

Niell, Silvina¹; Dorrego, Melina¹; Genolet, Romina¹; Archondo, Lucas¹; Garcia, Isabel¹; Besil, Natalia¹; Heinzen, Horacio²; Cesio, María Verónica²

sniell@cup.edu.uy

1. Universidad de la República, CENUR Litoral Norte, Paysandú, Uruguay.
2. Universidad de la República, Facultad de Química, Montevideo, Uruguay



INTRODUCTION

Anionic herbicides, particularly glyphosate, are herbicides that have been used worldwide for almost fifty years. In Uruguay, glyphosate is the most frequently used pesticide with the highest rates of kg/ha. For soil evaluations, it is interesting to evaluate which IC-MS/MS amenable herbicides and their important metabolites could be analyzed in a single analytical step. In this work, the simultaneous evaluation of glyphosate, AMPA, dicamba and dicamba desmethyl using IC-MS/MS is presented.

METHODOLOGY

Extraction

- 5 g soil + KOH 0.6 M + ultrasonic bath for 30 min.
- Adjustment to pH=4 with formic acid.
- Centrifuge at 4°C at 3500 rpm for 10 min

Combinations of RPC18 and GCB d-SPE evaluated

B	150mg C18	C	15mg GCB
D	30mg GCB	E	150mg C18 15mg GCB

- Vortex 1 min and centrifuge at 4°C at 3500 rpm for 10 min.

Clean-Up

Instrumental analysis



Dionex ICS6000 Ion Chromatograph Coupled to a Tandem-Triple Quadrupole Mass Spectrometer, TSQ Fortis Column: Dionex IonPac AS19 (2 x 250mm) Guard Column: Dionex IonPac AG19 (2 x 50mm) Eluent KOH

RESULTS AND DISCUSSION

Table 1. Recovery percentages of the tested methods at 50 µgkg⁻¹

Method	A		B		C		D		E	
	%Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
Glyphosate	115	13	100	37	96	9	100	26	100	8
AMPA	-	-	133	50	40	30	41	77	75	84
Dicamba	177	8	105	39	113	8	58	9	100	4
Dicamba desmethyl	161	3	74	24	91	7	67	17	68	15

The best recoveries for the analytes under study were obtained using only a small amount of GCB (0.015 g) **Method C**

Table 2. Validation parameters results of method C

Analyte	% Rec. 25 µg kg ⁻¹	% RSD	% Rec. 50 µg kg ⁻¹	% RSD	% Rec. 75 µg kg ⁻¹	% RSD	% Rec. 100 µg kg ⁻¹	% RSD	% Rec. 150 µg kg ⁻¹	% RSD	%ME	Linear range (µg kg ⁻¹)	LOQ (µg kg ⁻¹)
Glyphosate	78	73	96	9	54	12	75	6	53	2	-8	25 - 150	50
AMPA	-	-	40	30	47	10	69	16	69	8	-86	50 - 150	100
Dicamba	96	16	113	8	90	5	91	3	68	9	-21	25 - 150	25
Dicamba desmethyl	95	13	91	7	77	6	89	5	77	9	-1	25 - 150	25

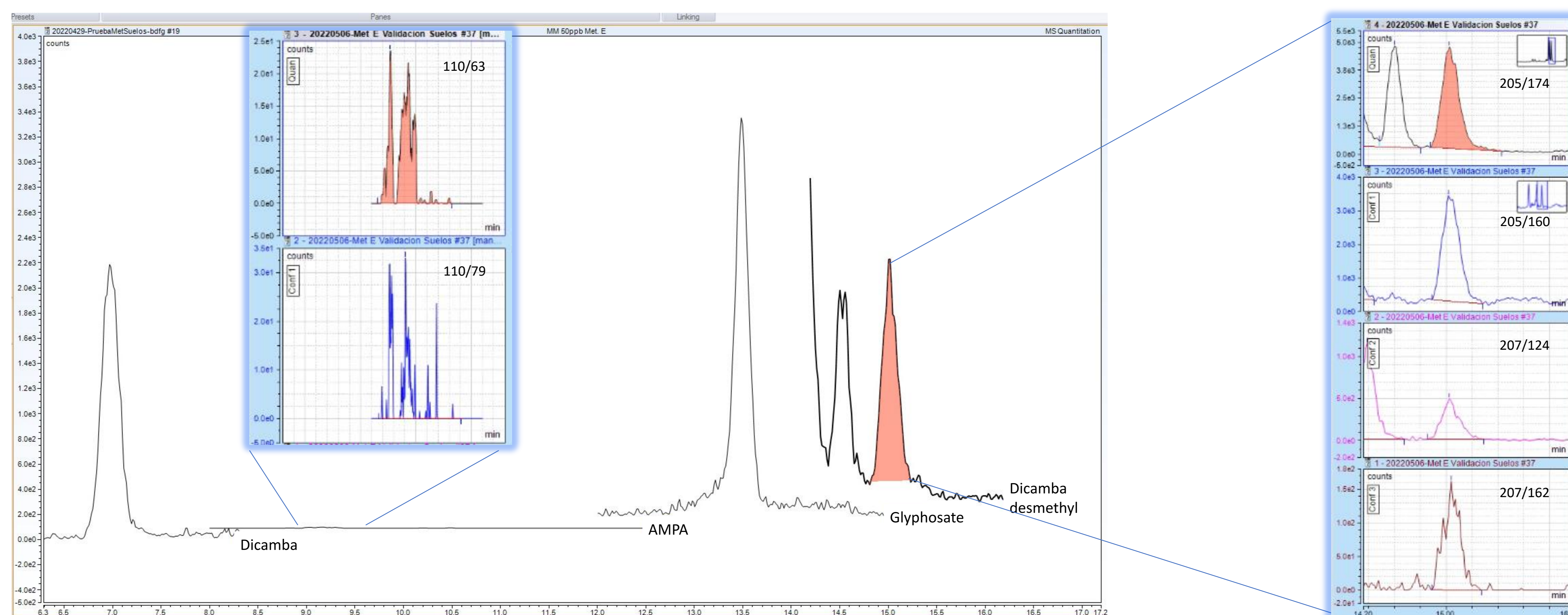


Figure 1. IC-MS/MS chromatogram of glyphosate, AMPA, dicamba and dicamba desmethyl in matrix matched calibration (50 µgkg⁻¹)

CONCLUSIONS

Glyphosate, dicamba and their metabolites can be analyzed with this single method by IC-MS/MS. LOQs are adequate, it would be useful to lower AMPA's LOQ. The validated methodology is suitable for environmental studies such as DT50 calculation and for soil monitoring purposes.

REFERENCES

De Gerónimo, Eduardo, et al. "Evaluation of two extraction methods to determine glyphosate and aminomethylphosphonic acid in soil." *Soil Science* 183.1 (2018): 34-40.
Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. Document No. SANTE/11312/2021

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