High Mass Accuracy Provides Enhanced Selectivity for the GC/MS Analysis of Pesticides in Food

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Introduction

The analytical power of GC/MS with high mass accuracy is useful in two broadly-defined ways: for the identification of unknown compounds, and to provide increased selectivity for the determination of target compounds, especially in complicated sample matrices. Whether the theoretical gains for the latter application can be achieved in practice depends greatly on the mass accuracy of the mass spectrometer, its mass axis stability over time, and the nature of the matrix interferences (relative retention time, mass, and magnitude). We present some results obtained with typical food samples containing low levels of pesticides.

Experimental

Samples
Food samples (Astragalus, Chamomile) were ground and extracted using a QuEChERS-like method (J. Agric. Food Chem 2010, 58, 5884). The prepared samples were spiked with a mixture of 357 pesticides originally obtained from the U.S. EPA National Pesticide Standard Repository (Ft. Meade, MD) at a level of 10 ppb or 100 ppb each.

GC/MS System
The GC configuration and conditions were as shown in Table 1.

The MS was a prototype of a commercial quadrupole time-of-flight (Q-TOF) system with the following specifications: orthogonal acceleration/single reflectron configuration, 70 eV EI source, 1 m flight tube, 12.5 kHz rep. rate, 4 GHz sampling rate (32Gbps), 8 kV acceleration potential, 10-1700 Dalton mass range. Other operating conditions were as shown in Table 2. A full mass calibration using PFTBA was done prior to the start of the overnight sequence, but not between runs.

Data Analysis
Data files were mass corrected post acquisition based on the measured values of three to five fragment ions of the reference compound, perfluoroethyltriazine (CAS# 858-46-8) using a stand-alone program (Ed Darland, Agilent Technologies). Agilent MassHunter Qualitative Analysis was used to generate extracted ion chromatograms with extraction windows of ± 0.1 D or ± 20 (or 10) ppm.

Experimental

Gas Chromatograph	Agilent 7890A
Columns	(1) 15.0 m x 0.25 mm ID x 0.25 µm HP-5MS Ultra Inert (19091S-431SI), Inlet Air cooled Multimode Inlet, outlet Pressure controlled tee (2) 0.65 m x 0.15 mm ID x 0.15 µm DB-5MSUI, Inlet Pressure controlled tee at 4.0 psig (PCM), outlet Vacuum
Carrier gas	Helium
Carrier gas mode	Constant pressure
Column Head pressure	18.12 psi , Retention Time Locked to Chlorpyriphos methyl at 8.298 min
Injection Port	Air cooled, Multimode Inlet
Auto-sampler	Agilent 7693A
Injection mode	Cold pulsed Splitless, 25.0 psig for 0.5 min, Purge delay 1.0 min Purge Flow 50.0 ml/min at 1.0 min
MMI Temperature Program	70 (0.1) – 600 C/min – 300 C
Injection volume	1.0 µL
Injection port liner	Multi-baffle 2 mm, deactivated (5190-2296)
Oven program deg C (min)	70 (1) – 50 C /min – 150 (0) 6 – 200 (0) –16 –280 (5) C (Run time = 21.0 min)
Backflush conditions	Post run, 4 min Oven 280 C, PCM 60 psig, Inlet 1 psig

Table 1. GC Conditions

Mass Spectrometer	Agilent Prototype Q-TOF
Interface Temp	280 C
Source Temp	280 C
Quadrupole Temp	150 C
Quadrupole Mode	Total Ion Transmission, 70 m/z cutoff
Collision Gas	Nitrogen @ 1.5 ml / min
Scan Range	m/z 45 – 550
Net Data Rate	5 Hz (200 ms, 2615 transients / spectrum)
Acquisition Mode	2 GHz Dual Gain

Table 2. MS Conditions

Results and Discussion

Theoretical Target Masses

As no large library of exact masses of EI fragment ion exists, a small one was created for this project. The pesticide mixture was diluted in toluene to 100 ppb and injected. A reference-mass-corrected, background-subtracted spectrum of each of 50 pesticides was generated. Using the NIST MS Interpreter as a guide, three to six ions were selected from each spectrum, and the corresponding measured masses were compared to those generated by the MassHunter Mass Calculator tool based on the predicted structure of the fragment. If the mass difference was not deemed acceptable, the measured mass was entered into the MassHunter Formula Calculator tool. The formula closest in mass was accepted as the actual formula if a reasonable structure could be postulated. All EICs were based on the theoretical masses.

Effect of Matrix

It is well known that not all matrices are alike. Figure 1 compares the TICs of two samples run under the previously listed conditions: Astragalus (red) and Chamomile (green).

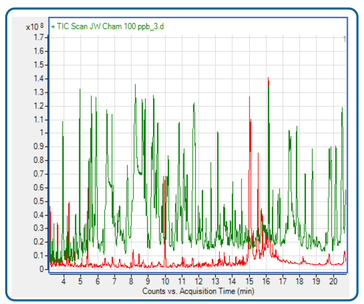

Figure 1. TICs of Astragalus and Chamomile Extracts

In the case of the former, cleaner matrix, few significant differences are seen in EIC peak areas or ratios between the two extraction window widths attributable to large coeluting matrix ions. One notable exception is Methacrifos, shown in Figure 2. Note how the analyte ion (theoretical m/z = 180.0005) is resolved from the coeluting matrix ion. The mass error is less than 2.3 ppm.

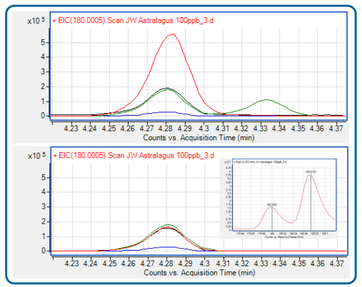

Figure 2. EICs of Methacrifos Ions at 0.1D and 20 ppm. Inset: Portion of Mass Spectrum at m/z 180

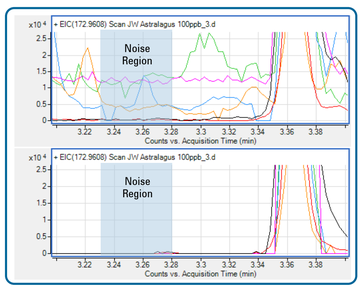

Figure 3. EICs of Dichlorobenzonitrile Ions at 0.1D and 10 ppm

m/z	± 0.1 D	± 10 ppm
100.0182	81.2	∞
136.9949	40.6	∞
137.9919	55.1	∞
170.9637	1174	∞
172.9608	2657	3731
174.9578	491	1538

Table 3. S/N (Height/RMS) of EICs of Dichlorobenzonitrile Ions. Noise Region 3.23-3.28 Min.

Results and Discussion

Even analytes with no specific coeluting interferences show an improvement in S/N. Figure 3 and Table 3 illustrate this for Dichlorobenzonitrile.

One would expect a much greater chance of encountering matrix interferences in the Chamomile sample, and that is indeed the case. Figure 4, which shows the mass spectrum averaged over the entire chromatographic run, and scaled appropriately for a relatively abundant analyte ion at 100 ppb concentration, illustrates the scope of the problem.

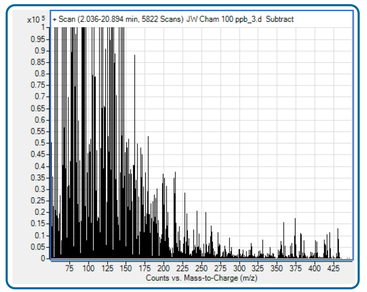

Figure 4. Background-Subtracted Mass Spectrum Averaged Over Entire Chromatogram

The abundance at every nominal m/z from 50 to over 200 is 10^4 counts or greater, which is comparable to that of a typical analyte ion at the 10 ppb concentration level. These are average values; peak values are of course much higher.

Figure 5 shows EICs for several of the characteristic ions of Flumetralin. The top plot is the result of an extraction window of 0.1 D. There are large matrix interferences at m/z 143.0058 (black) and 145.0029 (red). The bottom plot show the result using a 20 ppm window. The matrix interferences have been eliminated, and consistent peak shape can be seen for all analyte ions. The higher mass ions, 360.0283 and 404.0320, proved to be more immune to interference, as experience and Figure 4 would suggest.

The inset on the lower plot shows the results using the 20 ppm extraction window on the Chamomile sample spiked at the 10 ppb level. Excellent linearity is observed in the presence of a 40-fold excess of interferent abundance.

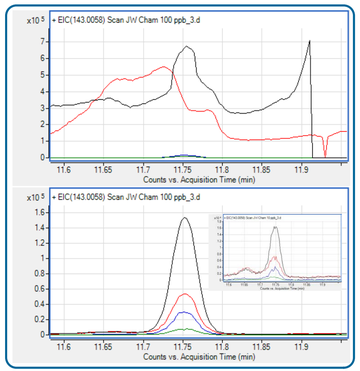

Figure 5. EICs of Flumetralin Ions at 0.1D (top) and 20 ppm (bottom). Note the difference in scale. Inset: Flumetralin at a Concentration of 10 ppb; 20 ppm (Matrix = Chamomile Extract)

Conclusions

A mass spectrometer with sufficient resolving power (in this case, ca. 5000 FWHM), mass accuracy (typically 5 ppm or less), and mass axis stability can provide improved selectivity for GC/MS analyses. This takes the form of reduced susceptibility to interference from matrix components in specific cases, and improved S/N in general.

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