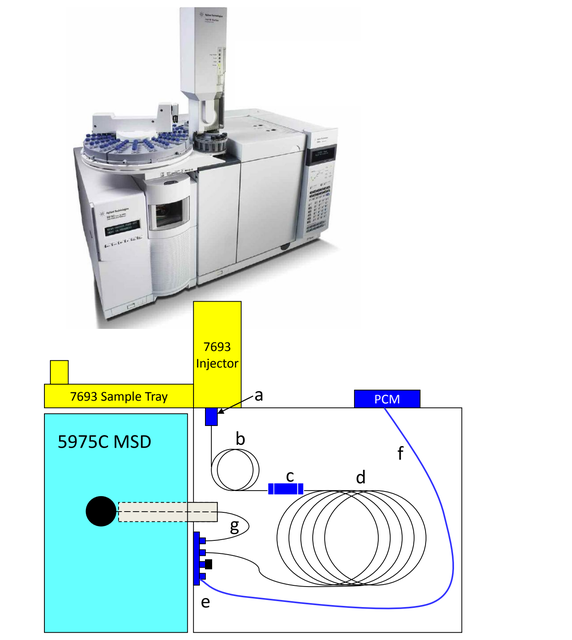
Comparing GC/QQQ to GC/Q Methods for the Analysis of Pesticide Residues in Fruits and Vegetables

Chris Sandy and Chin-Kai Meng, Agilent Technologies, Wilmington, Delaware USA

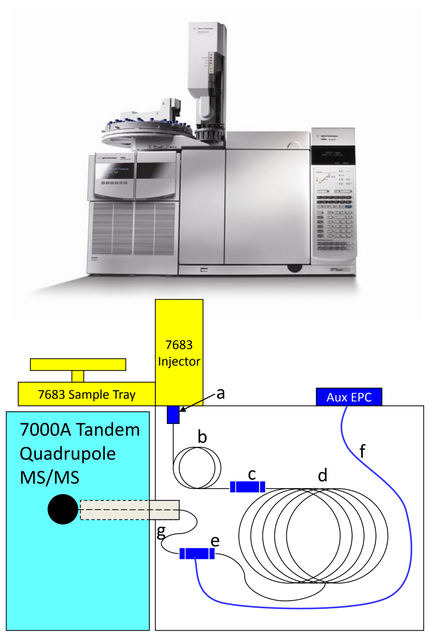
Overview

- High temperature source (up to 350°C) and quads (up to 200°C) reduce maintenance
- GC/QQQ method was developed for >300 pesticides
- GC/QQQ MRM method compared to GC/MS in SIM and Scan (using Deconvolution Reporting Software)
- The selectivity of the GC/QQQ MRM method improved pesticide detection limits considerably over either GC/MS method
- Column backflushing kept the source and GC column clean, reducing maintenance

Instrumentation



a. Multimode Inlet (MMI)
b. 2 m X 0.25 mm retention gap
c. Ultimate Union
d. 15 m X 0.25 mm X 0.25 µm HP-5MS UI
e. 2-way purged splitter (one port capped)
f. Helium purge flow from pneumatic control module
g. 80 cm X 0.15 mm deactivated restrictor



a. S/SL inlet
b. 2 m X 0.25 mm retention gap
c. Ultimate Union
d. 15 m X 0.25 mm X 0.25 µm HP-5MS UI
e. Purged ultimate union
f. Helium purge flow from Aux EPC
g. 65 cm X 0.15 mm deactivated restrictor

Method and Samples

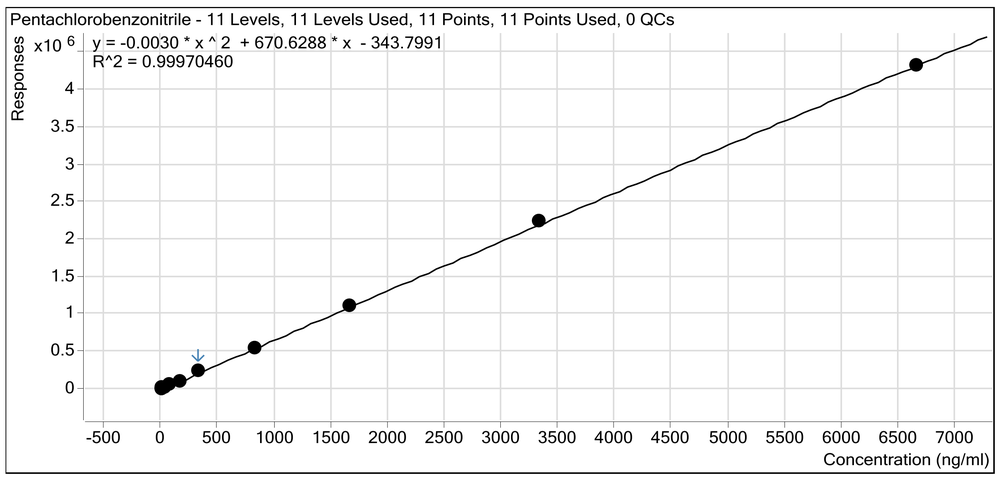
Injection volume:	Single Quad	5 µL cold splitless
	GC/MS/MS	1 µL hot splitless
Oven Temp:		70°C (1 min), 50°C/min to 150°C (0 min), 6°C/min to 200°C (0 min), 16°C/min to 280°C (5 min)
Backflushing:	Single Quad	5 min @ 280°C; purged splitter = 60 psi, inlet = 2 psi
	GC/MS/MS	3 min @ 280°C; purged union = 80 psi, inlet = 1 psi

Fruit and vegetable samples extracted using the QuEChERS method[1] with an additional activated carbon step (Toluene or Acetonitrile solvent)

Some samples were concentrated 4.5:1 (4.5 g original matrix:1 mL final extract)

Linearity in Carrot Matrix

Excellent linearity from 3.33 to 6670 ppb (Pentachlorobenzonitrile) in Carrot extract



Carrot Extract[2]

	GC/MS		GC/MS/MS[a]
	5 µL (Multimode Inlet)		1 µL
Pesticide	Cold SL Scan + DRS	Cold SL SIM	Hot SL (ppb)
Diclobenil			0.38[b]
Pentachlorobenzene			0.75[b]
Trifluralin			2.3[b]
Tefluthrin			0.53[b]
4,4'-Dichlorobenzophenone			1.2[b]
Chlorpyrifos			24.7
o,p'-DDE			3.7
p,p'-DDE	X	X	240
o,p'-DDD			9
p,p'-DDD	X		Sum = 45
o,p'-DDT	X		
p,p'-DDT	X	X	130
Fenazaquin	X	Not in method	Not in Method

a. The concentration of these compounds was lower in the original carrot sample by a factor of 4.5 since the extraction method results in 4.5 g of produce per mL of extract.

b. The reported values fall below the lowest point on the calibration curve.

Results

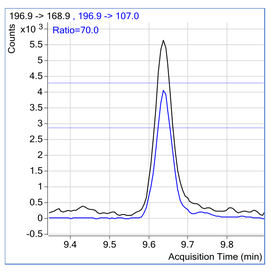
- **DRS Method:** 5 µL of carrot extract analyzed by GC/MS Scan mode – Data analysis using Deconvolution Reporting Software
  - Method has the capacity to identify any of the 927 pesticides and endocrine disruptors in the Agilent RTL Pesticide Database
  - Method was qualitative but not quantitative
  - DRS identified 4 DDT related compounds and Fenazaquin
- **SIM Method:** 5 µL of carrot extract analyzed by GC/MS using SIM
  - 3 SIM methods were run with 50-60 pesticides in each, ~160 pesticides total
  - Method was qualitative but not quantitative
  - Only p,p'-DDT and p,p'-DDE were identified
  - Fenazaquin not in the SIM method
- **GC/MS/MS method:** 1 µL injected using SRM method for 175 pesticides
  - p,p'-DDD and o,p'-DDT have similar RTs & use the same transitions –quantified together
  - 3 pesticides identified at < 1 ppb
  - 3 more pesticides identified at < 4 ppb
  - All DDT isomers & metabolites were quantified
  - Fenazaquin not in the SRM method

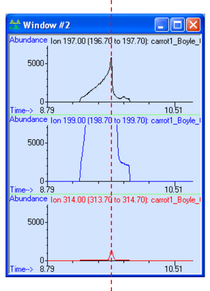
Comparing GC/MS Selectivity to GC/MS/MS

Incurred Chlorpyrifos at 25 ppb in Carrot Extract

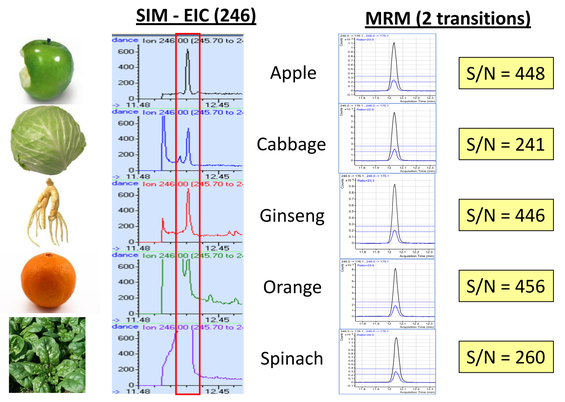
1 µL
7890A/7000A GC/MS/MS
Transitions 196.9 -> 168.9
196.9 -> 107.0

5 µL
7890A/5975C GC/MS
Extracted SIM Ions 197, 199, 314





Analysis of spiked p,p'-DDE at 10 ppb (All injections = 1 µL)



Conclusions[2]

1. New Agilent 7000A GC/MS/MS system proved to be highly selective and sensitive
2. Many pesticides can be detected at < 1 ppb with 1 µL injected
3. 1-µL injections using GC/MS/MS gives better results than 5-µL injections using GC/MS in Scan + DRS or SIM modes
4. Scan + DRS method has the capability to identify non-target pesticides – Good compliment to GC/MS/MS methods for comprehensive screening

Acknowledgements and References

The authors wish to thank Dr. Jon Wong of the US Food and Drug Administration (College Park, MD, USA) and Dr. Steven Lehotay of the U.S. Department of Agriculture (ARS, ERRC, Wyndmoor, PA, USA) for providing numerous standards and food extracts.

1) M. Anastassiades, S. J. Lehotay, D. Stajnbaher, and F. J. Schenck, *J AOAC Int,* 86 (2003) 412.
2) Philip L. Wylie and Chin-Kai Meng, "A Method for the Trace Analysis of 175 Pesticides Using the Agilent Triple Quadrupole GC/MS/MS", Agilent Application Note No. 5990-3578EN.