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Nota applicativa

Oasis PRiME HLB Cartridge for Clean-up of QuEChERS Extracts of Soybean Pods Prior to UPLC-MS/MS Determination of Free Acidic Herbicides

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Abstract

In this application note, a QuEChERS extraction and UPLC-MS/MS analysis method is demonstrated for multiresidue analysis of free (unbound) acidic herbicides, highlighting a clean-up protocol, part of a multiresidue analytical method, suitable for unbound (free) acidic herbicides and also suitable for base/neutral herbicides in soybean pods.

Benefits

- Efficient, time-saving multi-class/multi-residue methodology
- Simple, rapid, and effective sample clean-up suitable for determination of acidic herbicides
- Simultaneous extraction and clean-up of neutral and basic pesticides
- Fast, sensitive UPLC-MS/MS analysis

Introduction

Acidic herbicides are commonly used for agricultural weed control. To help insure public health and safety, reliable analytical methods are necessary to determine residues of these herbicides in fruits and vegetables grown for human or animal consumption. For the analytical chemist, it is desirable to screen for multiple acidic herbicides with a single analytical method in order to maximize throughput and minimize costs. It is even more cost effective if the same single analytical extraction and clean-up method can be used to screen for acidic, neutral and basic pesticides. In this application note, a QuEChERS extraction and UPLC-MS/MS analysis method is demonstrated for multiresidue analysis of free (unbound) acidic herbicides in soybean pods. This vegetable (known as edamame) is a popular and nutritious foodstuff. However, this commodity is challenging for pesticide analysis; typically edamame is about 5–6% total fat and 0.3% phospholipid (lecithin) with significant amounts of pigments such as chlorophyll and carotenes. The presence of these co-extracted substances in the QuEChERS extract can lead to interference in the UPLC-MS analysis, contamination of the analytical column, and other components of the UPLC system, and contamination of the mass spectrometer itself. The Oasis PRiME HLB Cartridge is highly effective for removing fats, phospholipids, and chlorophyll from QuEChERS extracts of edamame. A QuEChERS extraction method has been successfully applied to the analysis of free acidic herbicides, but dSPE clean-up was not employed.[1] Common dispersive SPE methods

(dSPE) using PSA sorbents for clean-up cannot be used for acidic herbicides because the acidic compounds are retained on the sorbent.[2] However, pass-through clean-up with the Oasis PRiME HLB Cartridge provides good recovery for acidic herbicides. Therefore, the same QuEChERS extract can be used to screen for acidic and non-acidic herbicides and other pesticides after a single pass-through clean-up using the Oasis PRiME HLB Cartridge.

This application note highlights a clean-up protocol, part of a multiresidue analytical method, suitable for unbound (free) acidic herbicides and also suitable for base/neutral herbicides. This is not a class specific method optimized for bound and unbound acidic herbicides; such an optimized method is currently under development. An application note or other publication will soon be presented for a class specific method for acidic herbicides and metabolites after basic hydrolysis.

Experimental

UPLC conditions

LC system:	ACQUITY UPLC I-Class
Column:	ACQUITY UPLC HSS T3, 1.8 µm, 2.1 × 100 mm
Mobile phase:	A: 0.02% Formic in water B: Acetonitrile:MeOH (50:50)
Injection volume:	10 µL
Injection mode:	Partial loop injection
Column temp.:	25 °C
Weak needle wash:	10:90 Acetonitrile:water (600 µL)

Strong needle wash:	50:30:40 Water:acetonitrile:IPA (200 µL)
Seal wash:	10:90 acetonitrile:water

Gradient:

Time	Time(mL/min)	%A	%B
0.00	0.400	95.0	5.0
5.00	0.400	5.0	95.0
6.00	0.400	5.0	95.0
6.10	0.400	50.0	50.0
6.50	0.500	50.0	50.0
6.80	0.500	95.0	5.0
7.00	0.400	95.0	5.0
8.00	0.400	95.0	5.0

MS conditions

MS system:	Xevo TQ-XS
Ionization mode:	ESI+
Source temp:	120 °C

Desolvation temp.:	300 °C
Desolvation gas flow:	1000 L/hr
Cone gas flow:	30 L/hr
Collision gas flow:	0.15 mL/min
Data management:	MassLynx v4.2
Monitored transitions:	see Table 1

Name	MRM	Cone (v)	Collision (eV)	Retention time (min)
Compounds Analyzed in ES-				
2, 4-DP	233.0>161.0 233 .0>125.0	28	10 30	4.80
2,4-D	218.9>161.0 218.9>125.0	26	15 40	4.45
2,4-DB	246.9>160.9 246.9>125.0	12	10 10	4.97
2,4,5-T	252.8>194.9 252.8>158.9	19	14 36	4.86
2,4,5-TP (Silvex)	268.9>196.9 268.9>161.0	28	15 30	5.16
3,6-Dichloro-2-hydroxy benzoic acid (Dicamba metabolite)	204.9>160.9 204.9>124.9	14	11 11	3.77
4-CPA	185.0>127.0	28	16	3.93
Bentazone	239.0>132.0	30	30	4.06
Bromoxynil	275.8>80.8 275.8>78.8	48	30	4.34
Dicamba	218.8>174.8 218.8>145.0	9	9 9	3.69
Fenoxaprop-P	332>151.9 332>115.9	70	50 32	5.24
Fluazafop-P (butyl)	384.1>282.1 384.1>328.1	38	22 16	5.78
Fluroxypyr	254.9>208.8 254.9>180.8	28	16 12	3.82
Fomesafen	437.1>195.0 437.1>222.0	59	30 30	5.14
Imazaquin	310.0>266.0 310.0>233.0	20	16 25	4.01
Ioxynil	369.7>126.8 369.7>215.0	40	30 30	4.65
MCPA	199.2>140.9 201.0>143.0	20	10 8	4.48
MCPB	227.0>140.9	15	20	4.99
MCPP	213.0>141.0 213.0>118.8	21	14 14	4.81
Triclopyr	255.9>220.1 255.9>197.9	20	5 10	4.68
Compounds Analyzed in ES+				
Cycloxydim	326.0>280.0 326.0>180.0	34	16 22	5.82
Imazapyr	262.2>86.1 262.2>69.2	38	26 26	2.76
Imazethapyr	290.2>245.2 290.2>177.1	45	20 25	3.67
Haloxyfop	362.0>288.0 362.0>272.0	28	26 32	5.26

- Good recoveries of acidic herbicides were obtained after pass-through clean-up with the Oasis PRiME HLB Cartridge; this is not possible using dSPE with PSA.
- Oasis PRiME HLB provides good cleanup for acid, base, and neutral pesticides in one step; dSPE with PSA cannot.

References

1. Carneiro RP, et. al. *Food Control.* (2013) 33: 413–423.
2. Lehotay S, et.al. *J AOAC Int.* (2005) 88(2): 595–614.

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ACQUITY UPLC I-Class PLUS System <https://www.waters.com/134613317>

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