The Benefits of Incorporating GC/QQQ into Pesticide Analysis Methods

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Pesticide residue analysis is a complex task because the analyst often has to search for hundreds of compounds in a wide variety of matrices. As required detection limits fall to 10 µg/kg (10 ppb) or lower for many pesticides, more sophisticated analytical tools are required. Matrices such as food, soil and even water can be very complex and one risks removing some target analytes if samples undergo too much clean-up.

For GC-amenable pesticides, many laboratories are using two complimentary techniques for screening and confirmation purposes. For broad screening at the 10–100 ppb level, GC/single quadrupole (GC-Q) is employed with Deconvolution Reporting Software (DRS) and the RTL Pesticide and Endocrine Disruptor library from Agilent Technologies.[1–3] This is a scan method to screen for 927 GC-amenable pesticides and endocrine disruptors in a single GC–MS run. Detection limits for most pesticides vary from ca. 10–100 ppb depending upon the matrix and the injection volume. For target pesticide analysis in the most complex matrices, Agilent's new 7890A/7000A GC/triple quadrupole (GC/QQQ) is unmatched. This paper illustrates the ability of Agilent's GC/QQQ to detect traces of pesticides when other techniques fail.

Figure 1: The Agilent 7890A/7000A GC/QQQ system.

Instrumental Design

The Agilent 7000A design is based upon the rugged and dependable 5975C single quadrupole MSD (Figure 1). It uses the same high temperature inert source along with the new high sensitivity triple axis detector that was recently introduced on the 5975C. The instrument uses two of the hyperbolic gold-plated quartz quadrupoles that have proved to be so stable and rugged in the 5973 and 5975 series MSDs. The ability to heat them up to 200 ºC means that cleaning is rarely, if ever, required. The collision cell is a shorter version of the hexapole used in Agilent's 6460 LC/QQQ instrument. Agilent's innovative use of helium quenching in the collision cell significantly reduces background noise and enhances the signal-to-noise ratio of the instrument. Finally, the 7000A is fully integrated to the 7890A GC and benefits from column backflushing and other capillary flow techniques.[4] The control software combines the familiar instrument control portion of Agilent's GC–MS ChemStation with the powerful MassHunter data analysis package that is now available on Agilent's LC-TOF, LC-Q-TOF, and LC/QQQ instruments.

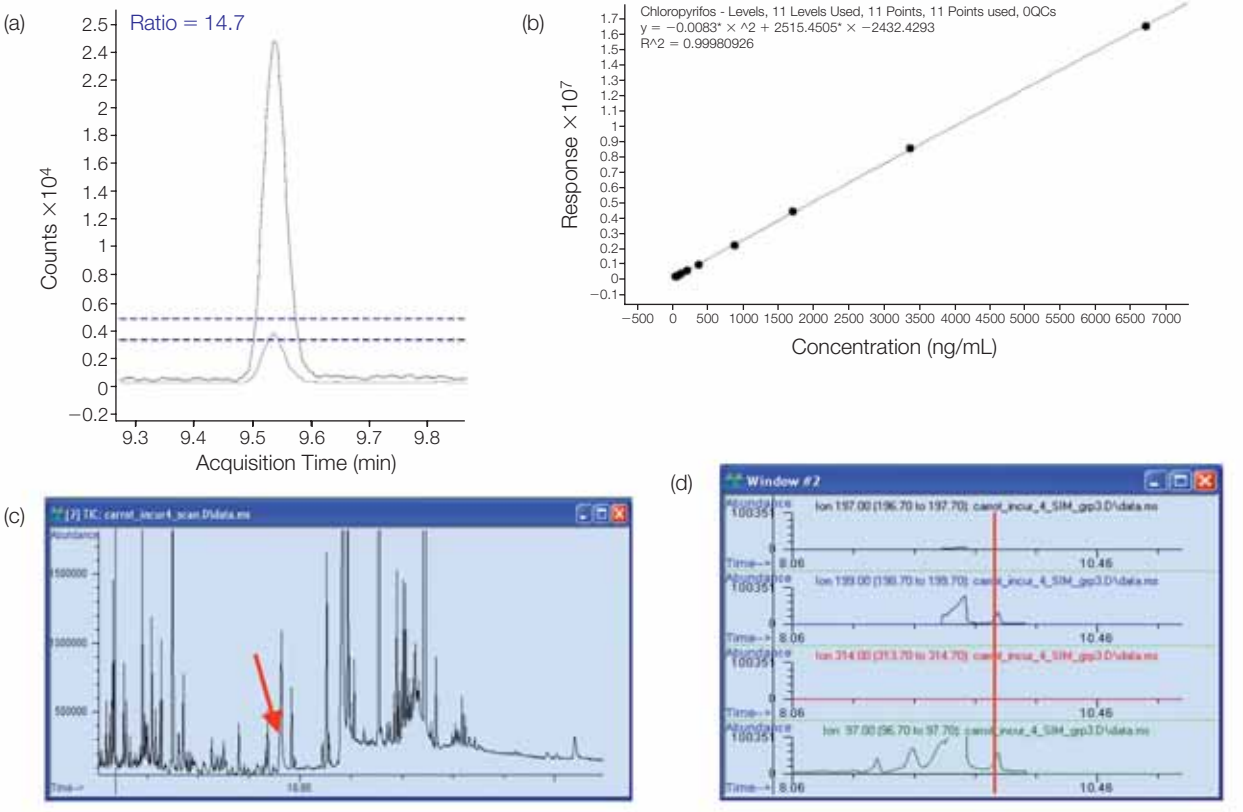
Experimental

GC:	Agilent 7890A
MS:	Agilent 7000A in the electron impact mode
Inlet:	Split/splitless @ 250 ºC
Capillary flow device:	2-way splitter with analytical column in and restrictor out to the QQQ; remaining port was capped; helium pressure provided by aux EPC @ 3 psi
Column:	Agilent J&W HP-5ms Ultra Inert 15 m × 0.25 mm × 0.25 µm HP-5MSUI (P/N 19091S-431UI)
Retention gap:	2 m × 0.25 mm deactivated fused silica
Restrictor:	80 cm × 0.150 mm deactivated fused silica
Carrier gas:	Helium @ 17.720 psi (constant pressure mode)
Oven temp:	70 ºC (1 min), 50 ºC/min to 150 ºC (0 min), 6 ºC/min to 200 ºC (0 min), 16 ºC/min to 280 ºC (5 min)
Backflush conditions:	Time = 3 min, inlet press. = 1 psi, aux EPC = 80 psi, oven temp = 280 ºC
Retention time locking:	Chlorpyrifos-methyl locked to 8.298 min
Collision cell gases:	N_2 @ 2.60 psi and He @ 6.25 psi

Results and Discussion

Monitoring ion transitions in a GC/QQQ is inherently much more selective than either scan or selected ion monitoring (SIM) with a GC-Q. With a clean sample in the scan mode, the Agilent 7000A is very similar in sensitivity to the 5975C MSD. It is the much-improved selectivity of the QQQ in the multiple reaction monitoring mode (MRM) that results in much lower detection limits for pesticides in dirty extracts. As described earlier[1–3] DRS uses full scan deconvolution to pull "cleaned" spectra from the matrix background. While this is extremely helpful and is applicable to large numbers of analytes, matrix interferences can eventually foil deconvolution. SIM methods can be more sensitive, but they

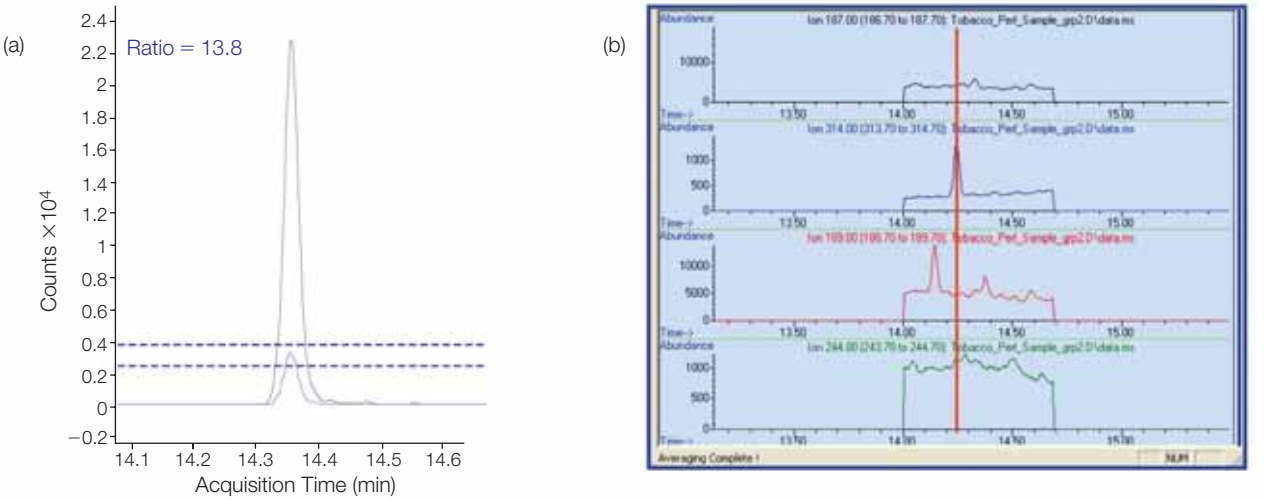
Figure 2: (a) Two transitions identifying chlorpyrifos in a carrot extract at 28 ppb. (b) Calibration curve from 3.33 ppb to 6670 ppb for chlorpyrifos in carrot extract. (c) GC-Q TIC of the carrot extract showing where chlorpyrifos elutes. (d) SIM analysis of the carrot sample showing that it was impossible to identify chlorpyrifos (expected RT indicated by red line) by this method.



too have problems with the interferences often found in food and environmental extracts.

In the MRM mode, the first quadrupole (Q1) isolates one or two ions per compound and accelerates them into the hexapole collision cell. These energetic ions collide with a neutral gas causing them to break up into smaller characteristic fragments. The charged products of this collision induced dissociation (CID) are monitored in Q3. It is generally accepted that a compound is positively identified when the ratio of two precursor-to-product transitions are in the correct abundance ratio.

Figure 3: (a) Transitions verifying the presence of iprodione in a tobacco extract at 44 ppb. (b) GC-Q SIM analysis could not identify iprodione in the tobacco extract at the expected RT (red line).



To compare analytical techniques, an un-spiked carrot extract was analysed by GC-Q (7890A/5975C) and by GC/QQQ (7890A/7000A) using a method for ca. 170 target pesticides. As shown in Figure 2(a), chlorpyrifos was easily found at 28 ppb by the GC/QQQ. The calibration curve for chlorpyrifos in carrot matrix gave an excellent fit from 3.33 ppb to 6670 ppb [Figure 2(b)]. Figure 2(c) shows a total ion chromatogram (TIC) of the carrot extract (GC-Q) with the retention time of chlorpyrifos indicated by the arrow. Chlorpyrifos is buried under a much larger ethyl hexadecanoate peak, making it impossible to identify chlorpyrifos in a SIM analysis [Figure 2(d)]. In addition to chlorpyrifos, the GC/QQQ found 6 DDT isomers and breakdown products from 5 to 180 ppb and eight more pesticides ranging in concentration from 0.2 to 21 ppb. Analysis using Agilent's DRS method identified only p,p'-DDT and p,p'-DDE.

A spiked tobacco extract was analysed by the same GC/QQQ method and several pesticides were identified between 35 and 250 ppb. Among these was iprodione, which was found at 44 ppb [Figure 3(a)]. There is too much background noise in the GC-Q SIM results [Figure 3(b)] to identify iprodione.

In the course of this work, several dozen injections were made of food extracts that were concentrated 4.5:1 (4.5 g of vegetable per mL of final extract). Experience with these samples has shown that backflushing is necessary to maintain chromatographic performance and to keep the source clean.[4] In this instance, the analytical column was connected to a purged 2-way splitter, one of Agilent's Capillary Flow Devices. A short restrictor ran from the splitter through the QQQ transfer line and the remaining port was capped. When the last pesticide had eluted, the pressures at the inlet and splitter were set to 1 psi and 80 psi, respectively. Thus, for a 3 minute post run period the flow through the analytical column was reversed, backflushing all high boiling materials off the head of the column and out through the split vent.

Conclusions

Laboratories that need to analyse pesticides at the low ppb level or below in complex food or environmental extracts will benefit from the increased selectivity and sensitivity of Agilent's new 7000A triple quadrupole mass spectrometer. The instrument is based upon the rugged, dependable and sensitive 5975C single quad MSD, using the same gold plated quartz quadrupole, source and triple-axis detector. The hexapole collision cell is based upon Agilent's 6460 LC/QQQ. With unsurpassed sensitivity and up to 500 MRMs/sec, it is possible to develop methods for analysing hundreds of pesticides in a single injection.

Acknowledgement

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