

Determination of acidic herbicides in water using liquid chromatography-tandem quadrupole mass spectrometry with direct injection

Waters™

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INTRODUCTION

Herbicides are a specific group of plant protection products used to treat a variety of weeds such as crop rotation, tillage, and fallow systems. Acidic herbicides comprise families of compounds that include derivatives of benzoic acid (e.g., dicamba), acetic acid (e.g., 2,4-dichlorophenoxyacetic acid [2,4-D]), and other miscellaneous acids. Herbicides can enter surface water bodies either directly through spray or indirectly via surface water runoff. Herbicides can also reach water-bearing aquifers below ground (groundwater) from applications onto crop fields and seepage of contaminated surface water. Surface and ground water is pumped, piped, or diverted for use in the supply of drinking water. The presence of pesticides in drinking water is monitored globally. The EU Drinking Water Directive sets a maximum limit of 0.1 µg/L for individual pesticide residues present in a sample (0.5 µg/L for total pesticides). In the USA, drinking water is regulated under the Safe Drinking Water Act, where there are varying maximum contaminant levels for each residue. There is a need for reliable analytical methods for monitoring acidic herbicides in drinking water. Historically, methods have been based upon using liquid-liquid extraction or solid-phase extraction (SPE) as a concentration step. This poster will demonstrate a rapid method for the determination of a range of acidic herbicides in water samples using large volume direct injection on Waters ACQUITY™ Premier HSS T3 column coupled with Waters ACQUITY Premier UPLC™ I-Class System and the Xevo™ TQ Absolute Mass Spectrometer to achieve a better degree of performance and ultra-high sensitivity quantitative method. The calibration curves were run from 0.01 to 0.2 µg/L in drinking water. Data were acquired and processed using waters_connect™ software

EXPERIMENTAL CONSIDERATIONS



Sample Preparation

Aliquots of drinking water samples (10 mL) were centrifuged and passed through a syringe PVDF filter (0.2 µm). Aliquots (1.5 mL) from each water sample were then transferred to deactivated glass vials and acidified (30 µL of 5% formic acid) prior to analysis. A sample of drinking water, were spiked with the compounds of interest at 0.01 and 0.2 µg/L to evaluate linearity. Data were acquired and processed with waters_connect™ software. Figure 3 summarizes conditions for all MRM transitions including the retention times. Soft ionization was enabled for MCPB, dicamba, 2,4-DB and triclopyr.

LC System: Waters ACQUITY Premier UPLC I-Class FTN Plus (250µL loop, 30µL needle, 250 µL syringe)

Column: ACQUITY Premier HSS T3 (1.8 µm, 2.1 x 100 mm),

Injection volume: 250 µL

Column temperature: 40 °C

Mobile phase A: 0.02 % FA in water, B: Methanol

MS System: Xevo TQ Absolute Mass Spectrometer

Source temperature 120 °C

Desolvation gas temperature 300 °C

Desolvation gas flow: 1000 l/hr

Cone gas flow: 150 l/hr

Capillary voltage: 1.0 kV NEG, 2 kV POS

Time (min)	%A	%B	Curve
Initial	80	20	-
6.0	0	100	6
8.0	0	100	6
8.1	80	20	6
10	80	20	6

Figure 3. Acquisition Method Editor (AME) showing MRM transitions, dwell time, soft ionization and other method parameters in waters_connect

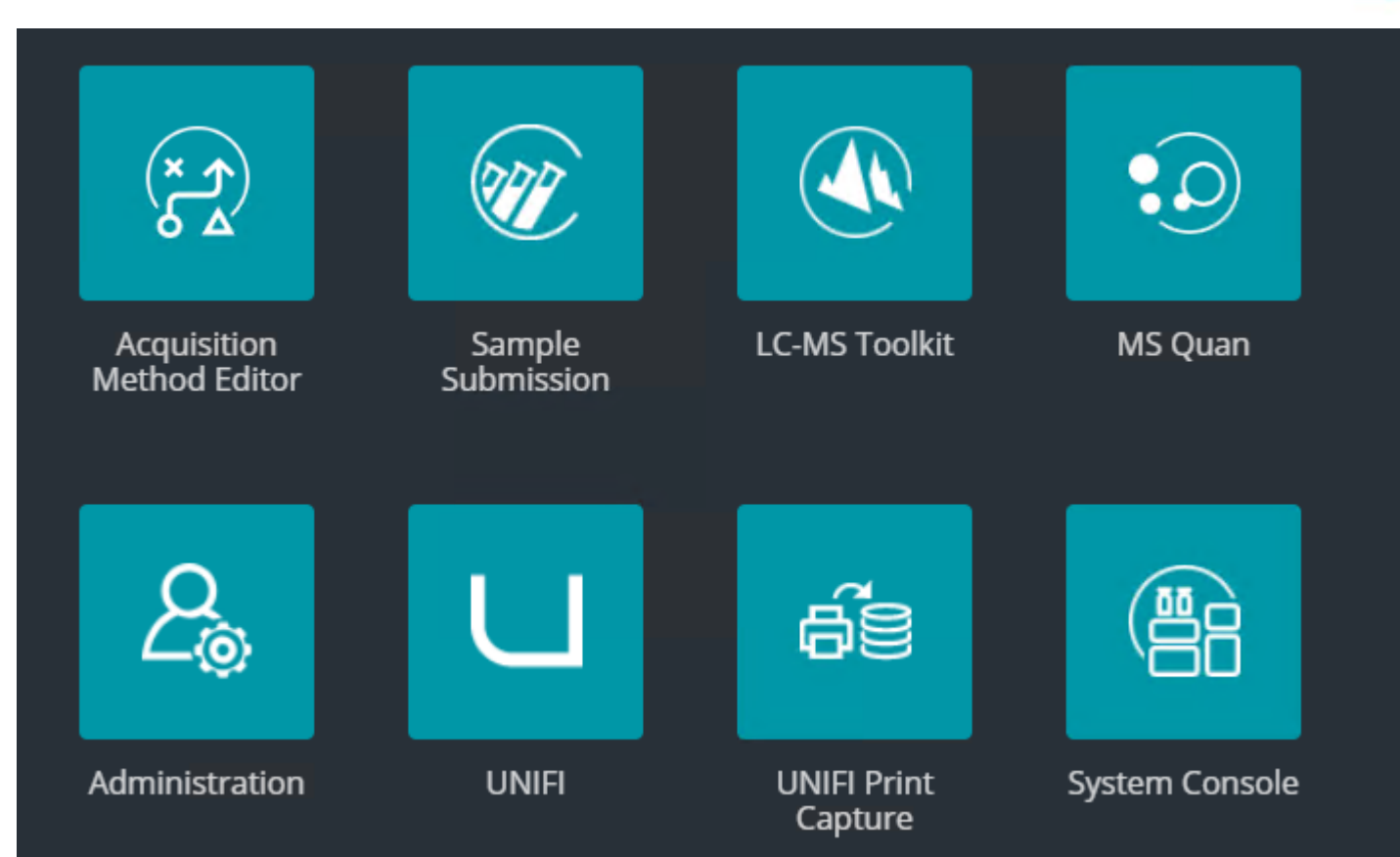


Figure 1. ACQUITY Premier UPLC I-Class with Xevo TQ Absolute Mass spectrometer

RESULTS AND DISCUSSION

Some of the compounds of interest, 2,4-DB, dicamba, MCPB and triclopyr, exhibited fragmentation within the source region under typical settings. Therefore, the temperature of the source block and the desolvation gas was reduced to 120 °C and 300 °C, respectively, which increased the response of the deprotonated molecular ion. These compounds were also acquired in soft ionization mode, a function enabled in the MS acquisition file that applies a shallower gradient of voltages to the StepWave™ XS ion transfer optics to reduce fragmentation during transmission of ions to the first quadrupole. Reducing fragmentation can result in significant improvements in sensitivity as shown previously¹. A range of acidic herbicides in drinking water were analyzed using large volume injection on Waters ACQUITY Premier HSS T3 column coupled with Waters ACQUITY Premier UPLC I-Class System and the Xevo TQ Absolute Mass Spectrometer and acquired with waters_connect software.

Excellent sensitivity and selectivity were demonstrated by the response for each compound detected from the analysis of drinking waters spiked at 0.02 µg/L, which is well below the maximum limits. Figure 4 shows an overlay chromatograms with 2 MRM transitions for all studied analytes in drinking water. Data processing using the MS Quan application in waters_connect for quantitation software platform allows for easy visual representation and review of data. Laboratories are expected to provide methods with lower limits of quantification (LLOQ) of at least one third of the EQS. The sensitivity observed suggests that detection and quantification of all compounds at lower concentrations should be possible.



Figure 4. Chromatograms for acidic herbicides in drinking water at 0.02µg/L acquired and processed in waters_connect.

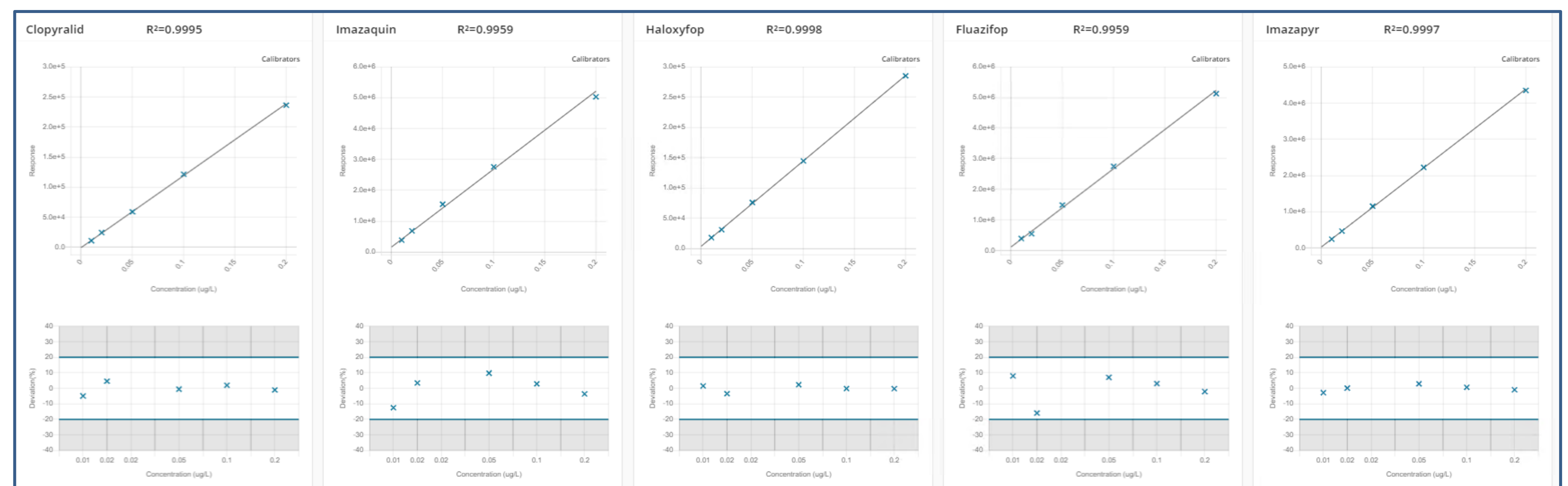


Figure 5. Calibration curve of example acidic herbicides in drinking water ranged from 0.01 to 0.2µg/L in MS Quan.

CONCLUSIONS

- This poster describes the performance of a method for the determination of 19 acidic herbicides by direct, large-volume injection of water samples by Waters ACQUITY Premier UPLC™ I-Class System and the Xevo™ TQ Absolute Mass Spectrometer and waters_connect™ software.
- The method is simple, fast, and reliable which avoids the time, costs, and achieve low level of detection with Xevo™ TQ Absolute Mass Spectrometer
- The MS Quan application with the new waters_connect™ quantitation software, which reduces the time taken to process data and review results

REFERENCES

1. <https://www.waters.com/nextgen/us/en/library/application-notes/2018/acidic-herbicides-water-liquid-chromatography-tandem-quadrupole-mass-spectrometry.html>

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