Practical Tools for GC-MS Analysis of Pesticides in Complex Matrices

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Practical Tools for GC-MS?

- Cost-effective
- Easy-to-use
- Reliable
- Rugged
- Sensitive
- Selective

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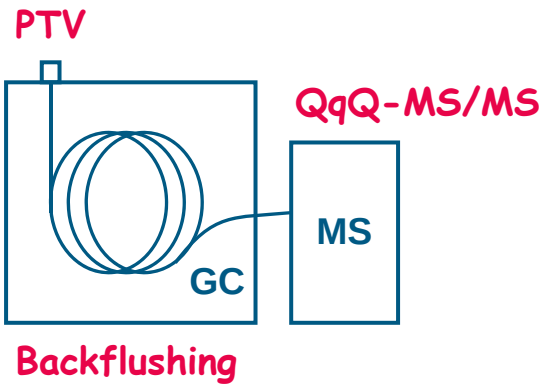

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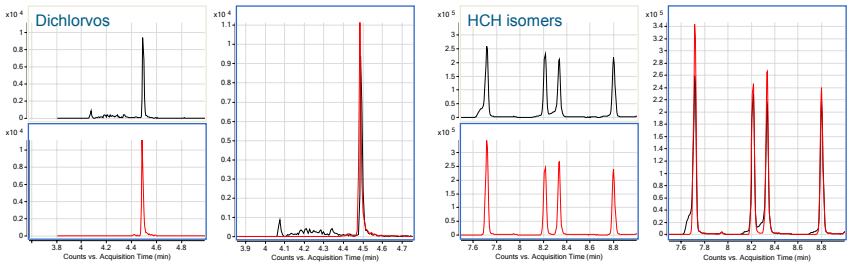
Programmable Temperature Vaporizer (PTV)

- Injection at a lower temperature → less discrimination, better results for thermally-labile analytes, reduced matrix effects
- Large volume injection (LVI) possibility
- Solvent elimination → LVI, better peak shapes of early eluting peaks in acetonitrile:



- Better column protection → better long-term performance, reduced matrix effects

Good PTV liner is the key to success!

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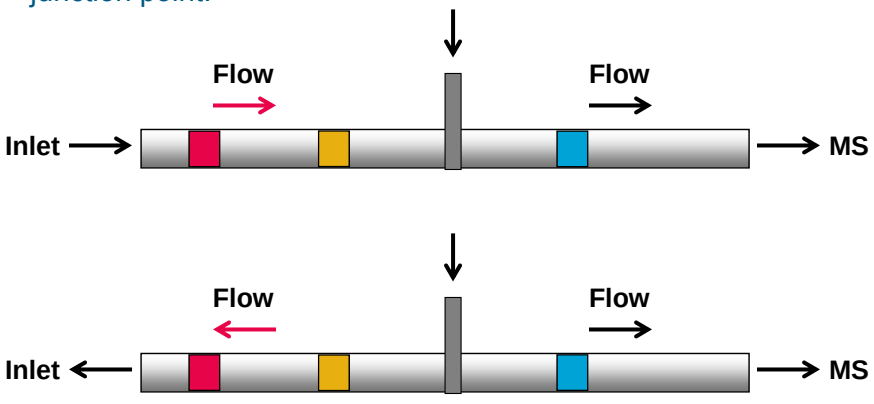
Column Backflushing

Backflushing can eliminate less volatile matrix components from the GC column by reversing the column flow at a pressure junction point:



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Column Backflushing

- **Post-Run Backflushing**
  - begins after the last analyte has been detected
  - the entire column is backflushed
  - typically uses a short restriction capillary installed at the column outlet
- **Concurrent Backflushing**
  - begins after the last analyte has eluted from the first "column"
  - different options:
    - retention gap = a short uncoated capillary
    - mid-column set-up (e.g. two 15-m columns)
    - short column = a short coated capillary

- time- and cost-effective
- good protection of the analytical column and MS

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Experimental Evaluation

- **GC-QqQ-MS/MS instrument:** Agilent 7980 GC/7000 QqQ, EI source, MMI inlet and a PCT backflushing system based on a purged ultimate union

- **GC columns:** HP 5-MS UI, 0.25 mm i.d., 0.25 µm film, length: 5 m (column 1) and 15 m (column 2)
- **Injection:** 5 µL PTV solvent vent (0.3 min vent time)
- **Inlet temperature program:** 60°C (0.35 min), then 900°C/min to 280°C (15 min), then 900°C/min to 300°C
- **Oven temperature program:** 60°C (1.5 min), then 50°C/min to 150°C, then 8°C/min to 240°C, then 50°C/min to 280°C (2.5 min), then 100°C/min to 290°C (2.05 min)

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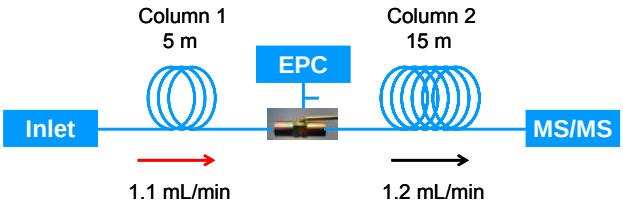
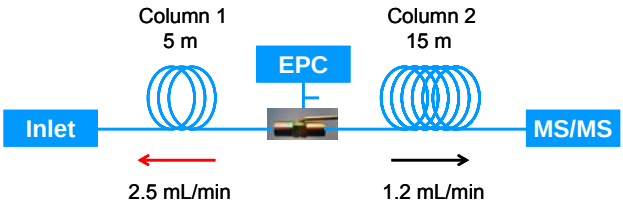
Column Flow Program

A) Elution of the analytes from the first column



B) Backflushing of the first column to remove less volatile matrix components



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Sample Preparation and Analysis

- **Samples:** 5 dietary supplement matrices representing root powders (ginseng and dandelion), fruit (freeze-dried) powders (saw palmetto berry and mangosteen) and full-plant powdered extracts (scutellaria)

- **Spiking level:** 50 ng/g

= lower limit for the majority of pesticides listed in the European Pharmacopoeia monograph 2.08.13

- corresponding matrix-matched standards (MMstd) and standards in acetonitrile (solvent std) were prepared at 5 ng/mL (equivalent to 50 ng/g)

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Sample Preparation and Analysis

- **Sample extraction:**
  based on the original QuEChERS method
  - addition of 4 g $MgSO_4$ and 1 g NaCl to sample (1 g), which was swelled/shaken for 30 min in 20 mL acetonitrile-water (1:1, *v/v*)
- **Dispersive SPE clean-up:**
  150 mg $MgSO_4$, 50 mg PSA, 50 mg C18 and 7.5 mg GCB per 1 mL of extract
- **GC-MS/MS analysis:**
  150 injections (incl. 125 matrix injections) consisting of 5 repeated sets of 30 runs, which included the following 6 injections for each of the 5 matrices:
  (1) solvent std
  (2) MMstd
  (3) spike 1
  (4) spike 2
  (5) spike 3
  (6) MMstd

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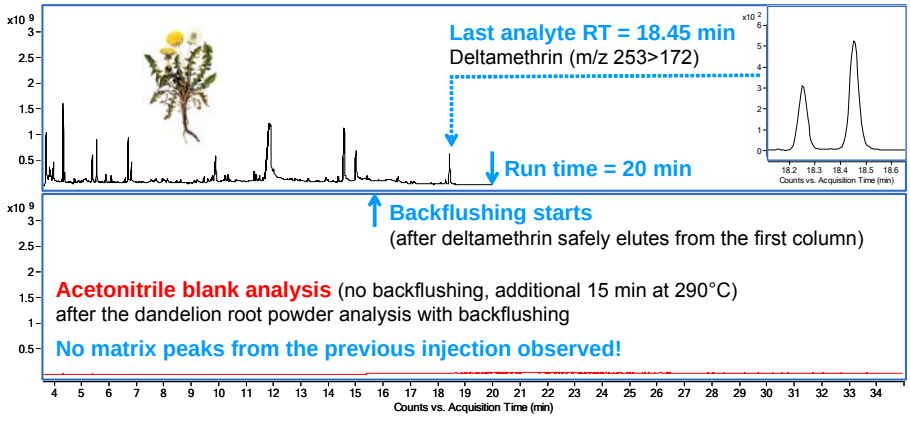
Elimination of Less Volatile Matrix Components

Dandelion root powder full scan (m/z 45-650) analysis with backflushing



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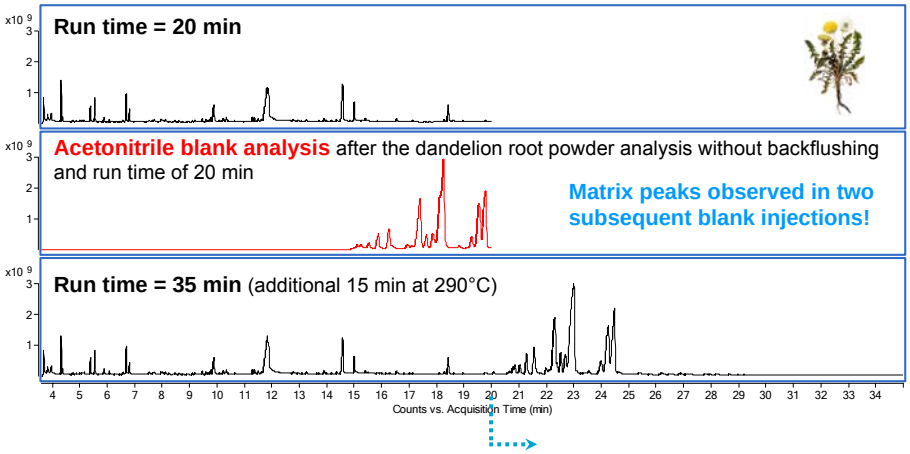

At least additional 10 min at 290°C needed to elute the less volatile matrix components (*e.g.* sterols).

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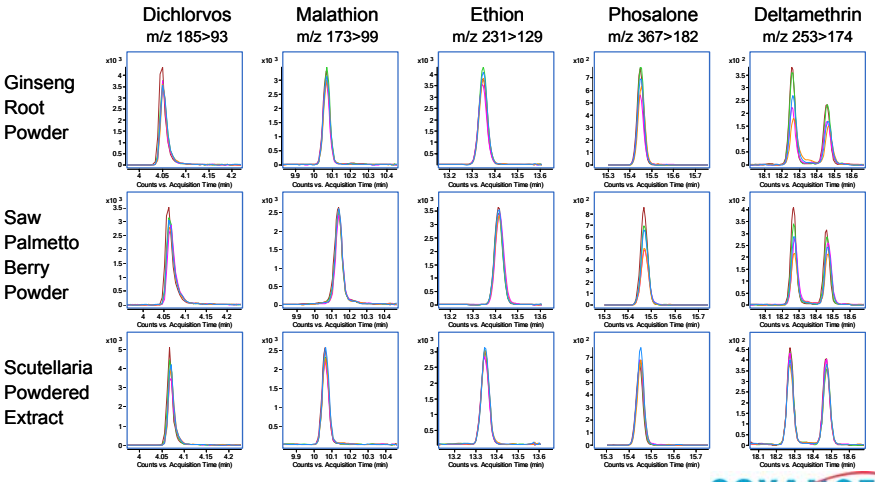
Long-term System Performance

Overlays of GC-MS/MS chromatograms for selected analytes in spiked samples obtained within the sequence of 125 matrix injections (sets: 1, 2, 3, 4, 5):



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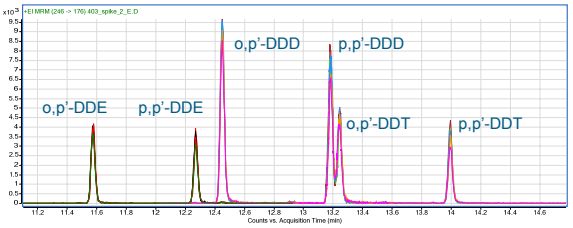
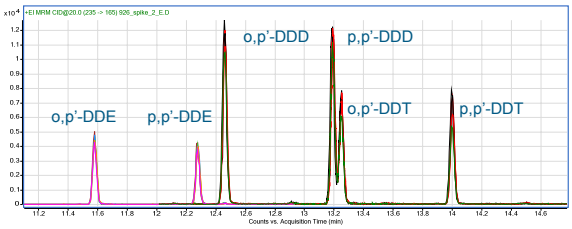
Overlays for DDE, DDD and DDT

Mangosteen freeze-dried powder



Ginseng root powder



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Liner Selection

Multi-baffled liner

Dimpled liner

- **sufficient surface for LVI**
- **inert**
- **good column protection**

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System Maintenance

- Liner replacement and removal of front part of the first column
- "Mechanical RTL" = replacement of a short (e.g. 25 cm) column piece instead of column trimming

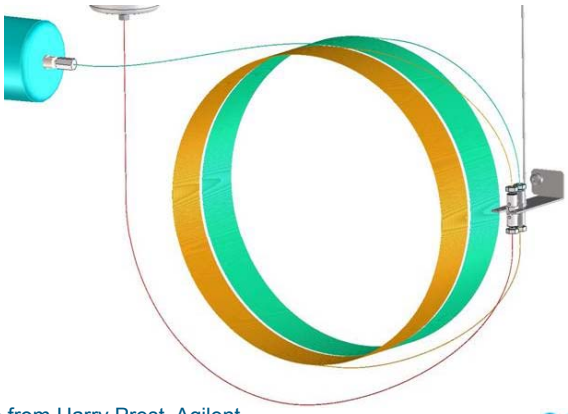

Figure from Harry Prest, Agilent

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Conclusions

- "Backflush baby backflush"
- Concurrent backflushing of the first, short column right after the elution of the last analyte prevents contamination of the second, longer column and the MS source and provides time-effective elimination of less volatile matrix components without a need for extended column bake-out.
- In combination with well-optimized injection (PTV, dimpled liner), very good long-term performance can be achieved even for dirty extracts.
- "Mechanical RTL" is a useful tool for the GC system and MS/MS method maintenance.
- QqQ-MS/MS with well-selected MRMs provides a high degree of selectivity for the analysis of dietary supplements.

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Acknowledgments

- **Agilent Technologies**:

Phil Wylie
Joe Weitzel
Harry Prest
Bill Wilson
Anthony Macherone

- **Restek Corporation**:

Jack Cochran

- **Covance Laboratories**:

Marcus Oakley
Dande Cornn
Sharon McKilligin

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Thank you for your attention!

Your questions?

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