

Robustness of the Agilent Ultivo Triple Quadrupole LC/MS With the ESI Source

10,000 Injections of pesticides spiked in black tea matrix



Figure 1. Ultivo triple quadrupole LC/MS with the Agilent electrospray ion source

Abstract

This Technical Overview demonstrates the robustness of the Agilent G6465B Ultivo triple quadrupole LC/MS coupled with the electrospray ionization (ESI) source for analytes in a complex matrix. Innovations such as the Cyclone Ion Guide, Vortex Collision Cell, and heated hyperbolic quadrupoles prevents contamination of optical elements or mass filtering components resulting in robust sample analysis regardless of matrix condition.

In the experiment shown, a mixture of model pesticides were spiked in black tea extract matrix and monitored for 10,000 nonstop-repeated injections. During this experiment, the instrument was operated without cleaning any components or readjusting the tune parameters. For each analyte, peak area was found to have a percent relative standard deviation (%RSD) of 10 % or less without internal standard correction.

Introduction

Routine analysis for pesticides or environmental contaminants is a common application of mass spectrometry analysis. The modern approach is the use of triple (tandem) quadrupole mass spectrometers operated in multiple reaction monitoring (MRM) mode to enable highly specific detection of analyte components of interest. Operating in this mode allows the instrument to disregard contaminants and chemical noise producing components.

Regardless of instrument specificity for a desired analyte, problematic sample components (that is, endogenous matrix components) can accumulate in the ion source and ion optics prior to MRM filtering. As accumulation of undesired components progresses, charging or presence of persistent ion suppressing contaminants can occur, manifesting as a severely reduced signal. Often, the resolutions to this issue are to tediously evaluate the instrument by re-adjusting tune parameters, or to shut down the instrument for a thorough cleaning.

Innovations built into the Ultivo triple quadrupole LC/MS such as the Cyclone Ion Guide, Vortex Collision Cell, and heated hyperbolic quadrupoles were specifically designed to be unaffected by the buildup of deposit in the ion source region, and to prevent accumulation of charged species in the ion optics and mass filtering elements. These innovations result in increased instrument uptime, robustness, and matrix tolerability regardless of the sample composition.

The aim of this experiment was to rigorously demonstrate the robustness of innovative Ultivo components using a representatively difficult and dirty matrix. In this case, black tea was chosen due to its notoriety for containing large amounts of interfering compounds (polyphenols, tannins, flavins, pigments, and so forth) that have the potential to deposit on the surface of instrument components—compromising instrument performance.

Experimental

LC Modules/columns

- Agilent 1290 Infinity autosampler (G4226A)
- Agilent 1290 Infinity binary pump (G4220A)
- Agilent 1290 Infinity thermostatted column compartment (G1316C)

Mass spectrometer

Ultivo triple quadrupole LC/MS with electrospray ion source (G6465B—option 100)

Software

- Agilent MassHunter Acquisition for Ultivo (Ver 1.1.2029.0)
- Agilent MassHunter Quantitative Analysis (Ver 9.0.625.0)
- Agilent MassHunter Qualitative Analysis (Ver 8.0.8208.0)

Instrument conditions

LC Parameters	
Pre-autosampler Column to Generate Stable Backpressure	Agilent InfinityLab Poroshell 120 EC-C18, 3.0 × 50 mm, 2.7 μm (p/n 699975-302)
Guard Column	InfinityLab Poroshell 120 EC-C18, 2.1 × 5 mm, 2.7 μm (p/n 821725-911)
Column Temperature	30 °C
Injection Volume	1 uL
Autosampler Temperature	4 °C
Needle Wash	1 second in wash port (3:3:3:1 ACN/MeOH/IPA/H ₂ O)
Flow Rate	0.500 mL/min
Isocratic Mobile Phase in Channel A and Channel B	80 % MeOH in H ₂ O with 5 mM ammonium formate and 0.1 % formic acid Channel A = 50 % Channel B = 50 %
MS Parameters	
Ion Source	Agilent electrospray ion source
Drying Gas Temperature	350 °C
Drying Gas Flow Rate	11 L/min (nitrogen)
Nebulizer Pressure	60 psi (nitrogen)
Capillary Voltage	4,000 V (Pos)/4,500 V (Neg)
Q1/Q2 Resolution	Unit (0.7 Da)
Time Filter	Enabled - 0.07 minutes

MRM Transitions						
Compound	Precursor Ion	Product Ion	Dwell	Fragmentor	Collision Energy	Polarity
2,4,5-TP (Silvex)	266.9	194.9	20	80	12	-
Acifluorfen	360.0	316.0	20	80	5	-
Aminocarb	209.1	152.2	20	105	12	+
Carbofuran	222.1	165.1	20	80	20	+
Dimethoate	230.0	125.0	20	70	16	+
Dinoseb	239.1	193.1	20	80	25	-
Metazachlor	278.1	210.1	20	70	4	+
Metoxuron	229.0	72.1	20	95	16	+

Results and discussion

For this experiment, 10,000 injections of black tea extract spiked with 100 ng/mL pesticides was injected into the instrument without having to readjust tune parameters or clean the instrument components. Throughput per sample was measured to be ~0.6 min/injection, resulting in nonstop operation of the instrument for at least four days with 100 % uptime.

Although a 1:5 matrix-to-solvent dilution was carried out, the sample was still visibly pigmented, as shown in Figure 2A. At the completion of the experiment, the ion source was examined and displayed a large degree of deposition of sample buffer and pigmented matrix components. Figure 2B shows the condition of the instrument immediately after completion. Notable observations were the accumulation of deposit around the MS inlet, resulting in browning of the spray shield and severe blackening of pigmented components on the ion injector cap.

Figure 3 shows raw abundance elution profiles for 10 evenly spaced injections (every 1,000) of each compound. The chromatograms demonstrate slight drift in chromatographic peak width and height due to degradation of the guard column over time. Peak area maintained consistency due to consistent flux of analyte ions to the mass spectrometer, regardless of peak width or peak height.

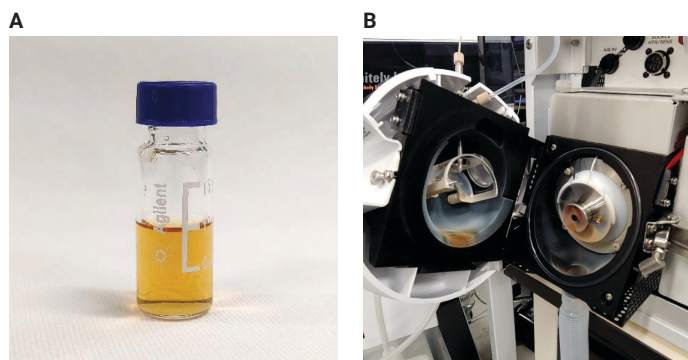


Figure 2. A) Image of sample vial with diluted matrix. B) Mass spectrometer inlet after analysis.

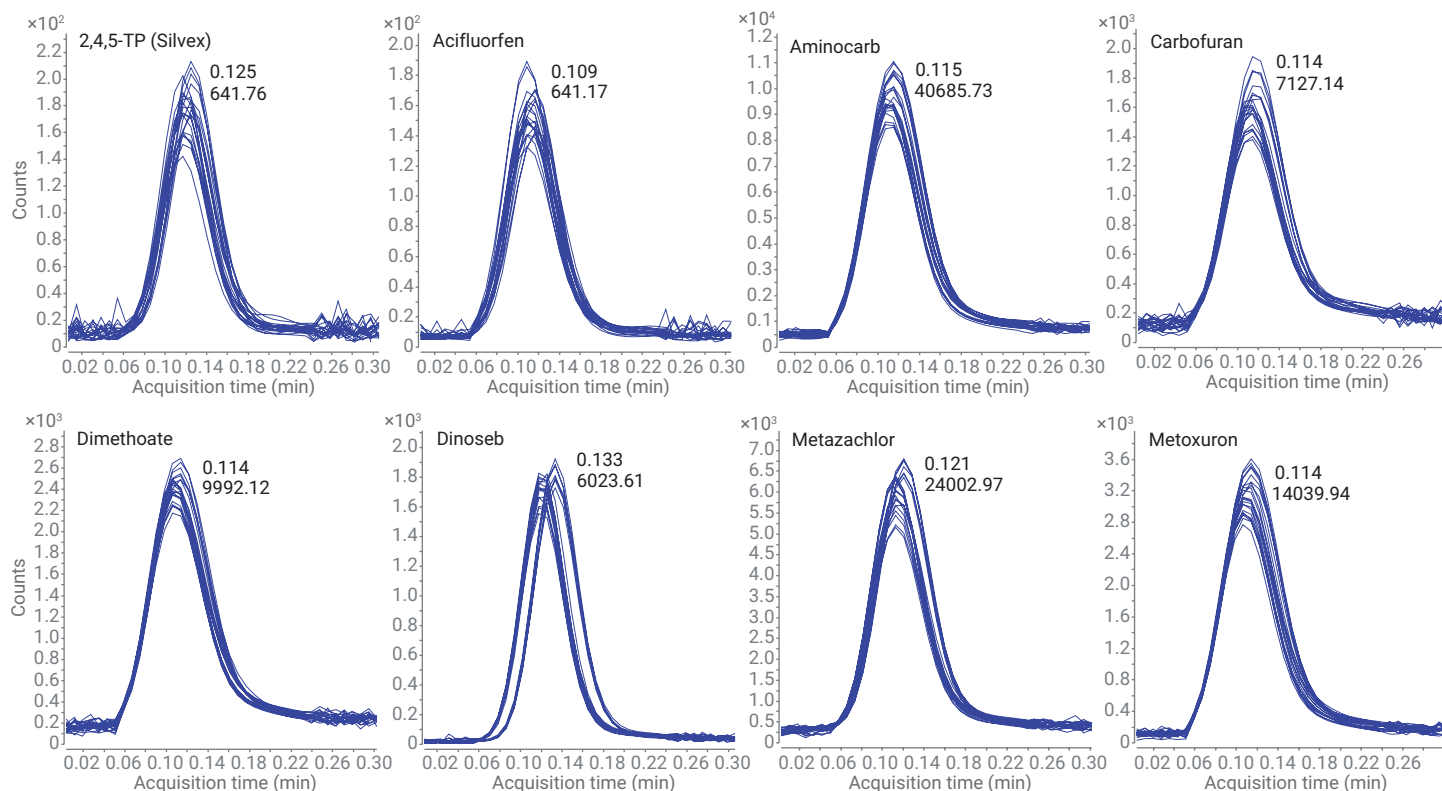


Figure 3. Sample chromatograms of each analyte for every 1,000 injections.

All 10,000 sample chromatograms were quantified using the Agile 2 parameter-less peak integrator algorithm, resulting in unbiased integration of the chromatographic peaks. Statistics for each analyte are summarized on the left side of Figure 4, displaying the mean, standard deviation (StDev), and percent relative RSD (%RSD).

Each analyte was found to have a %RSD of 10 % or less, demonstrating excellent signal stability over the duration of the experiment. The remainder of the figure displays the peak area of each injection over all 10,000 injections, demonstrating the variation in peak area values. Peak area variations most likely originated from the LC due to minor blockages caused by buildup of matrix components on the column and the ability for the mass spectrometer to recover abundance once those contaminants have eluted.

Conclusion

This Technical Overview demonstrates the robustness performance for 10,000 sample injections on the Ultivo triple quadrupole LC/MS coupled with an ESI source. Even when presented with a visibly component-rich sample, technical innovations in the Ultivo triple quadrupole LC/MS prevent issues that commonly cause instrument downtime such as charging, component breakdown and contamination, or inability to maintain tune conditions.

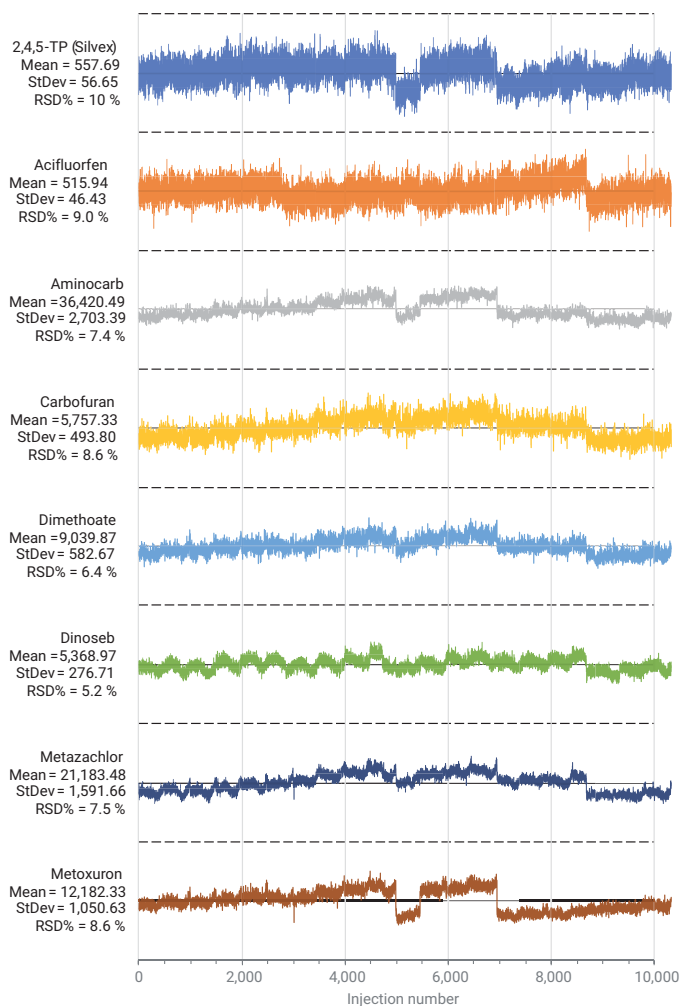


Figure 4. Peak area versus injection number with summary statistics.