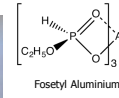
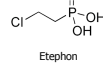
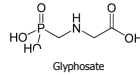


Results of glyphosate and other polar pesticides in stone and pome fruits and other matrices during 2018-2019, using liquid chromatography tandem mass spectrometry (LC-QQQ)

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INTRODUCTION

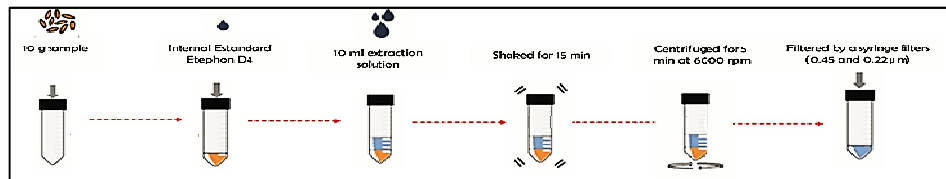
Glyphosate has been used worldwide as an active substance in plant protection products. Its role as a herbicide in agriculture, horticulture and even in some uncultivated areas made it suitable for weed control. However, Member States, the European Food Safety Authority (EFSA) and the European Chemicals Agency (ECHA) thoroughly evaluated Glyphosate for adverse effects on human and animal health and the environment. The European Union and EFSA established a Glyphosate Assessment Group (GAG) to report on a scientific assessment of Glyphosate, and the European Commission formally adopted it in Regulation (EU) 2019/724 on 10 May 2019. In order to determine Glyphosate (and other polar pesticides) it was decided to use the EURL-SRM QuPPE method (version 10) with few modifications. The extraction was performed with acidified methanol and a total of 9 polar pesticides were analysed. Separation was achieved in 18 minutes using liquid chromatography in a Xevo TQ-XS instrument (Waters Corporation). Several matrices with negative majority results were analysed and good sensitivity and selectivity was obtained at the limit of quantification of 0.1 mg kg⁻¹ for Glufosinate ammonium (sum of Glufosinate, its salts, 3-MPPA and NAG), Fosetyl, Glyphosate, Ethepon, Hydroxyethphon (HEPA) and AMPA, and for Phosphonic Acid it was 1 mg kg⁻¹. Following the criteria of SANTE/12682/2019, excellent recoveries between 70 and 120% were achieved with an RSD below 20%, as well as good linearity with r² ≥ 0.99. During routine testing in 2018-2019, 84 samples from various matrices included in different control projects were analyzed: from stone and pome fruits to corn, chard and other types, 7% were positive for Fosetyl.



METHOD

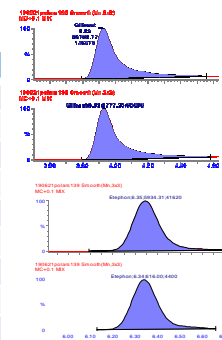


CONDITIONS UPLC / QQQ



UPLC CONDITIONS (previously remove metal ions)	
UPLC system	ACQUITY UPLC I-Class (Waters)
Column	Torus DEA 130Å, 1.7 µm, 2.1 mm x 100 mm
Mobile phase A	Water + 0.9% formic acid
Mobile phase B	Acetonitrile + 0.9% formic acid
MS CONDITIONS	
MS system	Xevo TQ-XS (Waters)
Ionization mode	ESI-
Capillary voltage	2.5 kV
Ion counting threshold	50
Desolvation temperature	600°C
Desolvation gas flow	1000 L/Hr
Source temperature	150°C
Cone gas flow	300 L/Hr
Collision gas flow	0.15 mL/min
Nebulizer gas pressure	7 Bar

TRANSITIONS		
COMPOUND	Quantifier transition	Qualifier transition
Glyphosate	168 -> 63	168 -> 150
AMPA	110 -> 63	110 -> 79
Ethepon	143 -> 107	145 -> 107
Hydroxy Ethepon (HEPA)	125 -> 95	125 -> 79
Glufosinate	180 -> 63	180 -> 85
NAG (N-acetyl glufosinate)	222 -> 136	222 -> 59
3-MPPA	151 -> 107	151 -> 133
Fosetyl	109 -> 81	109 -> 63
Phosphonic acid	81 -> 79	81 -> 63



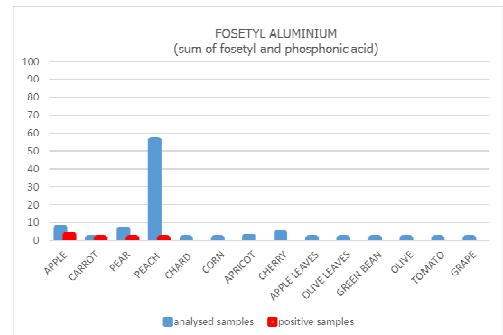
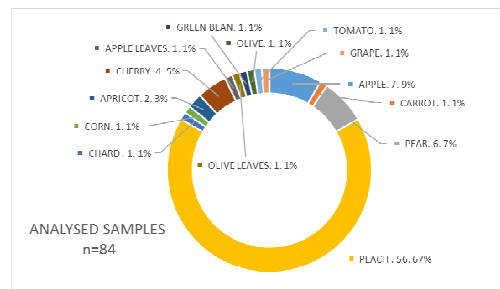
VALIDATION RESULTS

The method developed is suitable and complies with the specifications of the SANTE regulations. The extraction method allows the quantification of pesticides with satisfactory results in terms of accuracy (70-120% recoveries), precision (RSD < 20%), linearity (r² ≥ 0.99) and selectivity (deviation ratio < 30%). The validated range for all analytes (except phosphonic acid) is 0.01 mg/Kg (QL) to 5 mg/Kg, and 1 mg/Kg (QL) to 5 mg/Kg for phosphonic acid. The 1/10th dilution was also evaluated for all the analytes showing good results. In addition, the requirements of the MRLs were compiled for all analytes, all limits of quantification (QLs) being lower than MRLs.

	CHERRY (stone fruit)		APPLE (pome fruit)	
	LQ validate (mg/kg)	MRL (mg/kg)	LQ validate (mg/kg)	MRL (mg/kg)
GLYPHOSATE	0,1	0,1	0,1	0,1
ETHEPON	0,1	5	0,1	0,8
GLUFOSINATE	0,1	0,15	0,1	0,1
PHOSPHONIC ACID	1	2	1	150
MPPA (3-methylphosphinico-propionic acid)	0,1	0,15	0,1	0,1
AMPA (aminomethyl phosphonic acid)	0,1	0,1	0,1	0,1
HEPA (2-hydroxyethyl phosphonic acid)	0,1	5	0,1	0,8
NAG (N-acetyl glufosinate)	0,1	0,15	0,1	0,1
FOSETYL	0,1	2	0,1	150

RESULTS TESTING ON 2018-2019

During 2018-2019, 84 samples of different kinds of agriculture were analysed (chards, peaches, pears, green bean, olive, olive oil, corn, cherries, tomatoes, grapes...) and only 7% proved to be positive. Fosetyl aluminium (sum of Fosetyl and Phosphonic Acid) was the only positive analyte found and in all cases below its maximum residue limit (MRL).



CONCLUSIONS

All samples evaluated have satisfactory results according to the criteria of the maximum residue limit (MRL). The limit of quantification values of the method are below or equal to the MRL. Following SANTE/11813/2017 criteria, excellent recoveries between 70-120% are achieved with a RSD below 20%, as well as good linearity with r² ≥ 0.99. The Agri-food laboratory is working to analyse at lower levels 0.05 mg kg⁻¹ for Glufosinate Ammonium (sum of Glufosinate, its salts, 3-MPPA and NAG), Fosetyl, Glyphosate, Ethepon, Hydroxyethylene (HEPA) and AMPA and 0.5 mg kg⁻¹ for Phosphonic Acid.

REFERENCES

- Directive 2009/128/CE Commission Regulation (EU) 396/2005
- SANTE/11813/2017
- EURL-SRM QuPPE method (version 10) M1.6 "Glyphosate & Co. on Torus DEA" de EU Reference Laboratories for Residues of Pesticides Single Residue Methods

ACKNOWLEDGEMENTS

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