DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF SURFACTANTS IN TOMATO BY UHPLC-ORBITRAP-MS AND UHPLC-QqQ-MS/MS

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INTRODUCTION

Surfactants are a large group of adjuvants which show surface and interface activity. These compounds have a wide range of applications, such as water purification or even crude oil recovery. They are also used in Plant Protection Products (PPPs) as emulsifiers and wetting agents. Moreover, previous analytical studies have detected and characterised some surfactants in PPPs. Thus, there is a current need for studies focused on their determination on foodstuff treated with PPPs, which supported by the following facts:

- ❖ Few previous academic studies on their determination in vegetables.
- ❖ Their possible cytotoxic effects on humans.
- ❖ The undervaluation of that potential toxicity and relevance, which results in the lack of any European regulation regarding their presence in foodstuff treated with PPPs, unlike pesticide residues.

OBJECTIVES

- Development and validation of an analytical method the determination of the surfactants sodium dodecyl sulfate and nonaethylene glycol monododecyl ether in tomato by ultra high performance liquid chromatography (UHPLC) coupled to high (Exactive Orbitrap) and low resolution (Triple Quadrupole, QqQ) mass spectrometry.
- Application of the validated method to marketed samples.

EXPERIMENTAL CONDITIONS

CHROMATOGRAPHY

Injection Volume	10 µL
Flow rate	0.2 mL/min
Mobile phase	A: MeOH B: Water 0.1 % HCOOH NH_4COOH 4 mM
Elution mode	Gradient
Column	Agilent ZORBAX Eclipse Plus C18 (100 mm x 2.1 mm, 1.8 µm)

Gradient			
Time (min)	B (%)	Time (min)	B (%)
0	95	14	0
1	95	15	95
4	0	18	95

EXTRACTION

10 g of homogenized sample

10 mL of acetonitrile
Shake 1 min

3700 rpm, 10 min

LC-MS Analysis

QqQ MRM ACQUISITION

Analyte	Rt ± ΔRt (min)	Pecursor ion (m/z)	Product ions (m/z)	Collision Energy (eV)	Fragmentor voltage (V)
Sodium dodecyl sulfate (SDS)	6.43 ± 0.27	265.2	96.9 (Quantif.)	30	90
			80.0 (Confirm.)	70	

ORBITRAP ACQUISITION

Analyte	Rt ± ΔRt (min)	Exact mass (*m/z*) Adduct	Mass error (ppm)	Exact mass (*m/z*)	Molecular formula	Mass error (ppm)
	Characteristic ion			Fragment ions		
Nonaethylene glycol monododecyl ether	8.37 ± 0.17	600.46838 $[C_{30}H_{62}O_{10}NH_4]^+$	0.10	177.11214	$[C_8H_{17}O_4]^+$	-0.90
				133.08624	$[C_6H_{13}O_3]^+$	2.00

RESULTS AND DISCUSSION

SANTE/12682/2019 VALIDATION PARAMETERS

C1: 10 µg/kg
C2: 100 µg/kg
C3: 500 µg/kg

Analyte	Recovery (%) (n=10)			Intraday precisión RSD (%) (n=10)			Interday precisión RSD (%) (n=10)			Matrix Effect (%)	R^2 Solvent	R^2 Matrix	LOQ (µg/kg)
	C1	C2	C3	C1	C2	C3	C1	C2	C3				
SDS	-	118	115	-	9	8	-	15	13	+26	0.9981	0.9964	100
Nonaethylene glycol monododecyl ether	117	99	-	7	15	-	12	16	-	-23	0.9968	0.9946	50

✓ 0/10 samples negative for Nonaethylene glycol monododecyl ether.

✓ 3/10 samples positive for SDS (107, 116 and 124 µg/kg).

CONCLUSIONS

- ➢ A method has been successfully developed and validated to determine two surfactants in tomato.
- ➢ SDS has been detected in three out of ten tomato samples, from 107 to 124 µg/kg.
- ➢ Nonaethylene glycol monododecyl ether has not been detected in any samples.