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Off-Line Hydrogen Cleaning of GC/MS Ion Source Increases Sample Throughput for Pesticides in Foods

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Introduction

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction approach has streamlined pesticides in foods analysis by hyphenated mass spectrometry. With speed and ease, however, comes the challenge of high-matrix samples that can adversely affect the performance of the instrument over time and, thus, increase maintenance requirements. Triple quadrupole GC/MS/MS analysis in a high-throughput laboratory may require that the ion source be cleaned as often as every few weeks. This maintenance interval may be extended by an integrated hardware option which allows for either simultaneous or off-line cleaning by hydrogen. The use of off-line cleaning with hydrogen (between analytical runs) was found to be optimal for pesticides in foods and increased the interval between source cleanings by several-fold.

Experimental

Instrument conditions

Run Time	40.5 min.
Post Run Time	2 min.
Oven	
Temperature	
(Initial)	60 °C
Hold Time	1 min
Post Run	310 °C
Program	
#1 Rate	40 °C/min
#1 Value	120 °C
#1 Hold Time	0 min
#2 Rate	5 °C/min
#2 Value	310 °C
#2 Hold Time	0 min

He Quench Gas	On 2.25 mL/min
N2 Collision Gas	On 1.5 mL/min

Injection Volume	1.5 µL
Injection Type	2-layer Sandwich
L1 Airgap	0.2 µL
L2 Volume	0.5 µL
L2 Airgap	0.2 µL

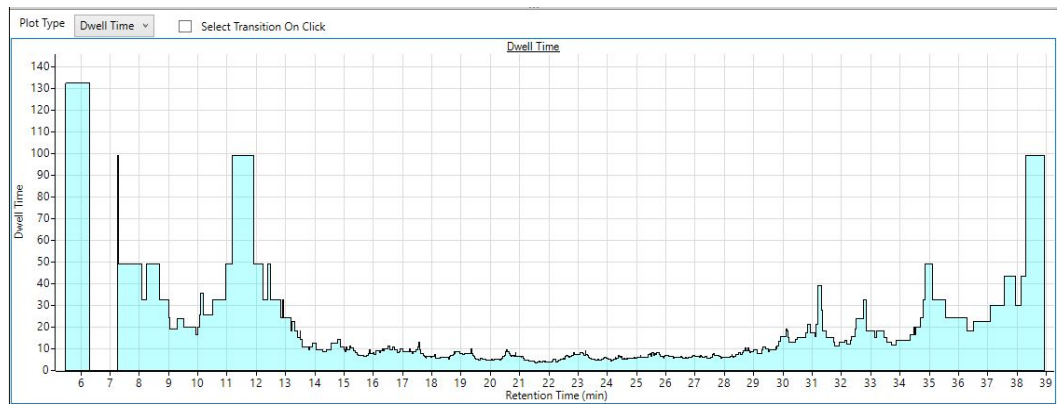
Front MM Inlet He	
(Initial)	60 °C
Hold Time	0.35 min
Post Run	310 °C
Program	
#1 Rate	900 °C/min
#1 Value	280 °C
#1 Hold Time	15 min
#2 Rate	900 °C/min
#2 Value	300 °C
#2 Hold Time	1 min
Mode	Solvent Vent
Pressure	On 13.291 psi
Total Flow	On 54.191 mL/min
Septum Purge Flow	On 3 mL/min
Septum Purge Flow Mode	Switched
2 min (Post Run Total Flow)	25 mL/min
Gas Saver	On 20 After 4 min mL/min
Purge Flow to Split Vent	50 mL/min at 1.5 min
Vent Flow	25 mL/min per min
Vent Pressure	6 psi Until 0.3 min
Cryo Use Temperature	200 °C

MSD Transfer Line (AUX 2)	280 °C

Column #1	
(Initial)	1.1914 mL/min
Post Run	-6 mL/min
Rtx-5Ms w/Integra-Guard 15m + 5m Pre-column	
20 m x 250 µm x 0.25 µm	
In	Front MM Inlet He
Out	Backflush EPC
(Initial)	60 °C
Pressure	13.291 psi
Flow	1.1914 mL/min
Average Velocity	27.983 cm/sec
Holdup Time	1.1912 min

Column #2	
(Initial)	1.3914 mL/min
Post Run	6.4 mL/min
Rtx-5Ms w/Integra-Guard	
15 m x 250 µm x 0.25 µm	
In	He Backflush EPC
Out	MSD
(Initial)	60 °C
Pressure	4.4277 psi
Flow	1.3914 mL/min
Average Velocity	61.093 cm/sec
Holdup Time	0.40921 min

Plots of concurrent dMRM Transitions acquired (left) and dwell times (right) during a 40 minute analysis



dMRM Statistics

Total MRMs	981	Minimum dwell time (ms)	3.43
Number of MRM groups	361	Maximum dwell time (ms)	132.5
Minimum concurrent MRMs	3	Minimum cycle time (ms)	124.67
Maximum concurrent MRMs	94		

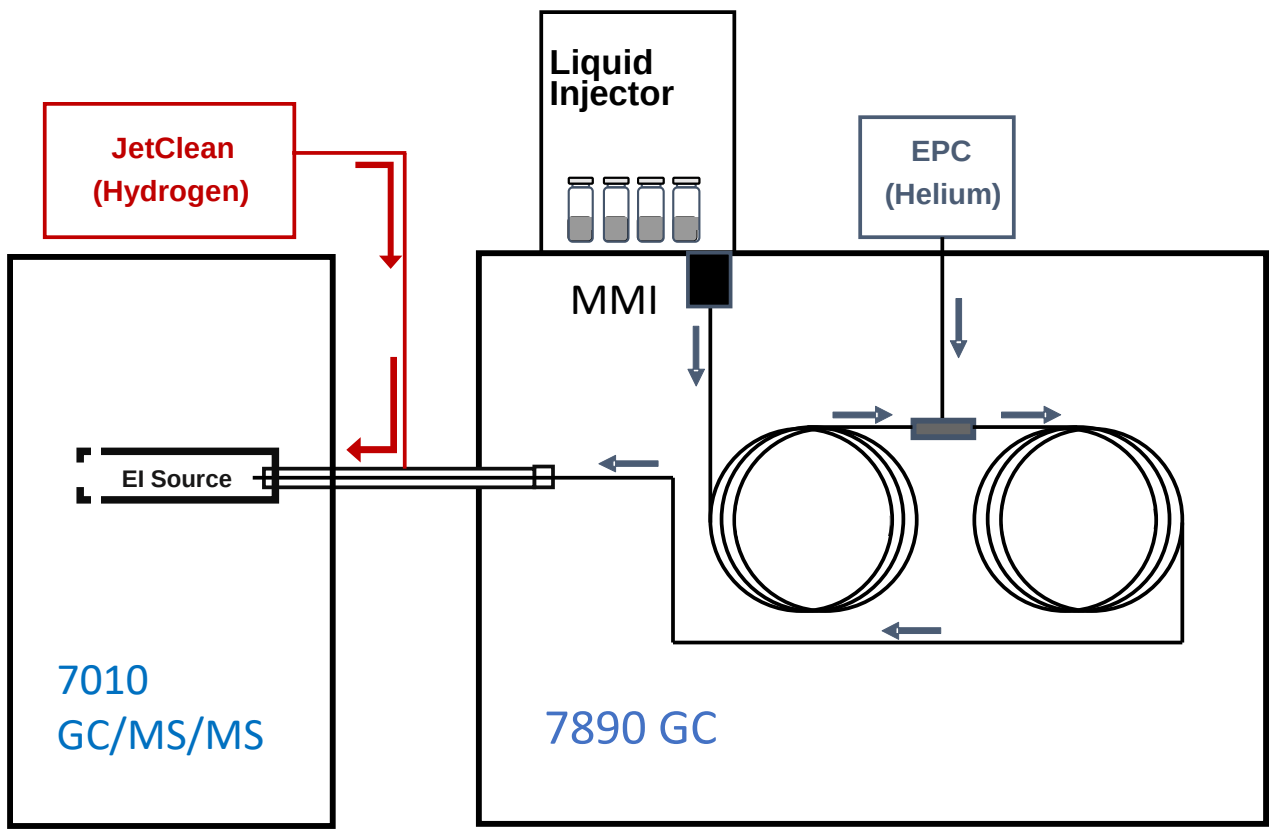
Batch analysis of vegetable matrices

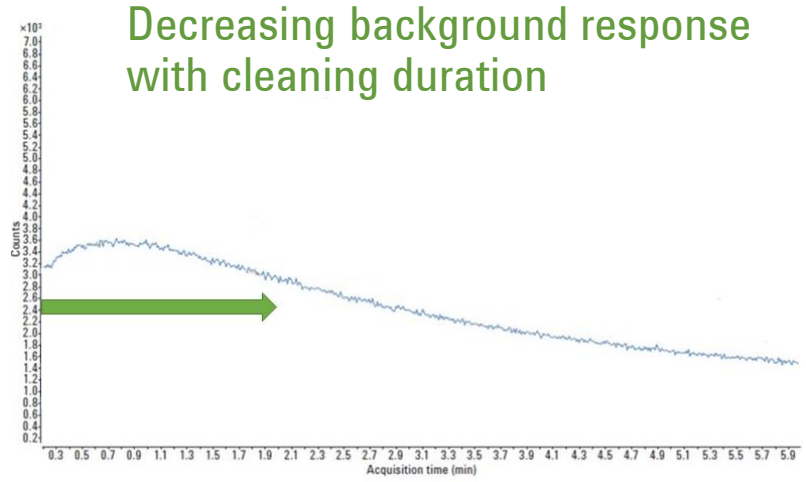
Samples of chard, apple, plum, peppers and spinach were extracted using a modified EN QuEChERS method. Food extracts were prepared and analyzed on the same day. Calibration curves were generated for each vegetable or fruit by spiking blank matrix with a standard mixture of 200 pesticide residues. ISTD Tris[2-chloro-1-(chloromethyl) ethyl]phosphate (TDCPP) was added at a final concentration of 100 ppb. Analyte protectant solutions as described in the official food testing regulation (3-ethoxy-1,2-propane diol, sorbitol, D-(-)-gluconic acid δ-lactone, and shikimic acid) were co-injected at a volume of 0.5 µL using sandwich injection. The working calibration range was 5 – 250 ppb in vial. Sample batches for analysis including quality control checks were set up in sequences using bracketed calibration. The total number of injections for each batch was approximately 25, excluding solvent blanks. SANTE Guidelines were used as acceptance criteria.

Off-line H2 cleaning during batch sequences of vegetable matrices

Sample analysis was carried out using triple quadrupole mass spectrometers equipped with a high efficiency or extractor source. The mass spectrometer was equipped with a hydrogen cleaning module, JetClean, which is fully integrated with software control. Off-line hydrogen cleaning, using Clean Only mode, was programmed into the software. Following column back flushing at the end of each run, hydrogen was introduced to exert a cleaning effect on the ion source:

Oven cooling after analytical run | **Introduce 0.7 mL/min. hydrogen** | **Duration = 2 minutes**



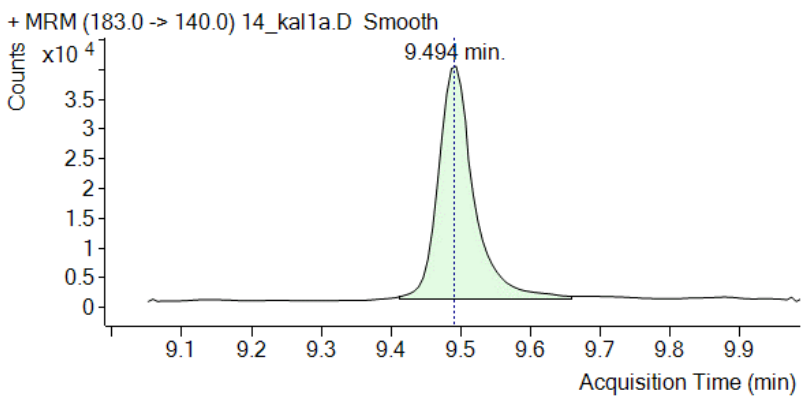


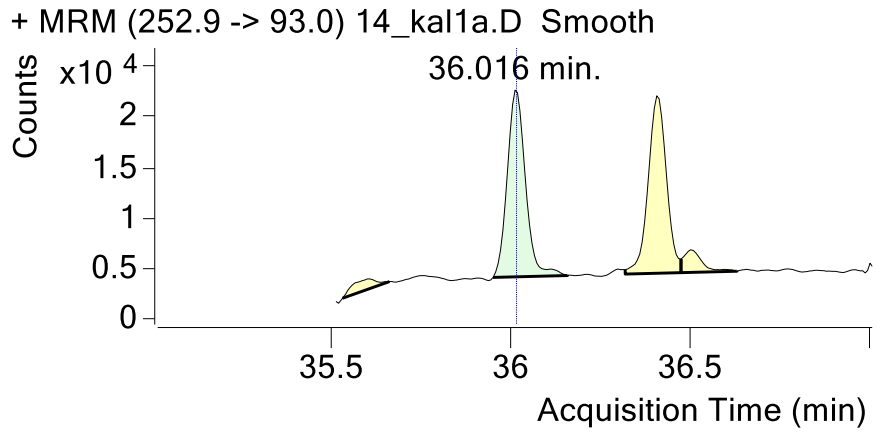
Instrument schematic (left). JetClean is a patented option that adds a controlled flow of hydrogen directly into the ion source to provide a cleaning action. The cleaning process occurs when the filaments are on and only affects the source. Cleaning can be done during the analysis (Acquire and Clean mode) or as a separate method following the analytical run (Clean Only mode). The latter case may take advantage of the fact that the oven is cooling during this time.

JetClean in Clean Only Mode (right). Trace for contaminating ion (or TIC may be used) showing decreasing signal during the cleaning process. Cleaning time is determined as part of method development and then may be applied on a routine basis.

Results

Chromatograms for etridiazole and deltamethrin in plum at the low calibration level of 5 ppb

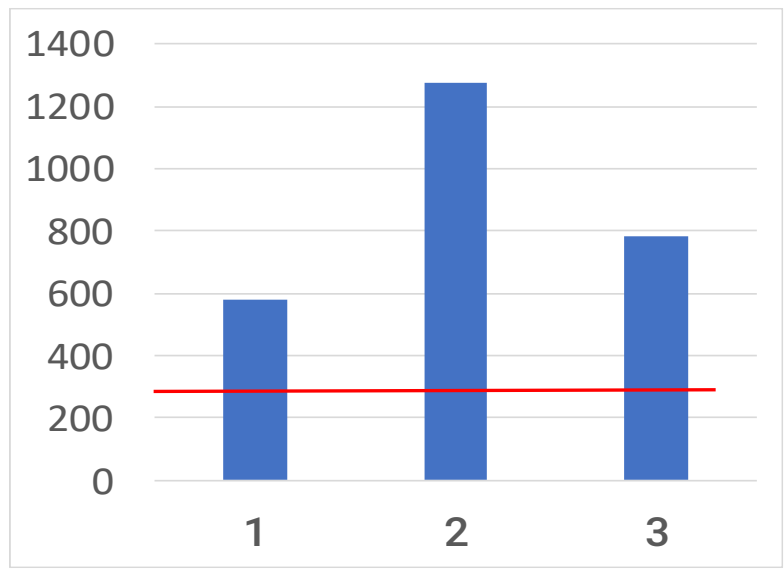




Longer maintenance interval durations for challenging residues analysis

The food matrices chard, plum, peppers and spinach are challenging in terms of the nature and amount of co-extractives that accumulate and activate the sample path, including the ion source. On one instrument, it was determined that 578, 1276 and 786 matrix injections, respectively, were made and passed batch performance criteria between source cleanings. This compares with 200-300 injections per maintenance interval expected if off-line cleaning were not used. Thus, instrument up-time was increased by as much as several-fold and associated cost-savings were realized.

Instrument up-time increased by as much as several-fold



Number of injections between ion source cleanings (blue bars) for model 7010 instrument with JetClean at CVUA. The red line represents the number of injections of challenging matrix that a laboratory might expect to perform between maintenance intervals when not using JetClean.

Conclusions

- JetClean is a patented option that provides *in situ* ion source cleaning using hydrogen.
- Cleaning occurs when the filaments are on and only affects the source.
- Acquire and Clean mode is done concurrently with the analysis.
- Clean Only mode may be used following the analysis without any increase in instrument cycle time.
- Instrument up-time was increased by as much as several-fold and associated cost-savings were realized when Clean Only mode was implemented in a food safety laboratory.

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