Waters Alliance™ Systems for LC/MS ESI/APCI Applications

Positive Ion APCI Analysis of an Herbicide Mixture Using the Waters Alliance™ LC/MS System Featuring the Platform LCZ Detector

Highlights: The following study involves the utilization of molecular ion (weight) information for confirmation of compounds in an herbicide standard mixture. Sensitive target compound analysis was achieved using Selected Ion Recording (SIR) mode in MassLynx software. Herbicide detection and confirmation in spiked barley extract analysis was also performed using ZSpray technology designed for robust complex sample analysis.

Atmospheric Pressure Chemical Ionization (APCI) is a useful ionization technique for the analysis of relatively small molecules, especially when the goal is molecular weight generation for target compound confirmation. APCI is both a sensitive and a robust technique. The Waters Alliance™ LC/MS System featuring the Platform LCZ detector utilizes either APCI or Electrospray Ionization (ESI) in either the positive or negative ion mode. The Platform LCZ also has two unique features: an extended mass range up to 4000 Da, and a dual orthogonal spray mechanism (ZSpray) for dirty or complex sample analysis. In this study, the sensitivity limits for herbicide analysis by Selected Ion Recording (SIR) on the Platform LCZ detector were approximately 1-10 pg on column, and the sensitivity limit for full scan analysis was approximately 10X higher. Barley extracts spiked with 0.1 ppm of a standard herbicide mix were successfully analyzed by positive ion APCI. The dual orthogonal extraction capability of ions from the source into the analyzer by the unique ZSpray technology enables robust analysis of samples with complex matrices (such as these extracts) with no interference observed from the sample matrix. The large sample cone orifice and efficient design of the ZSpray source also improves overall sensitivity. An isolation valve on this source also allows for easy cleaning. The sample cone may be removed and replaced without venting the system.

Experimental conditions:

- System: Waters Alliance™ LC/MS System Featuring the Platform LCZ Detector
- Column: Waters Symmetry C18 150 x 3.9 mm
- Eluent A: Water Eluent B: Acetonitrile
- Gradient : See table
- Flow rate: 0.5 ml/min
- Inj Volume: 10 ul

Time	%A	%B	Curve
Initial	60	40	---
8 min	40	60	7
10 min	40	60	---
12 min	60	40	6
15 min	60	40	---

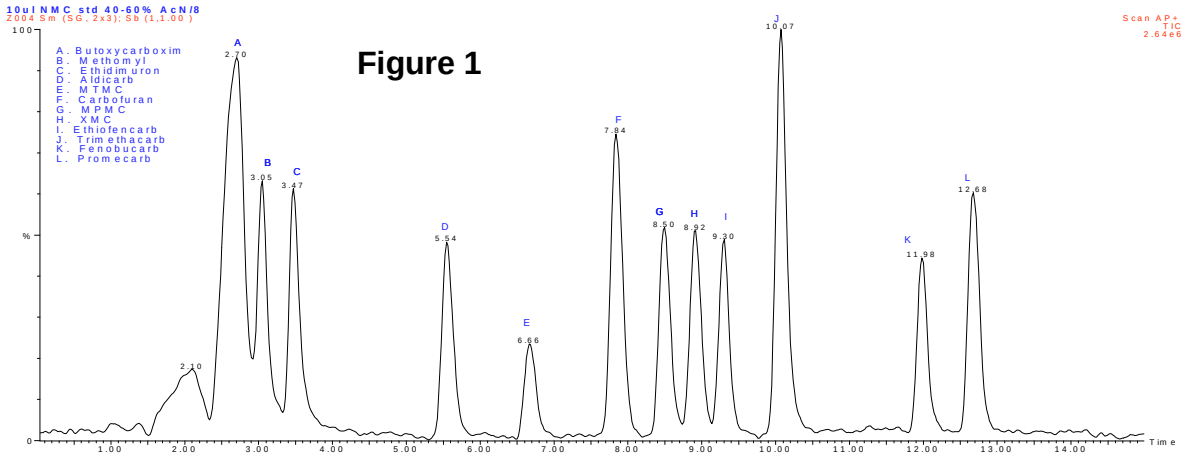
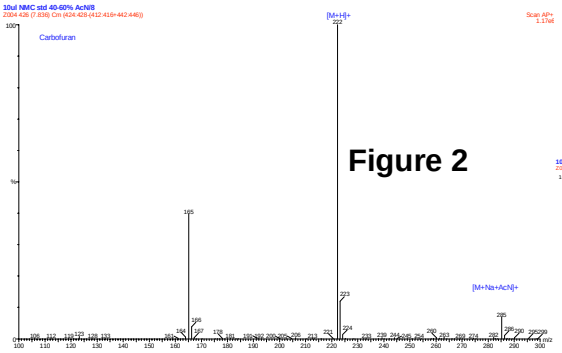


Figure 1 shows the total ion chromatogram (TIC) obtained from a 10 uL injection of NMC standard No.1 under the above conditions (100 ng on-column) using the Waters Alliance LC/MS System featuring the Platform LCZ detector. The mass spectrometer was scanned over a mass range from 100 to 300 amu every 0.5 seconds.

Herbicide API Spectra



Background-subtracted APCI spectrum of Carbofuran from a 10 ul injection of NMC Standard No. 1 (RT = 7.8 min).

Figure 2

Background-subtracted APCI spectrum of Ethiofencarb from a 10 ul injection of NMC Standard No. 1 (RT = 9.3 min).

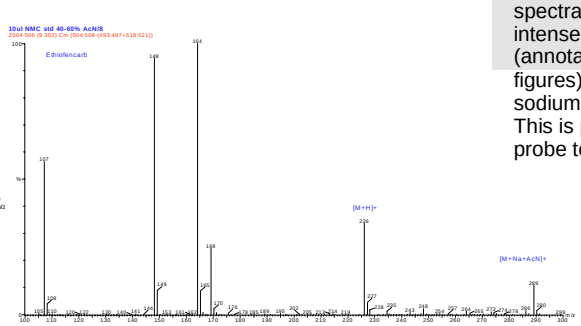


Figure 2 shows the background-subtracted mass spectra from two herbicides studied. These spectra are marked by relatively intense protonated molecular ions (annotated as [M+H]+ in these figures), as well as the presence of sodium and acetonitrile adduct ions. This is probably due to a low APCI probe temperature.

In order to determine the instrumental limits of detection, the standard mixture was diluted to yield a series of standard mixtures at concentrations of 0.1, 0.25, 0.5, 1, 5, 10, and 50 ng/ml in 30% methanol. 10 ul aliquots of each standard level were injected into the LC/MS system. In order to determine instrument sensitivity in the full scan mode, the mass spectrometer was scanned from 100 to 300 Da at a scan rate of 1 scan/0.8 seconds. Selected Ion Recording (SIR) sensitivity was determined by monitoring only the protonated molecular ions of each compound. In order to maximize sensitivity, these ions were only monitored during a short window centered on the retention time of each peak. The solvent standards were analyzed, and the [M+H]+ chromatograms of each analyte were inspected. Figure 3 compares the full scan and SIR chromatograms of a representative compound. The signal-to-noise ratio for the each peak (point to point) was determined using the MassLynx software, and is displayed in the chromatogram. As expected, SIR was 10-50 times more sensitive than full-scan analysis. Instrumental limits of detection were approximately 1 to 10 pg on-column for most compounds in SIR mode, and approximately 100-500 pg on-column for full-scan mode.

SIR vs. Full Scan APCI Analysis of Herbicides

Comparison of SIR data (upper trace) and full scan data (lower trace) extracted ion chromatograms following injection of diluted NMC Standard No. 1

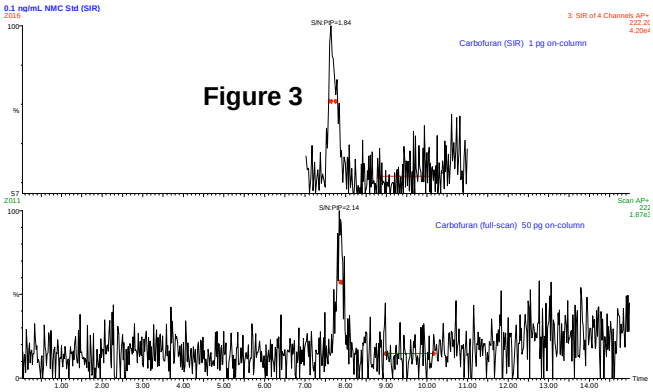


Figure 3

Spiked Barley Extract Analysis by APCI LC/MS

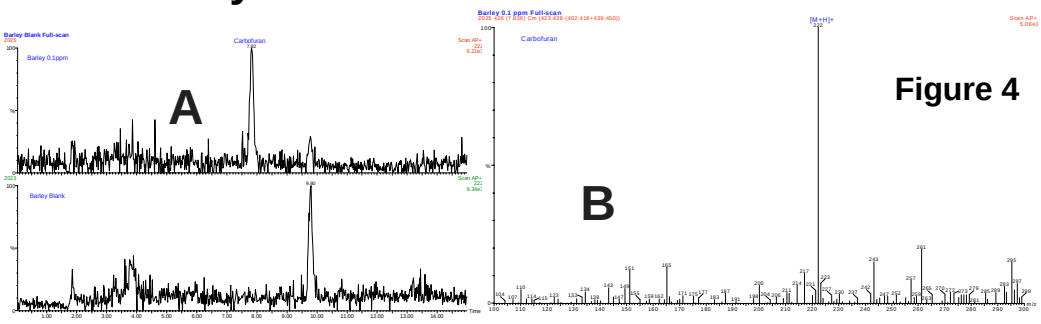


Figure 4

A: Comparison of full-scan extracted ion chromatograms for Carbofuran following a 10 uL injection of barley extract spiked at a level of 0.1ppm (upper trace) and blank (lower trace)

B: Background-subtracted mass spectrum of Carbofuran peak

Aliquots of blank extracts of barley were spiked with the herbicide standard mixture at concentrations of 0.1 ppm and analyzed in the full scan mode. Figure 4 compares the extracted [M+H]+ chromatogram from spiked (0.1 ppm) and a blank barley extract. The background-subtracted spectra of the analyte is shown. At this level, reasonable chromatographic peaks are observed for all analytes, with the exception of aldicarb and ethiofencarb. The mass spectra of these peaks show distinctive [M+H]+ and adduct ions. It should also be noted that no interference from the matrix was observed.