Solutions for addressing specific LC-MS problematic pesticide residues in multiresidue methods. Part I

Online videotutorial

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Problems related to reporting false positives and false negatives for specific problematic compounds

False positives and false negatives

EUPT SC03 (avocado)

7 laboratories reported **8** false positives

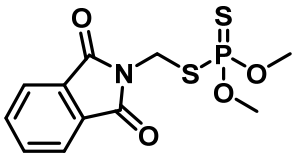
Code	Pesticide	RL (mg/kg)	Concentration (mg/kg)	Determination technique
Lab047	Azinphos-methyl	0.01	0.133732643	LC-QQQ-MS/MS
Lab012	Etofenprox	0.0	0.0878	LC-QQQ-MS/MS
Lab032	Formetanate (expressed as formetanate (hydrochloride))	0.01	0.241	LC-QQQ-MS/MS
Lab007	Prothioconazole (Prothioconazole- isomers)		0.21	LC-Orbitrap-MS
Lab062	Tebuconazole	0.01	0.02	LC-QQQ-MS/MS GC-QQQ-MS/MS

Lab047 False negative for Phosmet

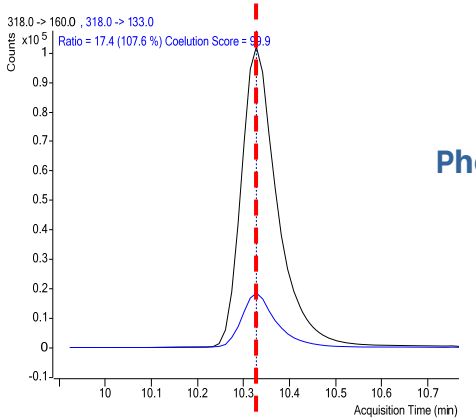
False positives and false negatives

Azinphos-methyl

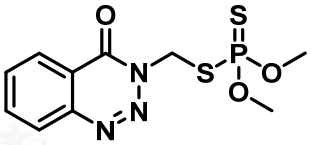
EUPT SC03 (avocado)



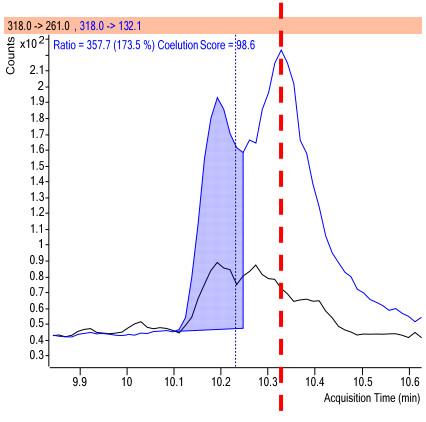
Phosmet



Phosmet (SC03 sample)



Azinphos-methyl



Azinphos-methyl acquisition window (SC03 sample)

False positives and false negatives

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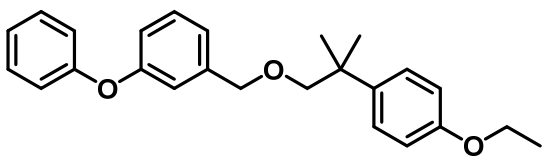
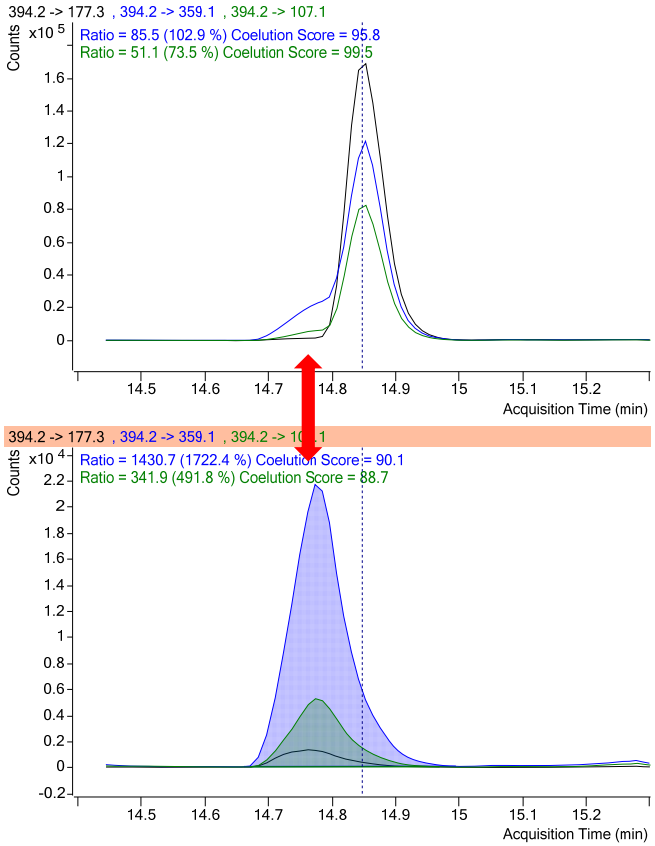
False positives and false negatives

Etofenprox



Etofenprox



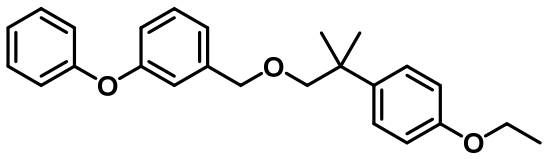
EUPT SC03 (avocado)

Std. etofenprox in avocado 0.500 mg/L

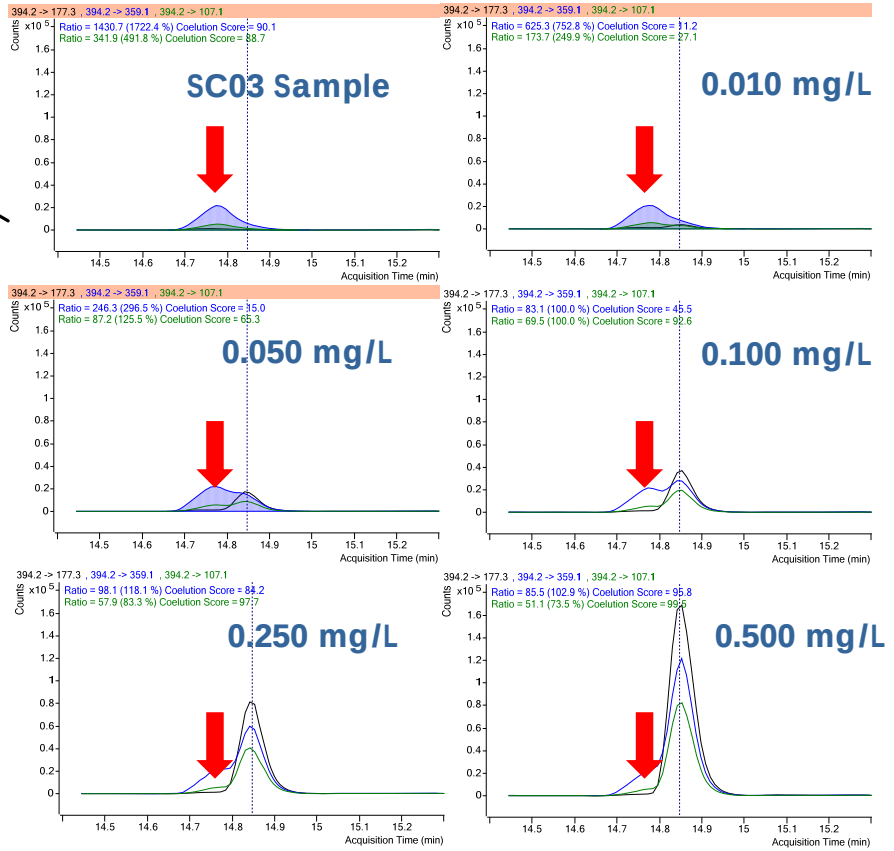
EUPT-SC03 sample

False positives and false negatives

EUPT SC03 (avocado)

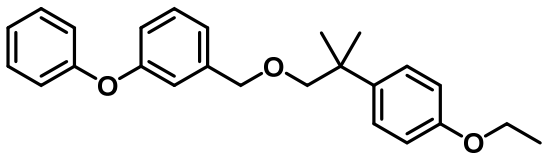


Etofenprox

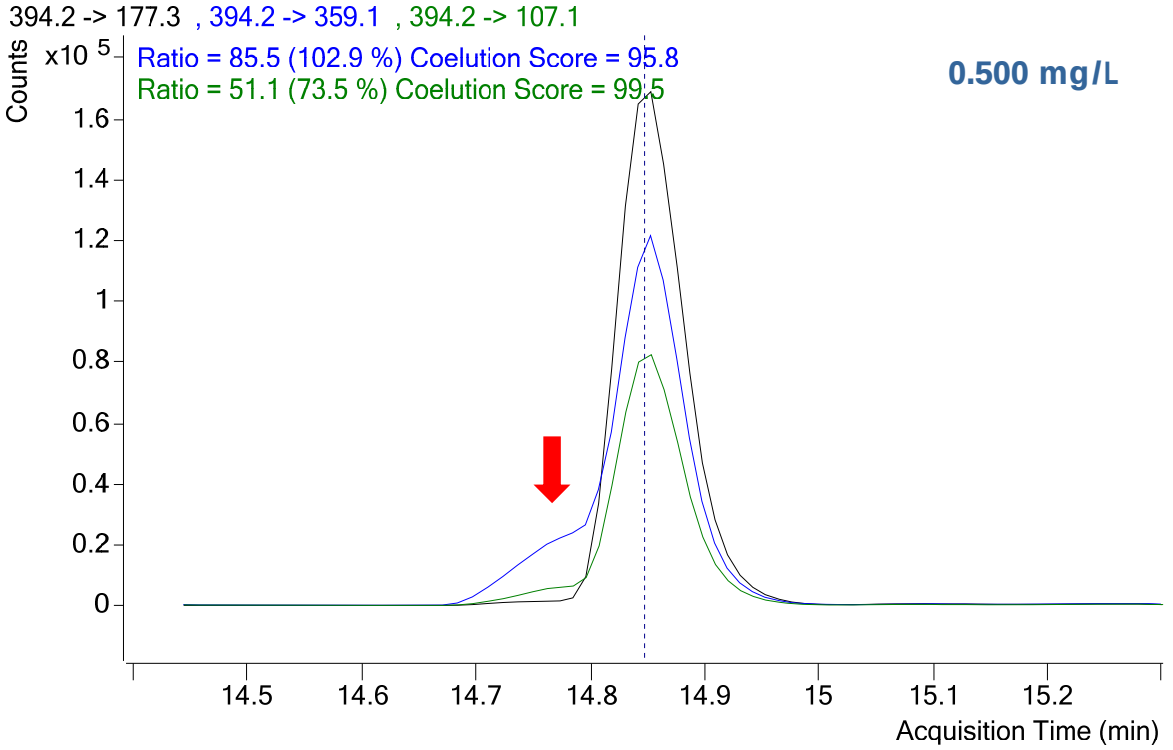


False positives and false negatives

EUPT SC03 (avocado)



Etofenprox



0.500 mg/L

False positives and false negatives

EUPT SC03 (avocado)

7 laboratories reported **8** false positives

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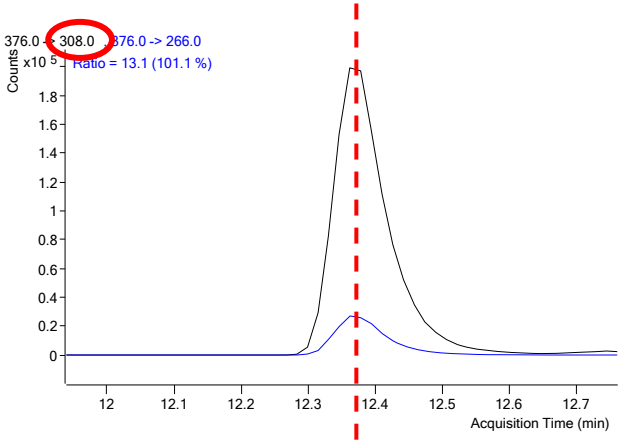
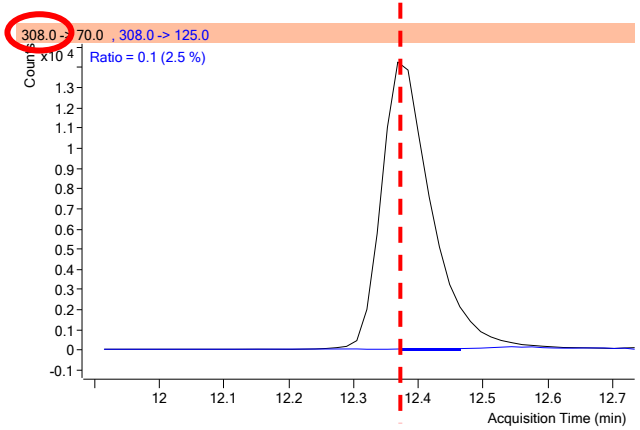
False positives and false negatives

EUPT SC03 (avocado)



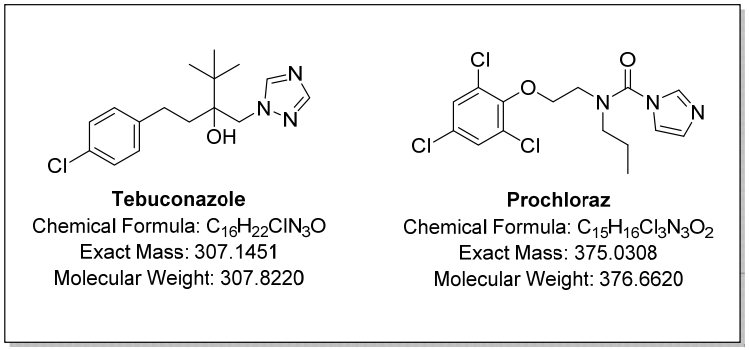
Prochloraz in SC03 sample (Prochloraz's acquisition window)



Prochloraz in SC03 sample (Tebuconazole's acquisition window)

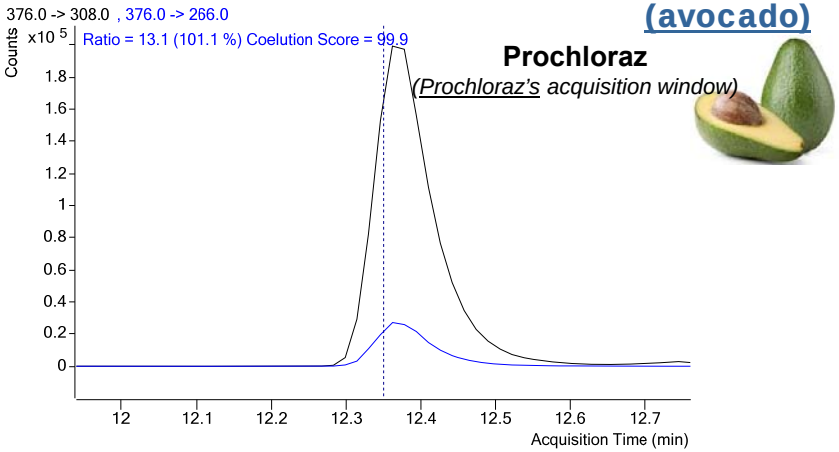
False positives and false negatives

EUPT SC03 (avocado)

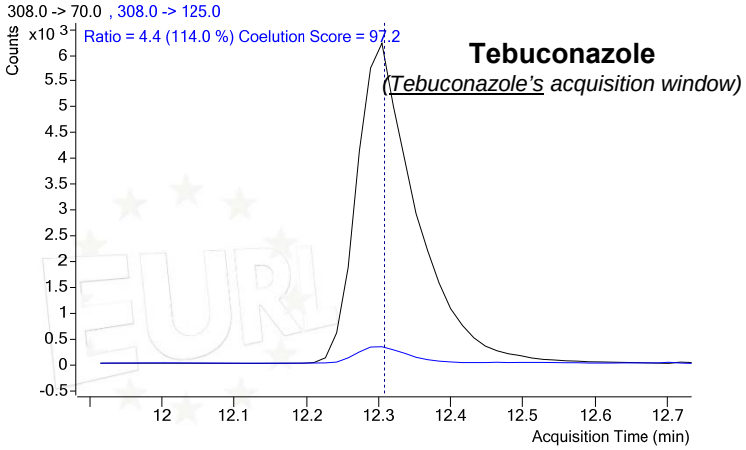


Tebuconazole
Chemical Formula: $C_{16}H_{22}ClN_3O$
Exact Mass: 307.1451
Molecular Weight: 307.8220

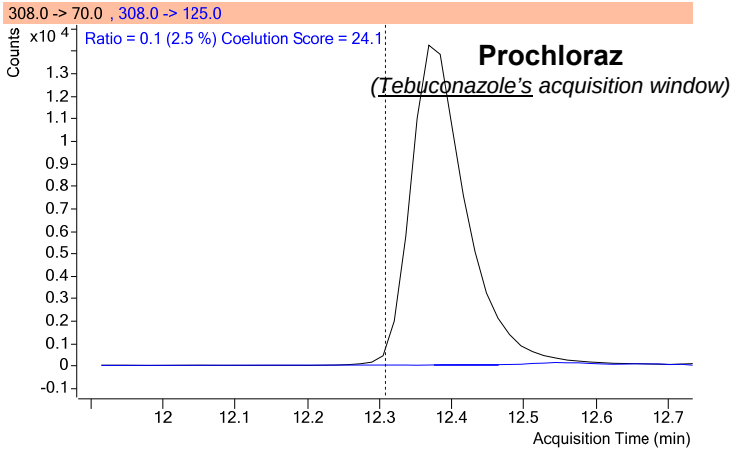
Prochloraz
Chemical Formula: $C_{15}H_{16}Cl_3N_3O_2$
Exact Mass: 375.0308
Molecular Weight: 376.6620



Prochloraz
(Prochloraz's acquisition window)

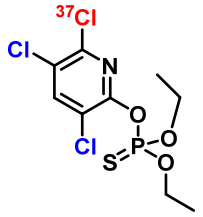


Tebuconazole
(Tebuconazole's acquisition window)



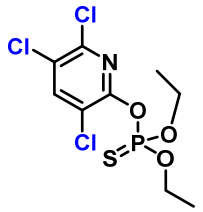
Prochloraz
(Tebuconazole's acquisition window)

Tentative false positives and negatives: common mass transitions



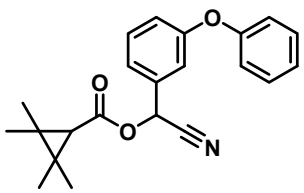
Chlorpyriphos ($^{37}Cl^{35}Cl_2$)
$C_9H_{11}Cl_2{}^{37}ClNO_3PS$
Exact Mass: 350,9233 Da

352 > 200
352 > 125



Chlorpyrifos ($^{35}Cl_3$)
$C_9H_{11}Cl_3NO_3PS$
Exact Mass: 348,9263 Da

350 > 198
350 > 125
350 > 97

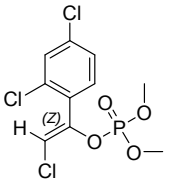


Fenpropathrin
Exact mass: 349.1678 Da

367 > 350
367 > 125
350 > 125
350 > 97

Depending on the selected mass transitions in LC-QqQ-MS/MS, false positives or negatives might be reported for chlorpyriphos and fenpropathrin

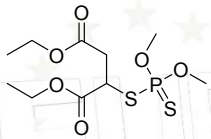
Tentative false positives and negatives: common mass transitions



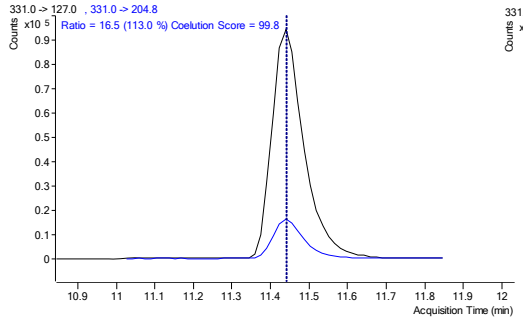
Dimethylvinphos (*Z* isomer)
Chemical Formula: $C_{10}H_{10}Cl_3O_4P$
Exact Mass: 329.9382
Molecular Weight: 331.5098

331 > 127

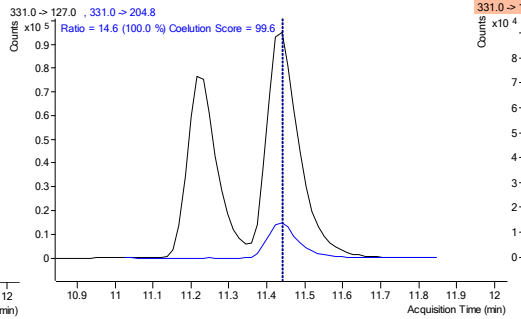
Hint: make use of the several chlorine atoms in dimethylvinphos to select a different precursor ion (333)



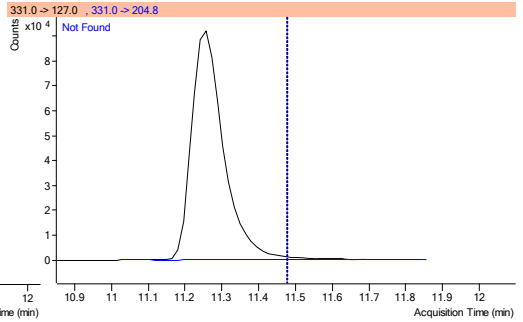
Malathion
Chemical Formula: $C_{10}H_{19}O_6PS_2$
Exact Mass: 330.0361
Molecular Weight: 330.3498



Dimethylvinphos
Dimethylvinphos monitored MRM transitions

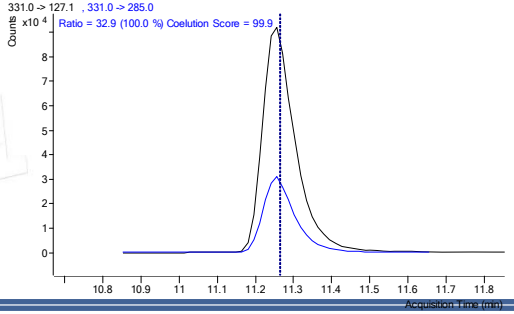


Dimethylvinphos & Malathion
Dimethylvinphos monitored MRM transitions

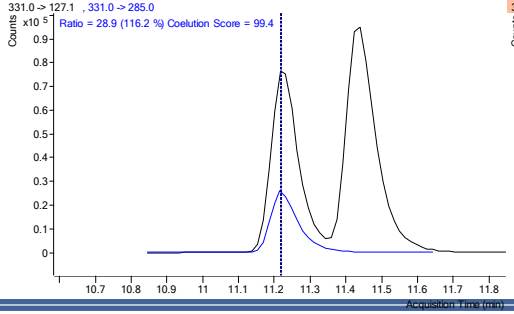


Malathion
Dimethylvinphos monitored MRM transitions

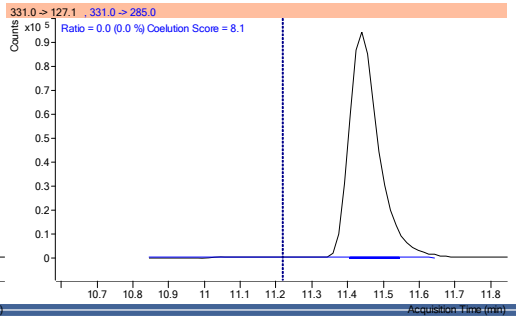
Malathion
Malathion monitored MRM transitions



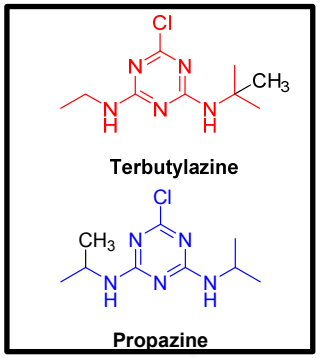
Malathion & Dimethylvinphos
Malathion monitored MRM transitions



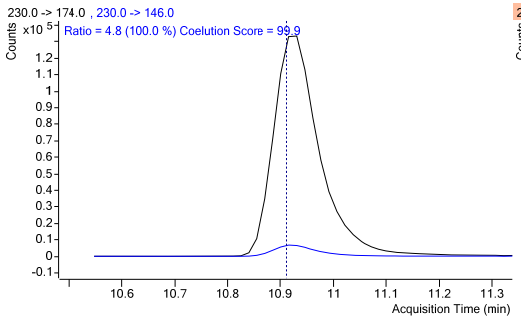
Dimethylvinphos
Malathion monitored MRM transitions



Tentative false positives and negatives: common mass transitions

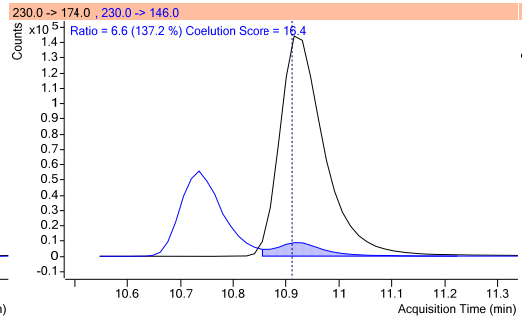


230 > 146



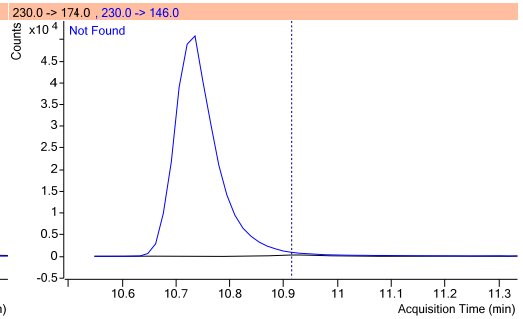
Terbutylazine

Terbutylazine monitored MRM transitions



Terbutylazine & Propazine

Terbutylazine monitored MRM transitions

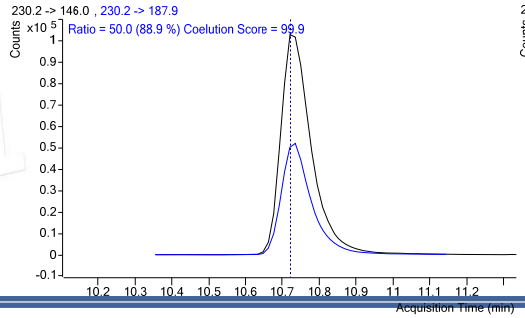


Propazine

Terbutylazine monitored MRM transitions

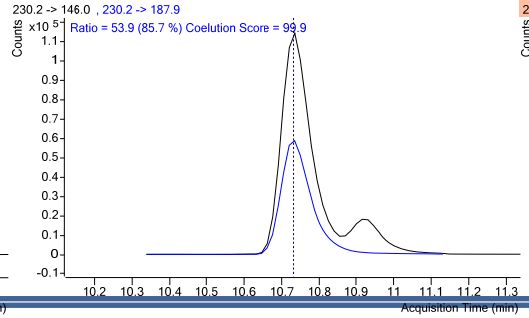
Propazine

Propazine monitored MRM transitions



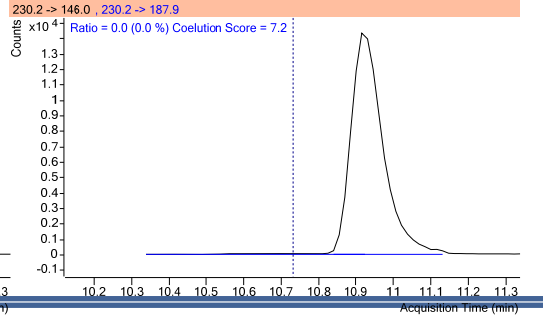
Propazine & Terbutylazine

Propazine monitored MRM transitions

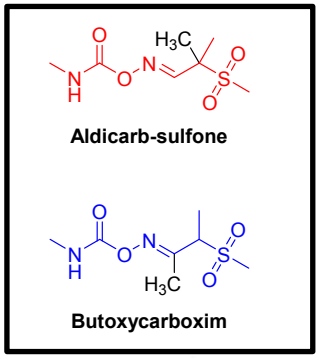


Terbutylazine

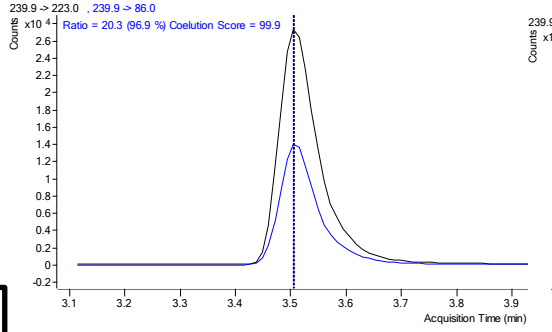
Propazine monitored MRM transitions



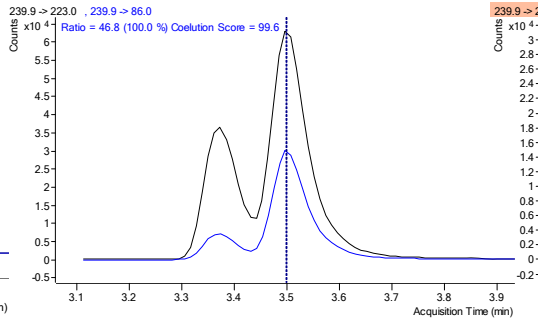
Tentative false positives and negatives: common mass transitions



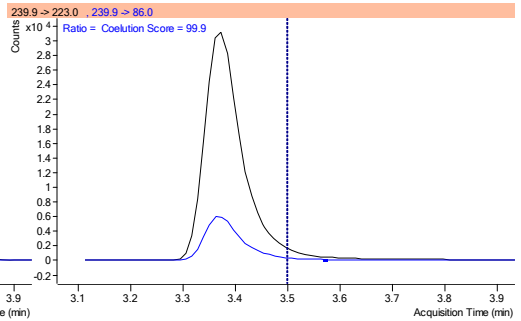
240 > 223
240 > 86
240 > 166



Aldicarb-sulfone
Aldicarb-sulfone monitored MRM transitions

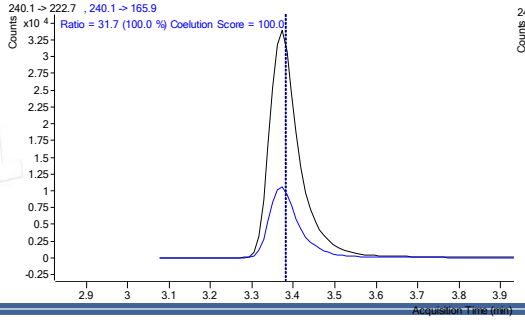


Aldicarb-sulfone & Butoxycarboxim
Aldicarb-sulfone monitored MRM transitions

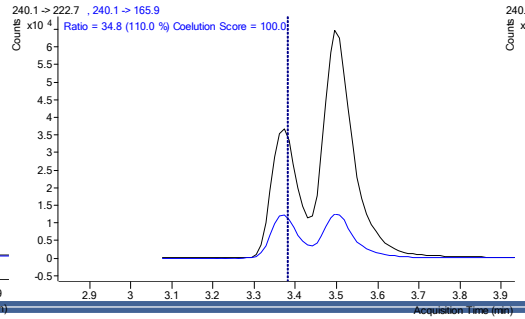


Butoxycarboxim
Aldicarb-sulfone monitored MRM transitions

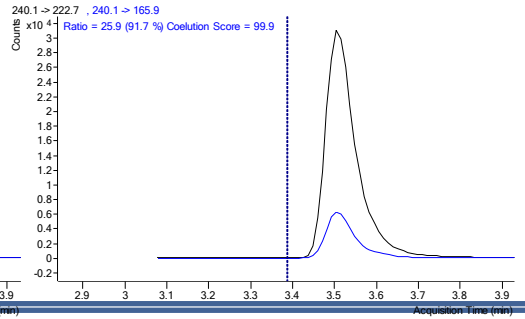
Butoxycarboxim
Butoxycarboxim monitored MRM transitions



Butoxycarboxim & Aldicarb-sulfone
Butoxycarboxim monitored MRM transitions

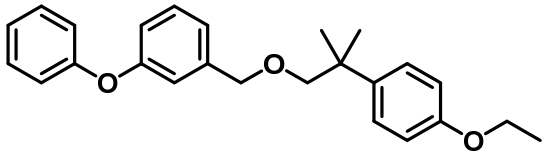


Aldicarb-sulfone
Butoxycarboxim monitored MRM transitions



Summary and key points

Coextracted matrix interferences (avocado) found within EUPTs



Etofenprox

Chemical Formula: $C_{25}H_{28}O_3$

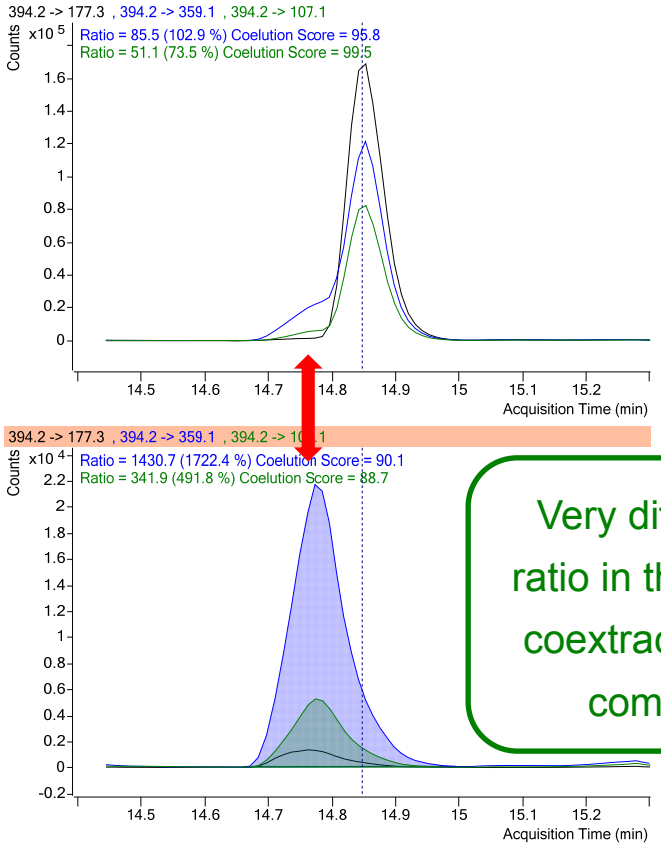
Exact Mass: 376.2038 Da

m/z: 376.2038 (100.0%), 377.2072 (27.0%), 378.2106 (2.7%)

394.2 > 177.3

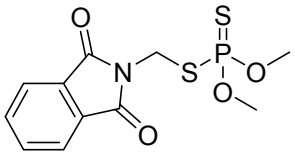
394.2 > 359.1

394.2 > 107.1



Very different ion ratio in the avocado coextracted matrix component

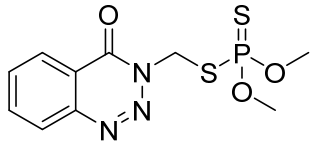
Compounds with common mass transitions found within EUPTs



Phosmet
Chemical Formula: $C_{11}H_{12}NO_4PS_2$
Exact Mass: 316.9945 Da
m/z: 316.9945 (100.0%), 317.9979 (11.9%), 318.9903 (4.5%), 318.9903 (4.5%)

318.0 > 160.0
318.0 > 133.0
Elutes earlier

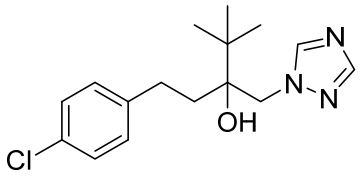
Pay attention to the retention times and exclusive mass transitions



Azinphos-methyl
Chemical Formula: $C_{10}H_{12}N_3O_3PS_2$
Exact Mass: 317.0058 Da
m/z: 317.0058 (100.0%), 318.0091 (10.8%), 319.0016 (4.5%), 319.0016 (4.5%)

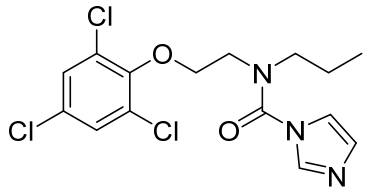
318.0 > 261.0
318.0 > 132.1
Elutes later

Compounds with common mass transitions found within EUPTs



Tebuconazole
Chemical Formula: $C_{16}H_{22}ClN_3O$
Exact Mass: 307.1451 Da
m/z: 307.1451 (100.0%), 309.1422 (32.0%), 308.1485 (17.3%), 310.1455 (5.5%)

A prochloraz fragment can be fragmented again to give rise to the 308.0 > 70.0 mass transition

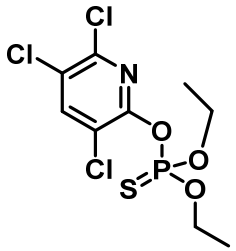


Prochloraz
Chemical Formula: $C_{15}H_{16}Cl_3N_3O_2$
Exact Mass: 375.0308 Da
m/z: 375.0308 (100.0%), 377.0279 (95.9%), 379.0249 (30.6%), 376.0342 (16.2%), 378.0312 (15.6%), 380.0283 (5.0%)

308.0 > 70.0
308.0 > 125.0
Elutes earlier

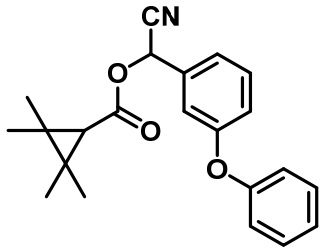
376.0 > **308.0**
376.0 > 266.0
Elutes later

Compounds with common mass transitions (other)

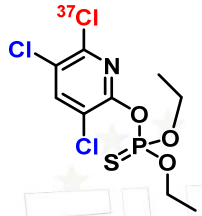


Chlorpyrifos
Chemical Formula: $C_9H_{11}Cl_3NO_3PS$
Exact Mass: 348.9263 Da
m/z: 348.9263 (100.0%), 350.9233 (95.9%), 352.9204 (30.6%), 349.9296 (9.7%), 351.9267 (9.3%), 350.9221 (4.5%)

Avoid the 350 m/z precursor for chlorpyrifos

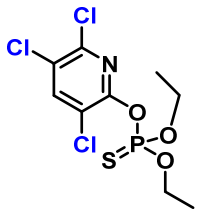


Fenpropathrin
Chemical Formula: $C_{22}H_{23}NO_3$
Exact Mass: 349.1678
m/z: 349.1678 (100.0%), 350.1711 (23.8%), 351.1745 (2.7%)



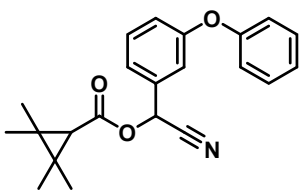
Chlorpyriphos ($^{37}Cl^{35}Cl_2$)
$C_9H_{11}Cl_2{}^{37}ClNO_3PS$
Exact Mass: 350,9233 Da

352 > 200
352 > 125
Elutes earlier



Chlorpyrifos ($^{35}Cl_3$)
$C_9H_{11}Cl_3NO_3PS$
Exact Mass: 348,9263 Da

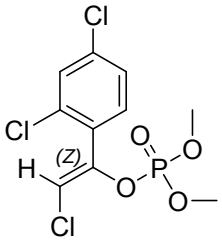
350 > 198
350 > 125
350 > 97
Elutes earlier



Fenpropathrin
Exact mass: 349.1678 Da

367 > 350
367 > 125
350 > 125
350 > 97
Elutes later

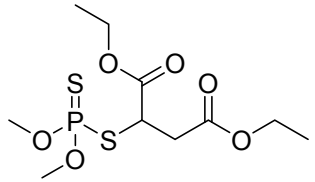
Compounds with common mass transitions (other)



Dimethylvinphos (*Z* isomer)
Chemical Formula: $C_{10}H_{10}Cl_3O_4P$
Exact Mass: 329.9382 Da
m/z: 329.9382 (100.0%), 331.9353 (95.9%), 333.9323 (30.6%), 330.9416 (10.8%), 332.9386 (10.4%)

331.0 > 127.0
331.0 > 204.8
Elutes later

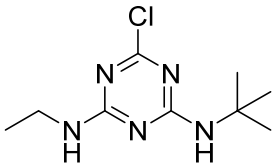
Employ the 333 m/z for dimethylvinphos



Malathion
Chemical Formula: $C_{10}H_{19}O_6PS_2$
Exact Mass: 330.0361
m/z: 330.0361 (100.0%), 331.0394 (10.8%), 332.0319 (9.0%), 331.0355 (1.6%), 332.0403 (1.2%)

331.0 > 127.1
331.0 > 285.0
Elutes earlier

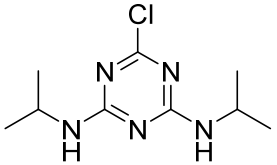
Compounds with common mass transitions (other)



Terbutylazine
Chemical Formula: $C_9H_{16}ClN_5$
Exact Mass: 229.1094 Da
m/z: 229.1094 (100.0%), 231.1065 (32.0%), 230.1128 (9.7%)

230.0 > 174.0
230.0 > 146.0
Elutes later

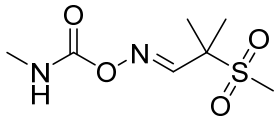
Pay attention to the retention times and exclusive mass transitions



Propazine
Chemical Formula: $C_9H_{16}ClN_5$
Exact Mass: 229.1094 Da
m/z: 229.1094 (100.0%), 231.1065 (32.0%), 230.1128 (9.7%)

230.0 > 146.0
230.0 > 187.9
Elutes earlier

Compounds with common mass transitions (other)

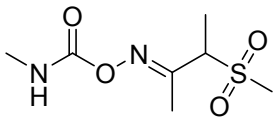


Aldicarb-sulfone
Chemical Formula: $C_7H_{14}N_2O_4S$
Exact Mass: 222.0674 Da
m/z: 222.0674 (100.0%), 223.0708 (7.6%), 224.0632 (4.5%)

239.9 > 223.0
239.9 > 86.0
Elutes later

Pay attention to the retention times.

Three mass transitions in common



Butoxycarboxim
Chemical Formula: $C_7H_{14}N_2O_4S$
Exact Mass: 222.0674 Da
m/z: 222.0674 (100.0%), 223.0708 (7.6%), 224.0632 (4.5%)

240.1 > 222.7
240.1 > 165.9
Elutes earlier

Thank you for your attention

This online tutorial is part of a series of online tutorials that will continue through the rest of the year:

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