LC-MS/MS Analysis of Anionic Polar Pesticides in Fruits and Vegetables using a Venusil HILIC column

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Overview

Many polar pesticides used in conventional agriculture are difficult to retain on standard C18 reversed phase HPLC columns.

In this application note we show a fast and robust method for the LC-MS/MS determination and quantification of several common anionic polar pesticides in fruits and vegetables after sample preparation using the QuPPe method. As the samples we tested were from plant origin, we followed the QuPPe-PO-Method suggested by the EU Reference Laboratories for Residues of Pesticides – Single Residue Methods (EURL-SRM).

Experimental

The experiments were performed on a Shimadzu® Nexera® system connected to a SCIEX® 6500+ triple quadrupole MS detector. The LC separation was performed on an Agela Venusil HILIC column under reversed phase gradient conditions.

LC Conditions

Column: Venusil HILIC 3 µm
Dimension: 100 x 2.1 mm
Part No.: VH931002-0
Mobile Phase: A: 0.1 % Formic Acid in Water
B: 0.1 % Formic Acid in Acetonitrile

Gradient:

Time(min)	%B
0.5	5
1.0	5
5.0	65
5.1	90
8.0	90
8.1	5

Flow Rate: 0.4 mL/min
Injection: 5 µL
Column Temperature: 40 °C
Detection: MSD

MS Conditions

Table 1. Source Parameters

Parameter	Value(-)
Gas Temp (°C)	450
Nebulizer Gas. GS1 (psi)	35
Heater Gas. GS2 (psi)	25
Curtain Gas (psi)	25
Ion Spray Voltage (V)	4500
CAD Gas (psi)	9

MS Conditions (continued)

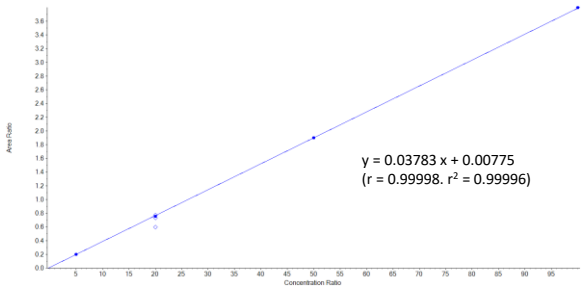
Table 2. MRM Transitions

Name	Q1 (m/z)	Q3 (m/z)	Expected t_R (min)	Start t (min)	End t (min)	Collision Energy (V)
AMPA ISTD	112.00	63.00	0.8	0.0	1.6	-28
AMPA 1	110.00	63.00	0.8	0.0	1.6	-24
AMPA 2	110.00	79.00	0.8	0.0	1.6	-34
Chlorate ISTD	89.00	71.00	2.7	1.8	3.5	-28
Chlorate 1	83.00	67.00	2.7	1.8	3.5	-28
Chlorate 2	85.00	69.00	2.7	1.8	3.5	-30
Fosetyl ISTD	114.00	82.00	2.7	1.9	3.5	-20
Fosetyl 1	109.00	81.00	2.7	1.9	3.5	-20
Fosetyl 2	109.00	63.00	2.7	1.9	3.5	-38
Glyphosate ISTD	171.00	63.00	1.5	0.7	2.4	-27
Glyphosate 1	168.00	63.00	1.5	0.7	2.4	-27
Glyphosate 2	168.00	79.00	1.5	0.7	2.4	-50
Glyphosate 3	168.00	81.00	1.5	0.7	2.4	-21
Phosphonic Acid ISTD	87.00	85.00	2.1	1.3	2.9	-21
Phosphonic Acid 1	81.00	78.80	2.1	1.3	2.9	-21
Phosphonic Acid 2	81.01	63.00	2.1	1.3	2.9	-32
Perchlorate ISTD	107.00	89.00	3.4	2.5	4.2	-33
Perchlorate 1	99.00	83.00	3.4	2.5	4.2	-33
Perchlorate 2	101.00	85.00	3.4	2.5	4.2	-35

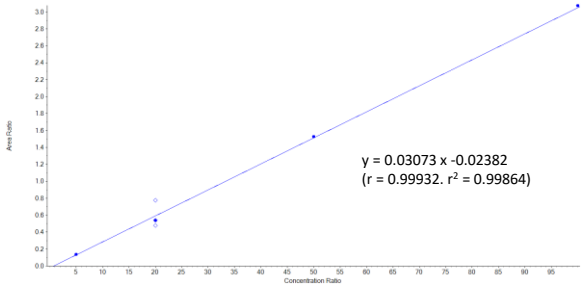
Calibration Curves and Chromatograms

Figure 1. Calibration Curves

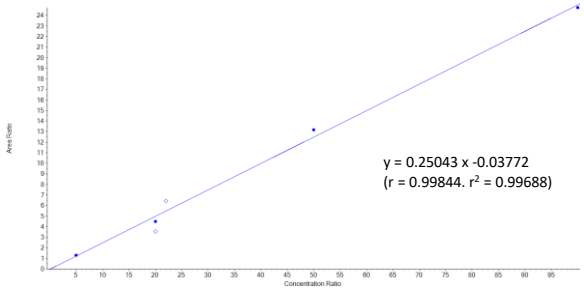
AMPA MRM 1



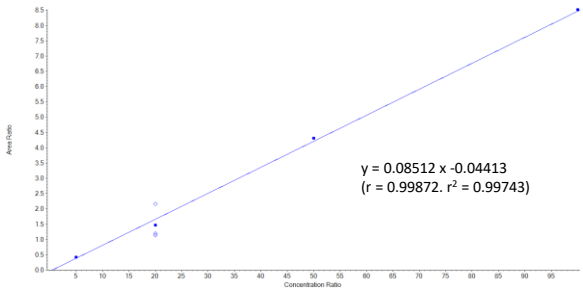
AMPA MRM 2



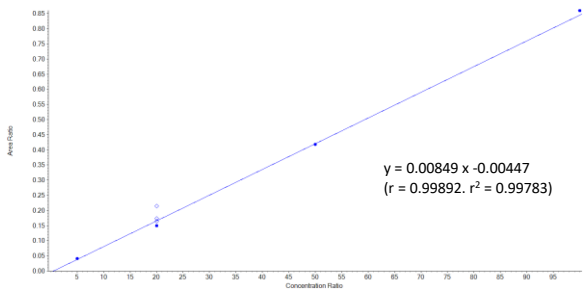
Chlorate MRM 1



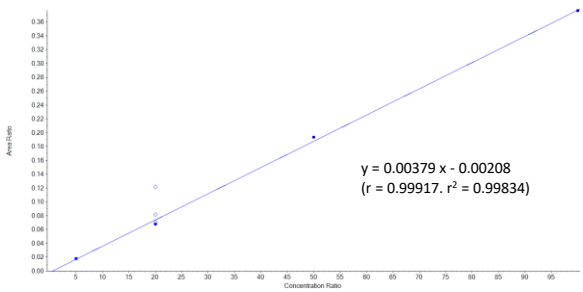
Chlorate MRM 2



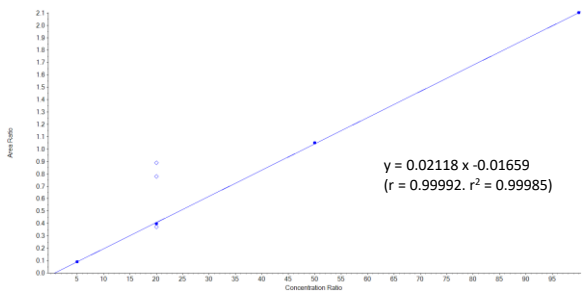
Fosetyl MRM 1



Fosetyl MRM 2



Glyphosate MRM 1



Glyphosate MRM 2

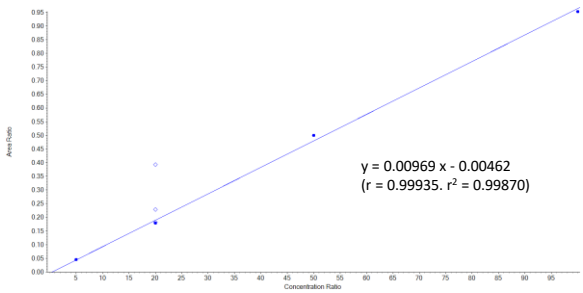


Figure 1. Calibration Curves (continued)

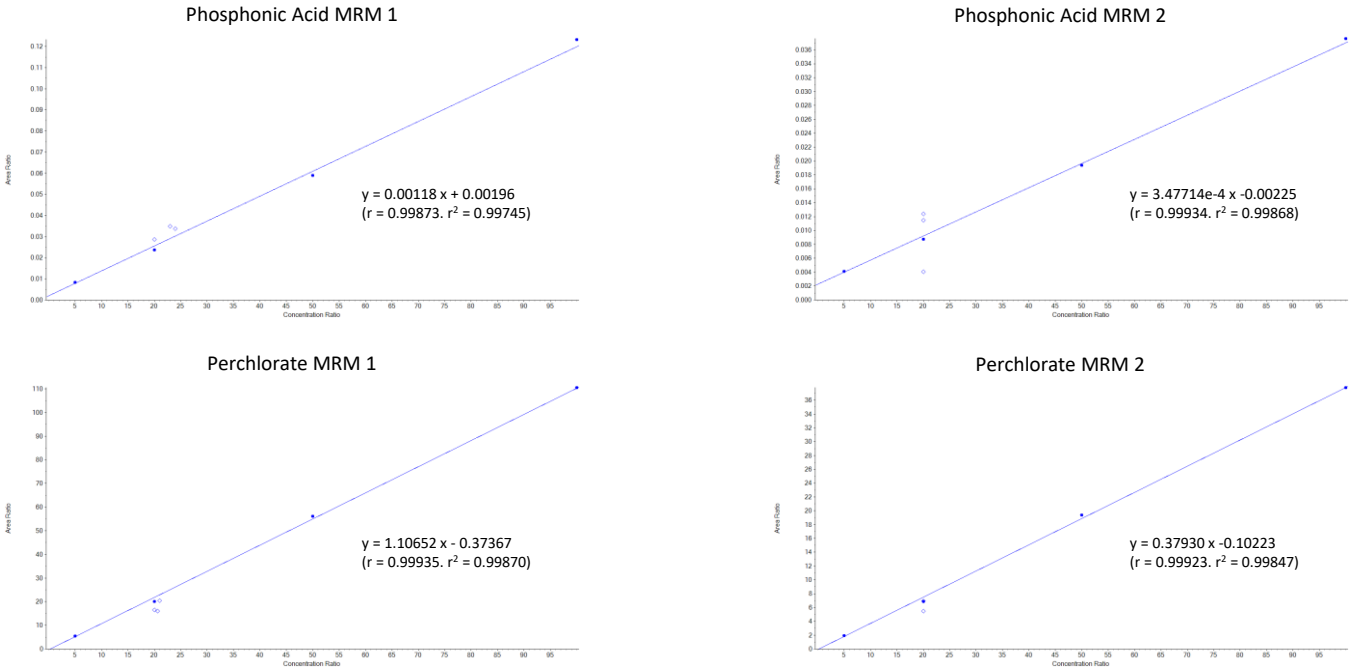


Figure 2. XICs

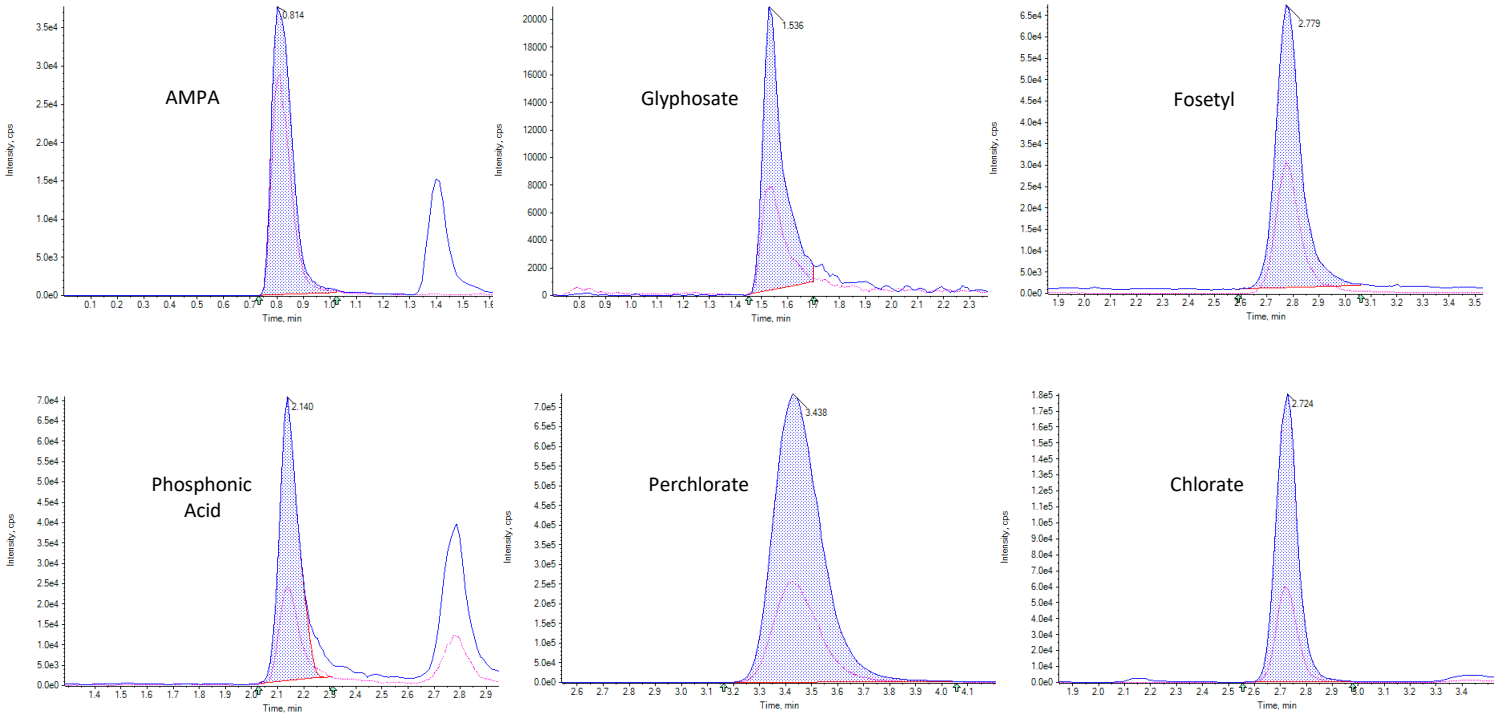


Table 3. Recovery data for various fruit and vegetable matrices

Analyte	Grape			Tomato			Tangerine		
	Spiked Conc. (ppb)	Exp. Conc. (ppb)	Accuracy (%)	Spiked Conc. (ppb)	Exp. Conc. (ppb)	Accuracy (%)	Spiked Conc. (ppb)	Exp. Conc. (ppb)	Accuracy (%)
AMPA 1	20	22.1	110.59	20	16.9	84.56	20	18.8	94.09
AMPA 2	20	31.4	156.95	20	20.5	102.43	20	20.9	104.64
Chlorate 1	20	16.6	83.22	20	14.7	73.36	20	15.1	75.25
Chlorate 2	20	17.1	85.53	20	14.8	74.12	20	15.9	79.37
Fosetyl 1	20	21.6	108.00	20	20.6	102.96	20	19.6	97.80
Fosetyl 2	20	23.1	115.50	20	21.4	106.97	20	21.1	105.34
Glyphosate 1	20	21.7	108.47	20	18.8	94.03	20	16.9	84.55
Glyphosate 2	20	20.6	103.24	20	19.8	98.96	20	19.5	97.72
Phosphonic Acid 1	30	29.4	98.02	20	21.6	108.13	28	29.3	104.65
Phosphonic Acid 2	30	34.2	113.87	20	19.6	98.19	28	29.8	106.37
Perchlorate 1	20	15.6	78.06	20	15.7	78.31	20	19.6	97.94
Perchlorate 2	20	15.4	76.93	20	15.4	76.99	20	19.4	97.04

Conclusion

The presented gradient reversed phase HPLC method using a Venusil HILIC column for the analysis of polar pesticides is a robust solution for this demanding application. The recovery of the analytes (**Table 3**) and linearity of the method for the tested analytes (**Figure 1**) demonstrates the suitability of this method for the routine analysis in food testing laboratories.

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