

## Highly Sensitive Analysis of Polar Pesticides in Food Matrices on the Xevo TQ-XS

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### GOAL

Develop a sensitive LC-MS/MS method for the robust analysis of highly polar pesticides in food commodities without the need of derivatization.

### BACKGROUND

Glyphosate is a non-selective broad spectrum herbicide, which accounts for more than 60% of global herbicide sales. While discussions on the toxicological concerns of glyphosate and associated compounds continue, maximum residue limits (MRLs) are enforced globally, varying on commodity of interest.<sup>1</sup> Due to certain physicochemical characteristics of glyphosate, its metabolites and similar compounds, generic "catch-all" multiresidue methods are not appropriate. Traditionally, derivatization has been utilized to allow for chromatographic retention on reverse phase columns. While good sensitivity and repeatability have been reported using this technique,<sup>2</sup> there is an interest in direct analysis to avoid timely sample preparation and derivatization. Ion chromatography offers an option for the direct analysis of such polar compounds; however, specialized equipment and the use of non-MS compatible solvent additives can be required.

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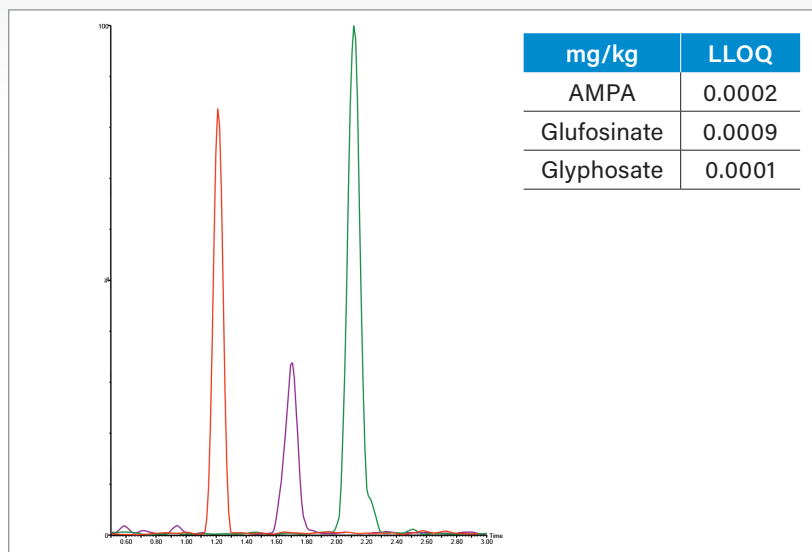


Figure 1. Example of chromatography for 1. AMPA, 2. glufosinate, and 3. glyphosate, respectively at 0.002 mg/L in solvent.

### THE SOLUTION

Using Waters' latest tandem quadrupole technology, the Xevo® TQ-XS, the sensitivity and repeatability was investigated for the simplified analysis of underivatized polar pesticides. A mixed mode, weak ion exchange/reverse phase analytical column allowed for MS friendly mobile phase of 50 mM aqueous ammonium formate (pH 2.9) to be readily used in electrospray negative ion mode.<sup>3</sup>

Waters® Xevo TQ-XS, coupled with the ACQUITY UPLC® System achieves sub parts per billion detection limits for glyphosate, glufosinate and aminomethylphosphonic acid (AMPA), as shown in Figure 1. Here an example of the chromatography obtained from the analysis of the three analytes of interest is shown at 0.002 mg/L in water, while inset shows the limit of quantitation achieved for each analyte based on signal-to-noise (S/N) ≥10.

System robustness, in terms of precision was observed from the analysis of a selection of spiked extracts of cereal-based foods and beverage. Extracts were prepared using a simple aqueous extraction, pass through SPE, spiked at 0.025 mg/kg, filtered and injected into the ACQUITY UPLC System coupled to Xevo TQ-XS. A summary of the results, run over almost 17 hours, and acquired from replicate injections in a single batch, is provided in Table 1, while an example of the chromatography achieved for each analyte in lentils is shown in Figure 2.

Linearity was evaluated for all analytes, in solvent and matrix. Excellent linearity was achieved using calibration curves bracketing the analytical run. An example is shown in Figure 3, where two curves are overlaid showing an  $R^2 \geq 0.995$  with residuals  $< 15\%$  for all concentration levels (0.0005 to 1 mg/kg). When comparing the slopes of the solvent and matrix matched calibration curves, significant matrix effects (namely ion suppression) were observed, especially for AMPA, which could be mitigated by the use of stable isotope analogue internal standards.

## SUMMARY

A fast and simple method has been demonstrated for the analysis of highly polar pesticides in extracts from a variety of foodstuffs. The sensitivity of the Xevo TQ-XS provides excellent limits of detection, suitable for monitoring MRL compliance for these challenging analytes and good quantitative performance, in terms of precision and calibration characteristics, even in the absence of internal standard, in compliance with SANTE 11954/2015 guidelines.

## References

1. <http://www.fas.usda.gov/maximum-residue-limits-mrl-database>.
2. Ehling S and Reddy T M. *J Agric Food Chem*. 63: 10562-10568, 2015.
3. Chamkasem N, Morris C, Harmon T. *J Reg Sci*. 2: 20-26, 201

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Table 1. Summary of precision data (%RSD) from the analysis of extracts from a variety of cereal based products, spiked at 0.025 mg/kg.

	Wheat	Lentils	Barley	Beer
<i>n</i> =	50	50	50	50
Glyphosate	13.7	12.5	13.6	11.6
Glufosinate	13.6	11.9	13.5	12.6
AMPA	15.9	13.5	18.3	14.3

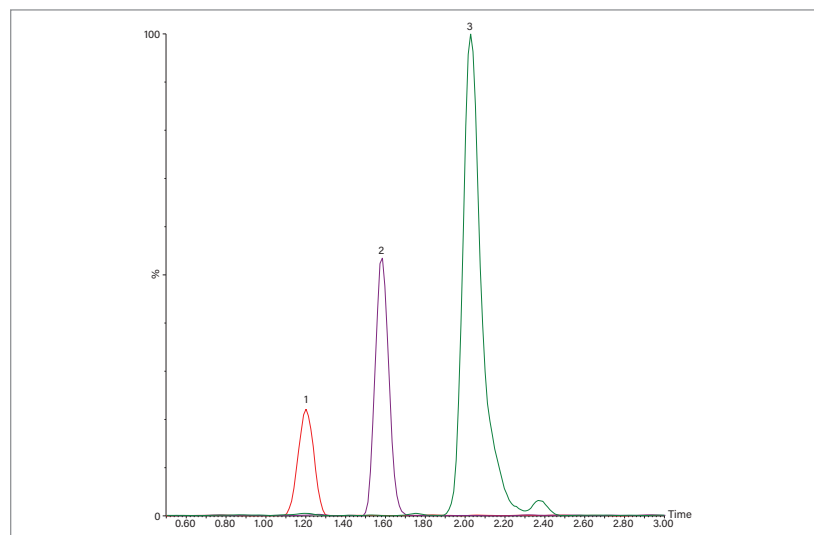


Figure 2. Example of chromatography for 1. AMPA, 2. glufosinate and 3. glyphosate, respectively at 0.025 mg/kg in lentils.

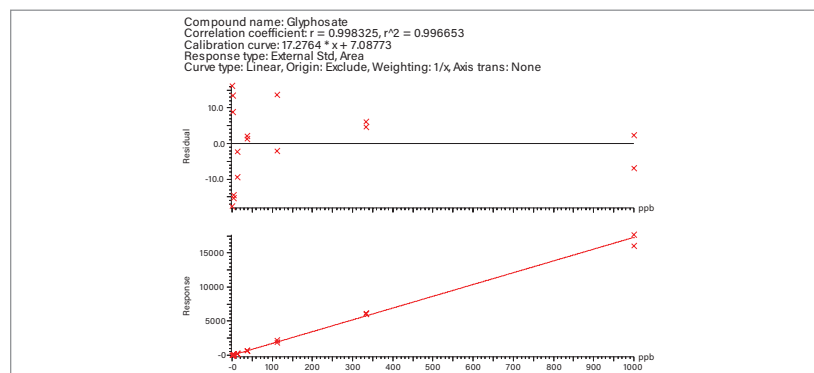


Figure 3. Example of calibration achieved for glyphosate in solvent from 0.0005 to 1 mg/L.

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