Determination of pesticides in food extract samples at low ppb levels using a new bench top GC-MS/MS system

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Introduction

The trace level detection, confirmation and quantitation of agrochemicals in food-stuff extracts by GC-MS is a well established technique. Whilst a single quadrupole GC-MS (such as the Agilent 5975C MSD) has the sensitivity to detect trace analytes using SIM, food extracts often contain matrix components that interfere with the analyte measurements and make confirmation and quantitation difficult, if not impossible at low ppb levels. Each type of food-stuff (fruits, vegetables, herbs, spices etc) can exhibit different concentrations and types of matrix interferences, despite extraction and clean-up with dispersive solid phase extraction techniques such as QuEChERS.

This poster shows the application of the new Agilent 7000A GC-QQQ system for the multi-residue analysis of agrochemicals in a vegetable and meat fat extract using MS/MS (MRM mode) and capillary flow technology with back-flushing.

The Analytical Challenge

The full scan TICs of 3 food extracts are shown in Figure 1. Each extract has different matrix interferents at wide ranging concentrations. The matrix components that co-elute with target analytes can prevent both confirmation and quantitation. An additional problem is that high-boiling matrix components which remain on the column between extract injections can cause chromatographic issues such as peak tailing and retention time shifts as well as contaminating the mass spectrometer ion source.

Full scan TICs of a blank injection of solvent following an injection of a Lettuce extract (no back-flush used) and a blank injection of solvent following an injection of a Lettuce extract (back-flushed used) are shown in Figure 2. Note the large amount of matrix material that remained on the column after the injection without back-flush, yet the use of back-flush removed all the matrix material from the column via the inlet split line, thus keeping the column clean between injections and preventing the high-boiling material from reaching the MS ion source, there-by causing contamination and subsequent loss in sensitivity.

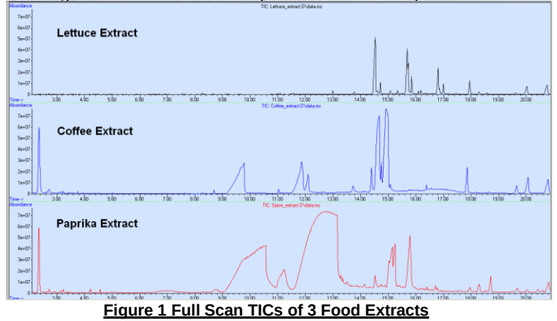

Figure 1 Full Scan TICs of 3 Food Extracts

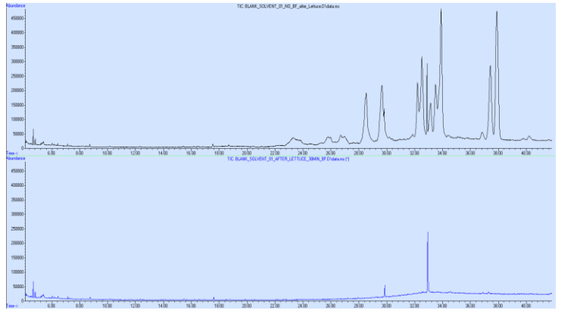

Figure 2 Full Scan TICs of Blank solvent injections after Lettuce Extract Injections without back-flushing (Top) and with back-flushing (Bottom)

Experimental

An Agilent 7890A GC fitted with a 30m x 0.25mm ID x 0.25um HP5-MS Ultra Inert column (19091S-433UI) was connected to an Agilent 7000A QQQ. Injections (1uL) were made using cold splitless injection with a PTV inlet and a 7683 auto-liquid sampler. The analytical method employed was the 1x RTL Pesticide method, locked to Chlorpyriphos methyl at 16.59 minutes. The QQQ was operated in MRM mode, each target analyte was measured using 2 transitions, one for quantitation, one as a qualifier. The list of target analytes is shown in Table 1.

1	a-HCH	21	Cyfluthrin	41	Linuron
2	Acephate	22	Cypermethrin	42	Malathion
3	Acrinathrin	23	Deltamethrin	43	Methacrifos
4	a-Endosulfan	24	Diazinon	44	Methamidophos
5	Azamethiphos	25	Dichlorvos	45	Mevinphos
6	Azinphos-methyl	26	Dicofol	46	Monocrotophos
7	Azoxystrobin	27	Dieldrin	47	o,p'-DDT
8	b-Endosulfan	28	Dimethoate	48	Omethoate
9	Bifenthrin	29	Endrin	49	p,p-DDE
10	Binapacryl	30	Ethion	50	Paraoxon-Methyl
11	Bitertanol	31	Fenpropathrin	51	Parathion-Methyl
12	Buprofezin	32	Flusilazole	52	Pirimiphos-methyl
13	Captafol	33	Folpet	53	Prochloraz
14	Captan	34	Heptachlor	54	Propargite
15	Chlorbenzilate	35	Heptenophos	55	Pyrifenox
16	Chlorfenvinphos	36	Hexachlorobenzene	56	Simazine
17	Chlorothalonil	37	Isofenphos	57	Tebuconazole
18	Chlorpyrifos	38	Isofenphos Methyl	58	Tecnazene
19	Chlorthal Dimethyl	39	l-Cyhalothrin	59	Tolylfluanid
20	Coumaphos	40	Lindane	60	Trifluralin

Table 1. Target Analytes Measured in Food Extract Samples

Matrix-matched calibration standards were prepared in blank Lettuce and blank Pork Fat extracts over the range of 1 – 100 ppb. Two lettuce extracts and one pork fat extract (prepared using the QuEChERS technique) spiked with 20 of the 60 analytes listed in Table 1 were supplied. The identity of the analytes and their concentrations were not supplied. Each food extract was analysed in triplicate.

Results

(1) Pork Fat Extract

19 of the 20 analytes spiked into the pork fat extract were confirmed and quantitated. Figure 3 shows a bar chart comparing the actual spiked values (in ppb, grey bars) to the mean determined values by GC-MS/MS (orange bars). The only analyte not detected was Folpet.

(2) Lettuce Extract #1

20 of the 20 analytes spiked into the first lettuce extract were confirmed and quantitated. Figure 4 shows a bar chart comparing the actual spiked values (in ppb, grey bars) to the mean determined values by GC-MS/MS (green bars).

(3) Lettuce Extract #2 (Lower level spike)

19 of the 20 analytes spiked into the second lettuce extract were confirmed and quantitated. Figure 5 shows a bar chart comparing the actual spiked values (in ppb, grey bars) to the mean determined values by GC-MS/MS (green bars). The only analyte not detected was Folpet.

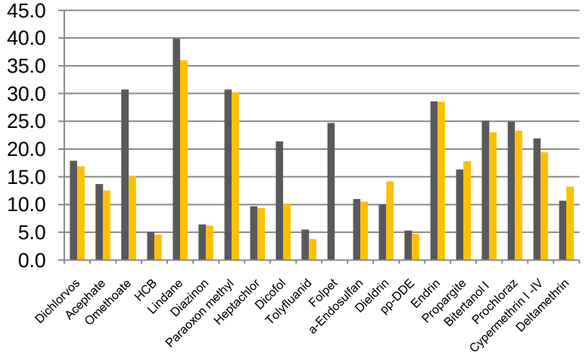

Figure 3. Quantitative Results (ppb) for analytes in Pork Fat Extract Spiked values (grey bars), mean of triplicate determinations (orange bars)

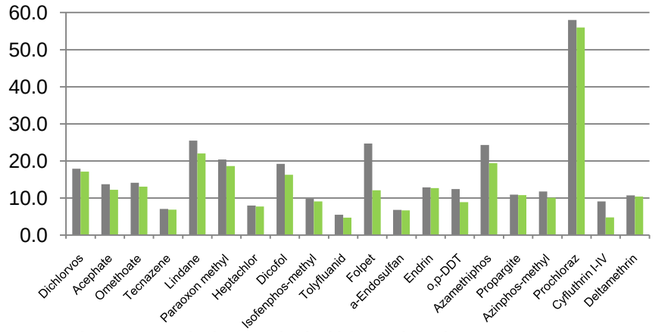

Figure 4. Quantitative Results (ppb) for analytes in Lettuce Extract #1 Spiked values (grey bars), mean of triplicate determinations (green bars)

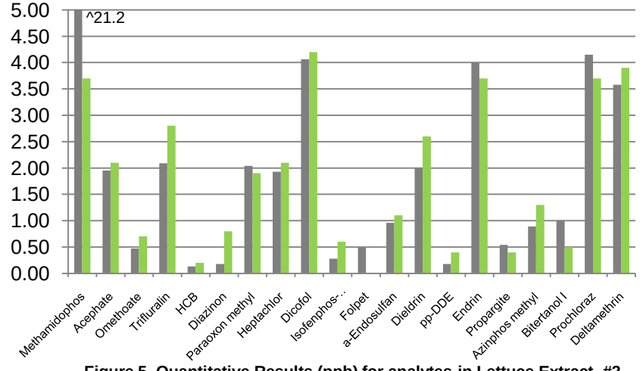

Figure 5. Quantitative Results (ppb) for analytes in Lettuce Extract #2 Spiked values (grey bars), mean of triplicate determinations (green bars)

Conclusion

The powerful combination of GC-MS/MS provided by the Agilent 7000A triple quadrupole mass spectrometer (giving the selectivity and sensitivity required to confirm and quantitate target analytes at low levels in complex sample extracts), retention time locking and capillary flow technology back-flushing (which maintains chromatographic integrity, analyte retention times and protects the mass spectrometer ion source from contamination with high boiling matrix components) provides a robust analytical solution for the multi-residue analysis of agrochemicals at trace levels in food extract samples.