Determination of Triazole Derivative Metabolites in Fruits and Vegetables Using the QuPPe Method and Differential Mobility Spectrometry (DMS)

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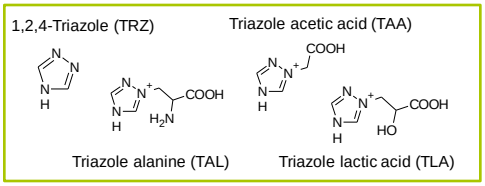
Introduction

Triazole fungicides such as triadimefon, cyproconazole, propiconazole, epoxiconazole and tebuconazole metabolize to 1,2,4-triazole (TRZ) and to further three common metabolites containing the 1,2,4-triazole moiety, namely 1,2,4-triazole, triazole alanine (TAL), 1,2,4-triazole acetic acid (TAA), and 1,2,4-triazole lactic acid (TLA). This group of metabolites are known as triazole derivative metabolites (TDMs).



The objective of this work was the inclusion of TDMs within the QuPPe method scheme, their successful validation in different commodities at low levels and the initiation of a monitoring program to assess the residue situation in different crops. This information will hopefully be of help when it comes to including TDMs in MRL-regulations, as proposed by EFSA.

TDMs are very polar in nature and their direct analysis by LC-MS/MS proved to be challenging due to strong signal interferences caused by co-eluting peaks, strongly compromising LOQs and accuracy. To improve selectivity, we employed Differential Mobility Spectrometry (DMS), a variation of Ion Mobility Spectrometry (IMS).

Analytical method

The experiments were performed using an AB Sciex 5500 Qtrap system with SelexION technology. The MS/MS-transitions and DMS settings of each compound are shown below:

	MRM	R.T. (min)	COV (V)	SV (V)
TRZ	70/43	0.94	-13.5	3000
TRZ-ISTD	75/46	0.95	-13.0	3000
TAA	128/70	5.78	-3.0	3000
TAA-ISTD	133/75	5.49	-3.0	3000
TAL	157/88	1.01	0.5	3000
TAL-ISTD	162/75	1.04	3.0	3500
TLA	158/70	5.01	-0.5	3000
TLA-ISTD	163/75	4.70	-0.5	3000

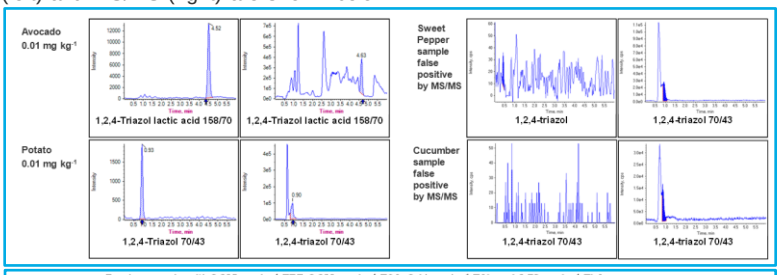
For the LC method a Hypercarb column (100 x 2.1, 5 µm) was used for the separation of the compounds. The gradient was 0 – 5 min 100%A to 10%A with a flow rate of 0.6 mL min^{-1}. The mobile phase consisted in A: 1% acetic acid in water + 5% MeOH; B: 1% acetic acid in MeOH. The injection volume was 5 µL.

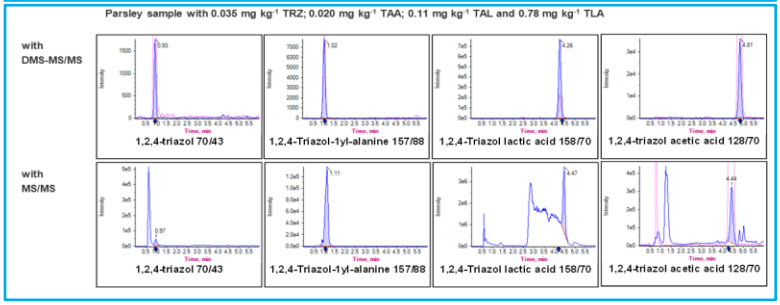
Results

Using DMS-MS/MS, highly satisfactory recovery and precision figures were achieved for all 4 TDMs on grape, potato, avocado and barley at 0.01 and 0.1 mg/kg. The results are summarized below:

Matrix	Level	TRZ	TAA	TAL	TLA
Grape	0.01 mg/kg	90 (7)	99 (3)	96 (1)	96 (4)
	0.1 mg/kg	86 (5)	99 (1)	104 (7)	99 (1)
Avocado	0.01 mg/kg	89 (1)	97 (2)	90 (10)	97 (3)
	0.1 mg/kg	112 (3)	98 (4)	99 (9)	102 (3)
Potato	0.01 mg/kg	100 (4)	96(5)	102 (10)	102 (5)
	0.1 mg/kg	106 (4)	105 (1)	99 (11)	108 (4)
Barley	0.01 mg/kg	115 (7)	109 (5)	119 (6)	99 (4)
	0.1 mg/kg	104 (4)	102 (2)	88 (9)	96 (2)

Typical chromatograms obtained by DMS-MS/MS (left) and MS/MS (right) are shown below:





1,227 samples (thereof 194 organic) were analyzed. **TAL** was detected in 385 conventional (31%) and in 42 organic samples (22%) at average levels of 0.092 and 0.054 mg/kg respectively. **TAA** was detected in 89 conventional (7%) and in 16 organic samples (8%) at average levels of 0.070 and 0.043 mg/kg respectively. **TLA** became available only recently, therefore no results can be presented.

Summary

TDMs were analyzed using QuPPe method and LC-MS/MS for screening and LC-DMS-MS/MS for quantification. Aiming to describe the overall residue situation >1200 samples were analyzed. Conventional samples contained TDMs at higher levels on average but the high frequency of findings in organic crops suggests a possible non-pesticide related TDMs source. Monitoring will continue.

Reference www.eurl-pesticides.eu

230

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