Analytical Methodology to Improve Pesticide Residue Analysis with Ion Trap GC/MS/MS

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ASMS 2011
WP 331

Agilent Technologies

Introduction

Pesticide residue analysis in heavy matrix can be labor and instrument intensive. Samples containing heavy matrix require longer run times to remove it from the GC column. Matrix that is passed through the GC into the mass spectrometer can contaminate the system reducing sensitivity, making frequent cleaning necessary. By utilizing backflush technology, we demonstrate that we can more efficiently remove heavy matrix from the column effluent. We observed improvements of baseline and retention time stability in spiked orange oil samples, while simultaneously reducing overall analysis time.

Experimental

Sample Preparation Procedure
Neat orange oil was prepared with a mixture of 5 pesticides to make a spiked concentration of 10 ppb.

Analytical Methodology
An Agilent 7890 GC/ 240 MS with a split/splitless inlet, operating in pulsed splitless mode was used in the analyses. The GC was operated in constant flow, and the GC conditions are outlined below. The Ion Trap operated in EI/MS/MS mode, and the ionization, isolation, scan, and ejection parameters were optimized using Automated Method Development (AMD).

Mid column, post-run backflushing was achieved by coupling two 15 m x 0.25 mm x 0.25 µm DB-5 ms columns with a purged ultimate union. The post-run flows are described below. The same setup was employed for the non-backflushing analyses but without changing the flow during the post run.

Split/Splitless Inlet Parameters:
Mode: Pulsed Splitless
Heater: 270° C

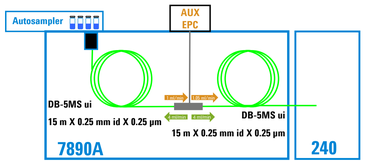

Figure 1: GC/MS System Configuration.

Experimental

GC temperature program:
Analysis: 50° C for 0.5 min
Ramp 15° min^{-1} to 260° C
Post Run: 280° C for 1.5 min.

GC flow program:

	With Backflush	Without Backflush
Analysis:		
Column 1:	1.00 mL/min	1.00 mL/min
Column 2:	1.05 mL/min	1.05 mL/min
Post Run:		
Column 1:	-4.06 mL/min	1.00 mL/min
Column 2:	4.00 mL/min	1.05mL/min

240 Parameters:
Trap: 230° C
Manifold: 50° C
Transfer Line: 280° C

Analyte	Pre → Prod	(Quant)	Waveform
o-Xenol	170 → 65:180	(141)	Resonant
Diazinone	304 → 116:314	(179)	Resonant
Carbanil	314 → 120:324	(258)	Non Resonant
2,4-DCPA	248 → 95:258	(213)	Resonant
2,4-D	234 → 89:244	(199)	Resonant

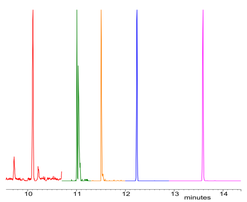

Figure 2: Normalized EI/MS/MS extracted ion chromatogram of orange oil spiked with 10 ppb pesticides

Results and Discussion

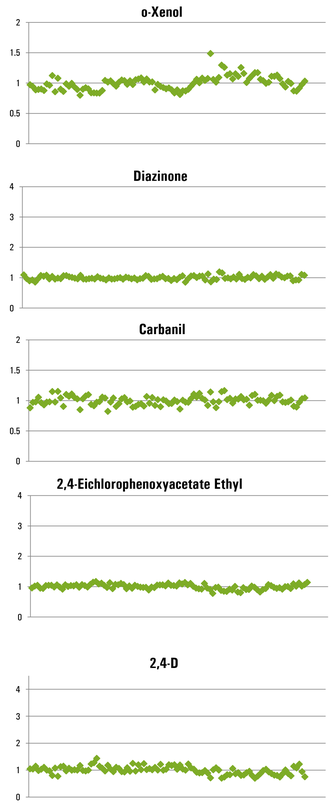

Figure 3 a-e: 100 replicate injections of orange oil spiked with 10 ppb pesticides using backflush

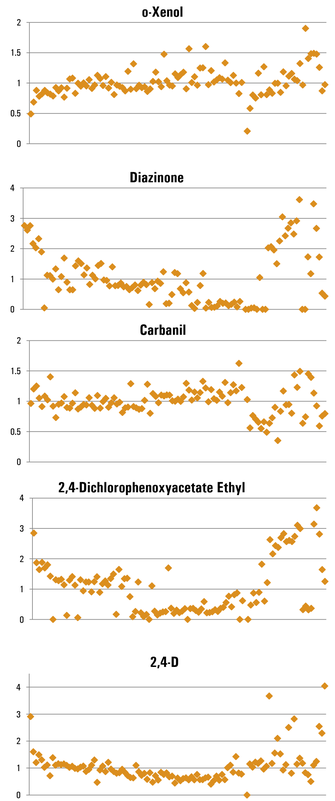

Figure 4 a-e: 100 replicate injections of orange oil spiked with 10 ppb pesticide without using backflush

Results and Discussion

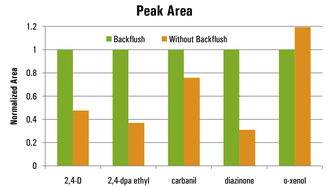

Figure 5: Peak area of 100 replicate injections of orange oil spiked with 10 ppb pesticides. Average areas normalized to set using backflush.

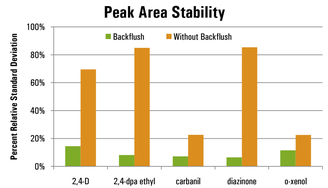

Figure 6: Relative percent standard deviation of peak area of 100 replicate injections of orange oil spiked with 10 ppb pesticides.

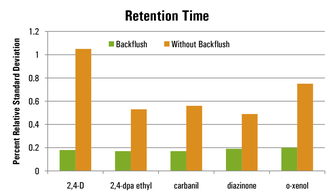

Figure 7: Relative standard deviation (ppm) of retention time of 100 replicate injections of orange oil spiked with 10 ppb pesticides.

The stability of response over a large number of injections is demonstrated in figures 3, 4 and 6. One hundred replicate injections of the 10 ppb spiked orange oil sample were made, and the peak areas were looked at. In figures 3 and 4, the peak areas for each of the five pesticides were normalized to the average of the hundred injections and plotted to demonstrate the comparable response stabilities. The corresponding relative percent standard deviations for each of the pesticides in backflushing and non-backflushing operation are represented in figure 6. The absolute peak area intensity is compared in figure 5 where in all but one case the data set that used backflushing provided a higher response.

The chromatographic stability of the instrument is demonstrated in figure 7, which shows the relative percent standard deviation of the retention times (RT) for the five analytes utilizing backflushing and without backflushing. The increase in RT stability provides reassurance in correctly identifying possible hits.

By increasing the post-run temperature to 320° C and holding for 8.5 minutes, the non-backflushing results became comparable to those utilizing backflushing. However, using backflushing decreased the analysis time by more than 40%. Additionally using backflushing, the lower temperature required to elute the orange oil matrix has the potential to increases the lifetime of the GC column. Furthermore, by using backflushing, the matrix is not introduced into the ion trap, keeping the MS cleaner, and therefore decreasing the frequency of maintenance and the need for recalibration.

Conclusions

The use of backflush increases the quality of pesticide residue analyses by increasing the precision of instrumental response and chromatographic stability. Analysis time is decreased, and the overall condition of the instrument is maintained for a longer period of time, increasing analytical productivity.