WAGENINGEN
UNIVERSITY & RESEARCH

Advances in HILIC chromatography applied to the determination of highly polar pesticides in food and feed

Jonatan Dias, Sonia Herrera Lopez, André de Kok, Hans Mol

Introduction and objectives

Hydrophilic interaction liquid chromatography (HILIC) is an alternative LC mode for separation of polar compounds. The highly anionic polar herbicide glyphosate and related compounds such as glufosinate, ethephon and fosetyl present some characteristics that makes their determination very difficult when reversed phase chromatography is applied due to the lack of retention of these compounds in this mode. HILIC appears in this context as a useful tool to solve those issues. In this work, the performance of several HILIC columns, namely Obelisc N (Sielc), APP (Waters), PolarX (Restek), HILIC-Z and Poroshell 120 CS-C18 (Agilent), were evaluated for the application on 14 highly polar anionic pesticides determination in several food and feed matrices.

Method

A methanol/water-based extraction method was employed.

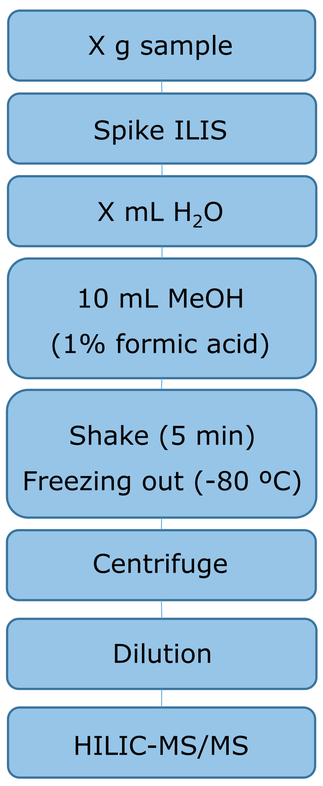

Figure 1. General extraction procedure.

Q-Trap 6500+ (Sciex), ESI interface operated in negative mode.

Columns evaluated:

- Obelisc N
- APP
- Polar X
- HILIC-Z
- Poroshell 120 CS-C18

Obelisc N
Eluent A: water 1% formic acid
Eluent B: acetonitrile

Dilution solvent:

Acetonitrile/water (6:4) + 0.2% TFA

APP
Eluent A: water 0.9% formic acid
Eluent B: acetonitrile 0.9% formic acid

Dilution solvent:

MeOH 1% formic acid /water (1:1)

PolarX
Eluent A: water 0.5% formic acid
Eluent B: acetonitrile 0.5% formic acid

Dilution solvent:

MeOH 1% formic acid /water (1:1)

HILIC Z
Eluent A: 1% formic acid
Eluent B: acetonitrile

Dilution solvent:

Acetonitrile/water (6:4) + 0.2% TFA

Poroshell 120 CS
Eluent A: water 0.1% formic acid
Eluent B: methanol 0.1% formic acid

Dilution solvent:

MeOH 1% formic acid /water (1:1)

Results

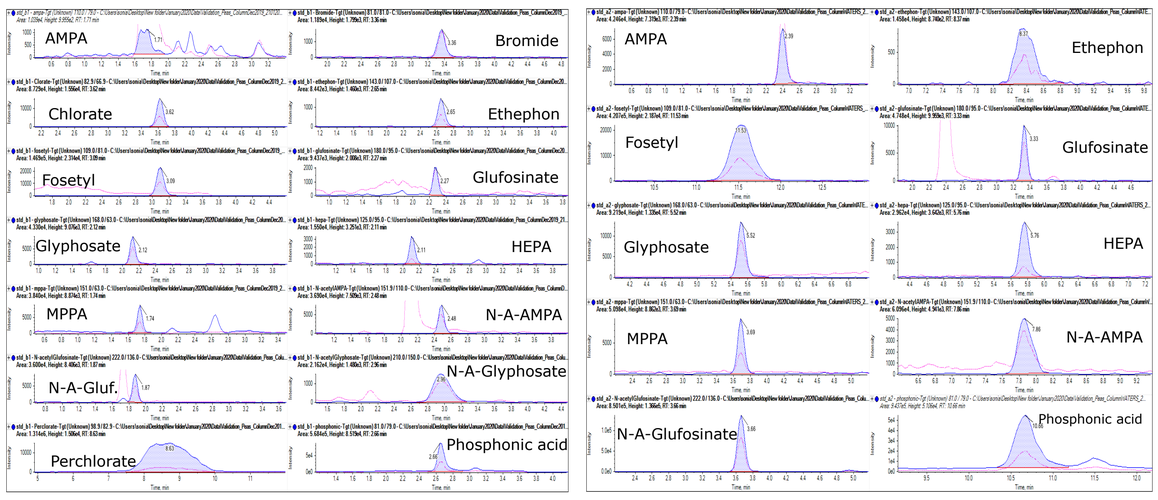

Figure 2. Recontructed ion chromatograms and peak shapes of the evaluated pesticides using Obelisc N and APP column, respectively. Standard solutions prepared in solvent at 0.5 ng mL^{-1}.

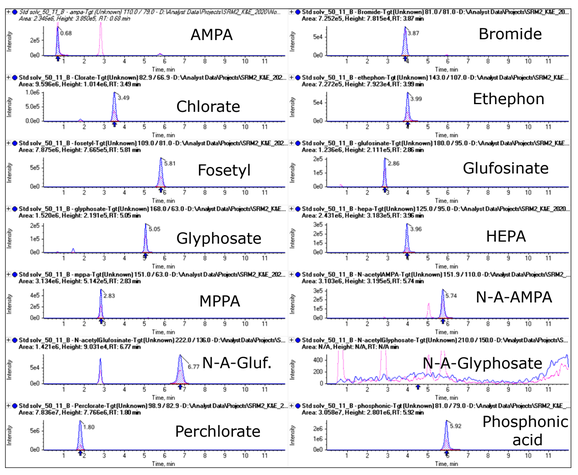

Figure 3. Recontructed ion chromatograms and peak shapes of the evaluated pesticides using PolarX column. Standard solutions prepared in solvent at 50 ng mL^{-1}.

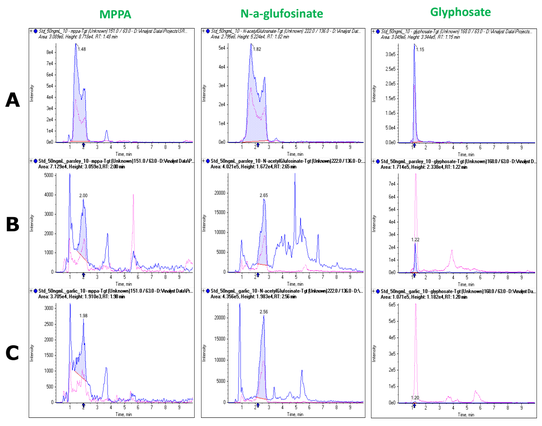

Figure 4. Recontructed ion chromatograms and peak shapes of MPPA, N-a-glufosinate and glyphosate using Poroshell 120 CS. Standard solutions prepared in solvent (A), powder parsley extract (B) and powder garlic extract (C) at 50 ng mL^{-1}.

Table 1. Performance evaluation of the tested columns.

Compound	Performance (peak shape and detectability)				
	Obelisc N	APP	HILIC-Z	PolarX	Poroshell 120
AMPA	✓*	✓	✗+#	✓	✓
Bromide	✓	nd	✓	✓*	✓
Chlorate	✓	nd	✓	✓	✓
Ethephon	✓	✓	✓#	✓	✓
Fosetyl	✓	✓	✓#	✓	✓
Glufosinate	✓	✓	✓#	✓	✓
Glyphosate	✓*	✓	(✗)#	✓*	✗*
HEPA	✓*	✓	(✗)	✓	✗*
MPPA	✓	✓	✓	✓	✗*+
N-a-AMPA	✓	✓	✓	✓	✗*
N-a-Glufosinate	✓	✓	✓#	✓	✗*+
N-a-Glyphosate	✓	nd	(✗)	nd	✓
Perchlorate	✓	nd	✗+#	✓	✓
Phosphonic acid	✓	✓	✓	✓	✗*

nd.: not detected under these conditions
*Strong suppression in some matrices
+Peak splitting
#Lack of retention
()Tailing

Conclusions

- Obelisc N covers a higher number of compounds (14) when compared to the other columns.
- APP showed improvements in LOQ for some compounds like AMPA, fosetyl, glyphosate, HEPA and MPPA. However, bromide, chlorate, perchlorate and N-acetyl-glyphosate can not be analysed by this column, in these conditions.
- PolarX presented good results, except for N-acetyl-glyphosate, which could not be eluted within acceptable time.
- HILIC-Z presented some selectivity and peak splitting issues, as well as lack of retention for most of the compounds.
- Poroshell 120 CS-C18 presented good retention for most of the compounds. However, high suppression and poor peak shape was observed for compounds like HEPA, MPPA, N-acetyl-AMPA and phosphonic acid when evaluated in matrix.

Wageningen University & Research
P.O. Box 123, 6700 AB Wageningen
Contact: jonatan.dias@wur.nl
T + 31 (0)317 48 69 18
www.wur.nl/food-safety-research