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Improving Gas Chromatograph-Mass Spectrometer System Longevity for Multi-Residue Pesticide Methods with Heavy Matrix Through Inert Microfluidic Retention Gap Technology

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Introduction

Analysis of pesticides in food

The analysis of pesticides in food is known to be complex. With increasing target compound and commodity lists, decreasing detection limit requirements, and the need for a wide linear dynamic range, pesticide analysis is demanding. Tandem mass spectrometry (MS/MS) is incredibly useful in screening, confirming, and quantifying a wide range of pesticides especially with its ability to minimize matrix interferences. However, despite these advantages and advances in sample preparation like QuEChERS, matrix can still contaminate the inlet liner, analytical column(s), ion source, etc., leading to peak tailing, loss of response, and even ion enhancement. Users often default to regular liner replacements, column trimming, and source maintenance. By employing an inert, microfluidic retention gap, system maintenance can be reduced and system longevity improved.

Agilent 9000 Intuvo Gas Chromatograph

A redesigned modular flow path featuring an inert, microfluidic retention gap (guard chip) protects the analytical column(s) and ion source from matrix and eliminates the need to trim the column. It also offers these additional advantages over conventional gas chromatographic systems:

- Simplified maintenance
- Improved inertness
- Smaller footprint

Experimental

Instrumentation

The analysis was conducted on an Agilent Intuvo 9000 Gas Chromatograph coupled with an Agilent 7000C Triple Quadrupole Mass Spectrometer. The system was configured with a split/splitless inlet equipped with an ultra-inert liner with wool and a single HP5-ms UI column (15m x 0.25mm x 0.25µm). Target pesticides were evaluated in seven different food commodities (honey, rice, orange, olive oil, black tea, cucumber, and onion). Calibration curves for the pesticides ranged from 1-1000 ng/mL and the 50 ng/mL standard was evaluated over the course of 60 matrix injections for accuracy. Column lifetime and required system maintenance comparison studies were also evaluated by spinach extract injections on both the Intuvo GC/MS/MS and 7890B GC/MS/MS systems. Instrument conditions are show below.

Parameter	Value
Agilent 9000 Intuvo GC & 7890B GC	
Inert flow path configuration	Simple MS
Sandwich injection	3-layer sandwich L1 (matrix) 1µL L2 (analyte protectant) 0.5µL L3 (sample) 1µL
Inlet	SSL; pulsed SL 280°C
Injection pulse pressure	30psi until 0.5min
Intuvo guard chip	Track oven
Intuvo bus temperature	290°C (default)
Column	HP5-ms UI 15m x 250µm x 0.250µm
Column flow	1.4mL/min
Column temperature program	60°C (1.5min) then 50°C/min to 160°C then 8°C/min to 240°C then 50°C/min to 280°C (2.5min) then 100°C/min to 290°C (1.1min)
Agilent 7000C GC/MS/MS	
Transfer line	280°C
Source temperature	280°C
Quad temperature	150°C

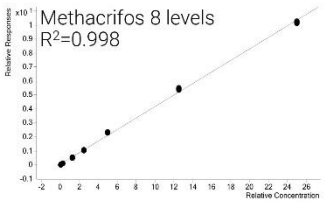
Results and Discussion

Calibration

A calibration curve consisting of eight levels run in triplicate was determined for each matrix. A subset of a larger list of pesticides typically analyzed was used throughout this study to allow for more rigorous examination of calibration coefficients and chromatographic performance. Deuterated polyaromatic hydrocarbons were used as internal standards.

Excellent linearity for concentrations ranging from 1ng/mL to 1000ng/mL was found. Correlation coefficients ranged from 0.972 to 0.998.

1. 1,4-dichlorobenzne-d4
2. Naphthalene-d8
3. Methacrifos
4. Acenaphthene-d10
5. Ethalfluralin
6. Sulfotep
7. Demeton-S
8. Simazine
9. Lindane
10. Phenanthrene-d10
11. Chlorpyrifos methyl
12. Fenitrothion
13. Aldrin
14. Pendimethalin
15. Tolyfluanid
16. Dieldrin
17. Buprimate
18. Triazophos
19. Chrysene-d12
20. Iprodione
21. EPN
22. Phosalone
23. Mirex
24. Coumaphos
25. Perylene-d12
26. Pyraclostrobin
27. Deltamethrin



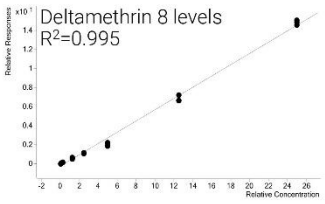


Figure 1. Calibration curves for methacrifos and deltamethrin in honey are representative of the 21 analytes evaluated in seven different matrices.

Accuracy and Chromatographic Consistency

After calibrating with the matrix of interest, 60 additional sandwich injections were evaluated for continuing calibration accuracy. Figure 2 shows the average accuracy of the 60 injections for each matrix and analyte.

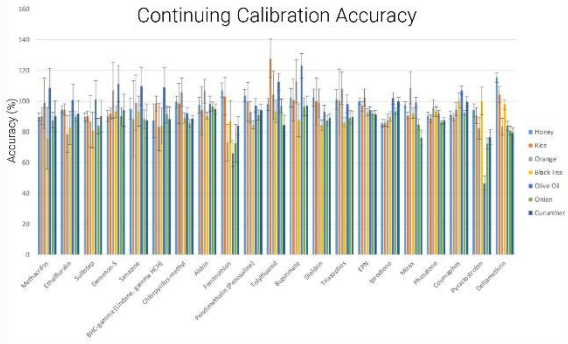


Figure 2. Continuing calibration accuracy for 21 analytes and seven matrices demonstrates consistent responses over 60 injections.

When examining Figure 2 there are a few analyte/matrix pairs that show a higher degree of variability (wider error bars) or a lower degree of accuracy. However, the majority of the analyte/matrix pairs demonstrate continuing calibration accuracy between 70% and 120% for an average of 60 matrix injections. These results indicate a high degree of consistency among the data with limited cases of response loss, peak distortion, or ion issues.

Overlaid chromatograms highlighting the start of the experiment, after batch completion, and after performing a guard chip replacement are shown in Figure 3.

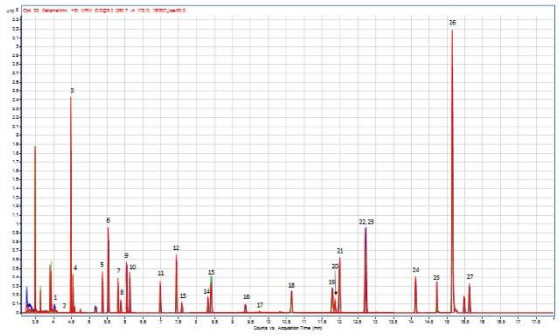


Figure 3. Overlaid chromatograms demonstrate the chromatographic consistency after calibration (blue), after completing an additional 60 matrix injections with black tea (red), and after guard chip replacement on the Intuvo system (green).

Results and Discussion

Comparison to Conventional Gas Chromatographs

To demonstrate further the added longevity afforded by the guard chip as part of the Intuvo inert flow path, a side-by-side comparison was done with a 7890B GC/MS/MS system. Spinach, a high pigment matrix, was used for this comparison study. Sandwich injections were used to introduce matrix, analyte protectants, and a 50ng/mL standard each injection. The accuracy of the 50ng/mL standard, compared to the calibration curve, was monitored and maintenance on either system was performed if the calibration accuracy fell outside of the 70-120% window.

In the previous study, the Intuvo system routinely completed nearly 100 injections in a given batch without suffering from analyte tailing or response loss. However, in conventional GC/MS/MS systems, where retention gaps are not typically used, peak shape degradation can be seen in as few as 30 matrix injections (Figure 4).

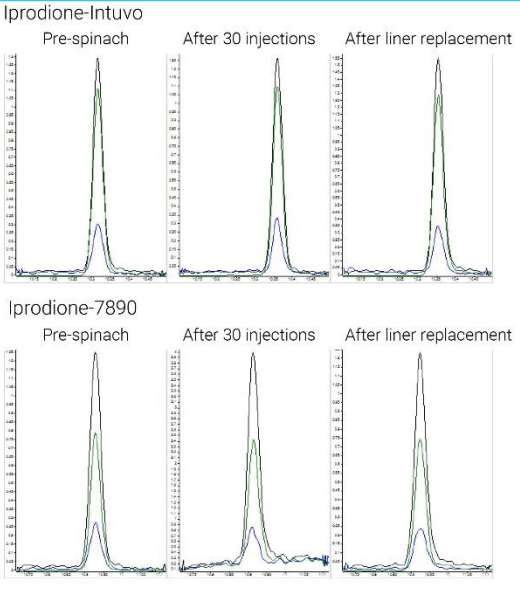


Figure 4. Multiple reaction monitoring target and qualifying ions are overlaid for iprodione. The peak shape differences between the two systems pre-matrix, after 30 injections, and after liner replacement highlight the benefit of including a retention gap.

With a single 15m column configuration, the Intuvo/7000C GC/MS/MS was able to withstand over 300 injections with liner or guard chip replacements. The system did not require retention time re-locking to maintain accurate time segments. In the case of the 7890B/7000C GC/MS/MS, less than 200 injections were completed. While liner replacements often improved performance on the 7890B/7000C GC/MS/MS system, column trimming was also required through the course of the experiment in order to maintain calibration accuracy within the 70-120% range. This shortened the column length to a point that a retention time locked chromatogram could no longer be achieved.

Conclusions

Improved chromatographic consistency and longevity

A calibration and matrix evaluation was performed on an Agilent Intuvo 9000 GC and an Agilent 7000C Triple Quadrupole Mass Spectrometer configured with an Intuvo HP5-ms UI column. Twenty-one pesticides were evaluated with seven matrices to represent a range of commodities, with varying levels of difficulty. The instrument showed excellent calibration linearity and continuing calibration accuracy. With the implementation of the Intuvo guard chip, the following was observed:

- The need to trim the column to maintain peak shape was eliminated
- The ion source did not require maintenance for the duration of the experiment
- Excellent peak shape and calibration accuracy was maintained on a simple, single column configuration

In this evaluation, calibration curve coefficients were usually 0.995 or better, regardless of matrix complexity. The average calibration accuracy for a 50ng/mL standard across 60 matrix injections was ~100% for the seven food commodities evaluated. Consistent peak shape and response was also observed through the experiment.

When comparing to conventional GC/MS/MS systems, the Intuvo guard chip preserves chromatographic fidelity for a greater number of injections while eliminating the need to trim the column. This resulted in a 50% increase in column longevity since the column length was maintained.

With regular maintenance of the liner and guard chip, Intuvo GC/MS/MS systems could last 500 injections without column or ion source maintenance.

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