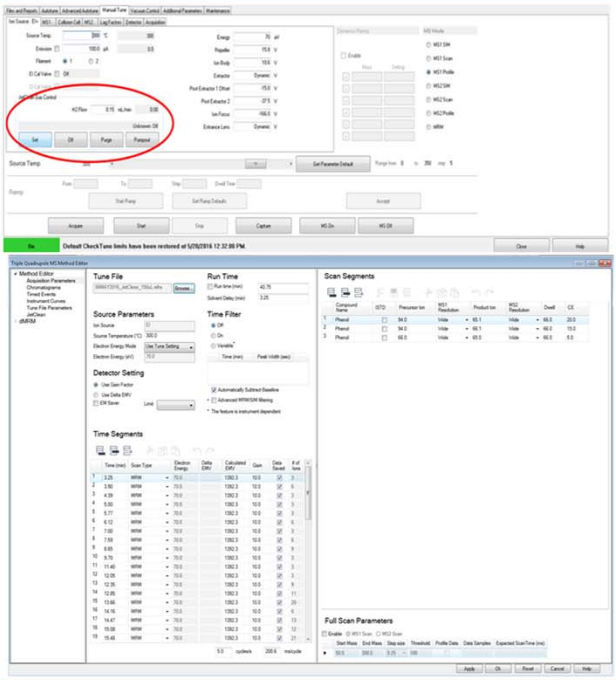
*The dwell times in each TS were the same, all with values over 10msec, resulting in a scan rate of ~5 scans/sec for the TS.

Table 4. Matrix Selection and Sample Preparation Used for Optimal MRM Application

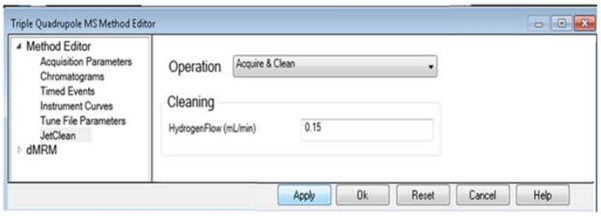
Category	Matrix	Sample Prep
High Sugar	Organic Honey	5 g honey/5 mL water, EN salts, EN dSPE General

Experimental

Operation: JetClean was initiated in the acquire and clean mode for this application. The MassHunter software allowed for the simple setup and operation of the process, all controlled in the MS domain.



Tuning of the MS:
Acquire and Clean mode of operation

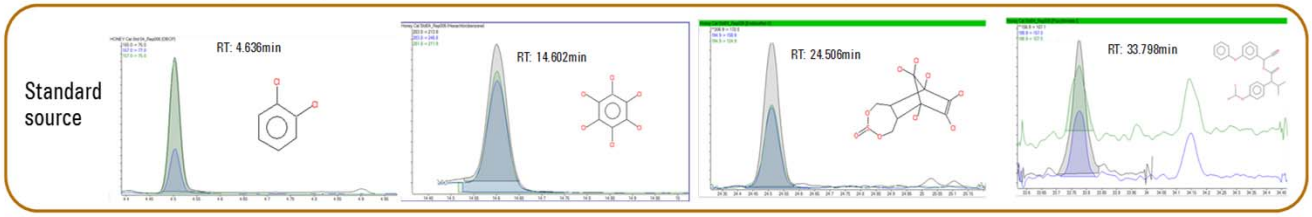


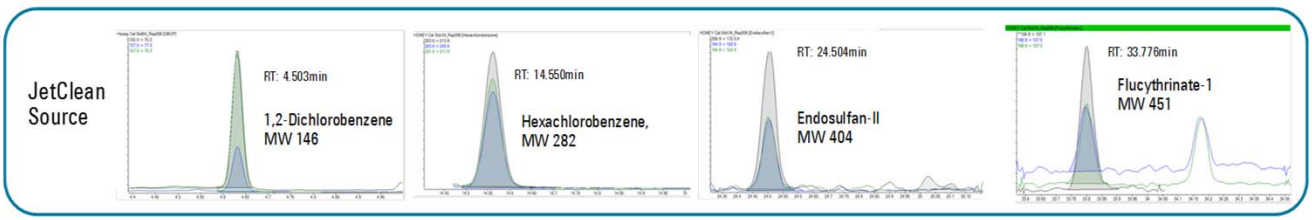
Incorporating the tune file and JetClean parameters in the acquisition method for GLP and easy transportability.

Results and Discussion

Agilent's Self-cleaning ion source has been successfully used for the extended, 64 analyte PAH analysis in environmental[1] and labs and also in food laboratories, resulting in remarkable precision, accuracy, linearity and detection levels, which were sustained for extended periods of time (many months) without manual cleaning. Considering the benefits of the Self-cleaning ion source for PAH analysis, the use of the JetClean applied for cleaning the MS source for pesticide analysis.

Chromatographic Performance: The following chromatograms show analytes at 2.5 pg concentrations, eluting at the beginning, middle and at the end of the chromatographic run. The ion plots are of target compounds and their respective matrix optimized MRM transitions in organic honey using standard source configuration and with the JetClean source. The JetClean benefits on peak shape and baseline are more obvious on the later eluting, higher MW analytes.





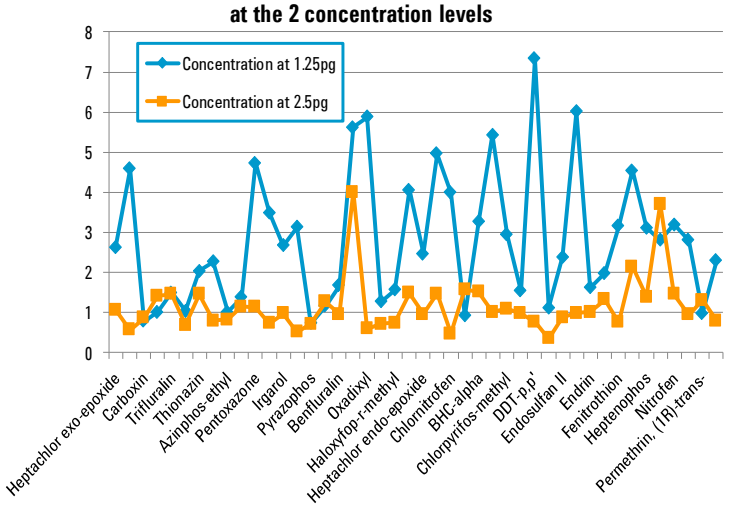
Results and Discussion

Quantitative results: Table 5 lists the R^2 values and the statistically derived MDLs for representative target analytes of the over 170 various pesticides tested. The calibration ranged from 0.12 pg/ul - 50pg/uL for the majority of the analytes, although some were not included at the lowest level. The resulting R^2 values were very comparable by both source type. The MDLs were calculated from 10 replicate measurement of 1.25 pg/µL concentration spiked honey extract using 99% confidence level. Lower MDLs were obtained for the majority of the analytes using the JetClean source, with an average of 0.151 pg MDL for the standard source and 0.081pg for the JetClean source. The replicate measurements performed at 1.25pg level resulted lower %RSD using the JetClean source, although they were comparable at the 2.5 pg level.

Table 5.

Analyte	R^2		MDL (pg)	
	STD	JetClean	STD	JetClean
Heptachlor exo-epoxide	0.994	0.992	0.085	0.022
Endrin ketone	0.993	0.996	0.041	0.016
Carboxin	0.991	0.994	0.021	0.025
Profenofos	0.994	0.996	0.023	0.036
Trifluralin	0.997	0.994	0.088	0.033
Alachlor	0.996	0.978	0.119	0.050
Thionazin	0.994	0.994	0.097	0.038
Dimethoate	0.999	0.992	0.150	0.028
Azinphos-ethyl	0.999	0.995	0.063	0.071
Fenthion sulfone	0.996	0.994	0.046	0.040
Pentoxazone	0.998	0.993	0.137	0.034
Iprodione	0.993	0.999	0.041	0.029
Irgarol	0.993	0.997	0.117	0.037
Phosphamidon II	0.996	0.988	0.235	0.031
Pyrazophos	0.994	0.996	0.042	0.056
Terbufos	0.994	0.996	0.078	0.032
Benfluralin	0.991	0.994	0.143	0.042
Ethofenprox	0.996	0.992	0.161	0.036
Oxadixyl	0.994	0.994	0.245	0.030
Endosulfan I	0.995	0.996	0.027	0.032
Haloxyfop-r-methyl	0.999	0.994	0.085	0.060
Tetrachlorvinphos, E-isomer	0.998	0.996	0.112	0.029
Heptachlor endo-epoxide	0.999	0.992	0.100	0.042
Methoxychlor, p,p'-	0.994	0.996	0.170	0.046
Chlornitrofen	0.996	0.997	0.070	0.020
Bendiocarb	0.994	0.937	0.719	1.263
BHC-alpha	0.995	0.995	0.221	0.098
Chlorobenzilate	0.996	0.995	0.557	0.118
Chlorpyrifos-methyl	0.994	0.993	0.270	0.075
DBCP	0.995	0.986	0.155	0.208
DDT-p,p'	0.993	0.996	0.427	0.105
Dichlorobenzene, 1,2-	0.999	0.993	0.129	0.184
Endosulfan II	0.991	0.998	0.037	0.040
Endosulfan sulfate	0.997	0.996	0.136	0.036
Endrin	0.992	0.994	0.045	0.025
Ethoprophos	0.995	0.995	0.072	0.016
Fenitrothion	0.993	0.991	0.313	0.060
Flucythrinate I	0.997	0.992	0.040	0.023
Heptenophos	0.992	0.996	0.264	0.045
Hexachlorobenzene	0.999	0.997	0.227	0.116
Nitrofen	0.990	0.995	0.097	0.030
Parathion-methyl	0.994	0.995	0.272	0.070
Permethrin, (1R)-trans-	0.997	0.968	0.033	0.105
Pirimiphos-methyl	0.996	0.994	0.152	0.042

%RSD ratio of the Standard source / JetClean source results obtained at the 2 concentration levels



Conclusions

Approximately 170 various pesticides were analyzed in organic honey on the 7010 Series Triple Quadrupole GC/MS using standard and JetClean source in the Acquire and Clean mode, utilizing carefully introduced hydrogen flow. The JetClean control is included in the MassHunter software with easy setup and operation.

The chromatographic peak shape and baseline was improved using the Jetclean source particularly for the late eluting compounds. The calibration resulted very comparable R^2 values by both source, while the MDLs obtained at 1.25 pg level resulted lower values using the JetClean source. The %RSDs were comparable at higher, 2.5pg/µl level. The results indicate that the JetClean source meets and exceed the performance delivered by the standard source.

Further study is undergoing to identify how the source maintenance period is extended when JetClean is applied compared to the standard source.

Reference

[1]Anderson, Kim A., et al. "Modified ion source triple quadrupole mass spectrometer gas chromatograph for polycyclic aromatic hydrocarbon analyses." *Journal of Chromatography A* 1419 (2015): 89-98.