QuEChERS Pesticide Analysis for Fresh Produce*

UCT Products:

ECMSSC50CTFS-MP (6 grams $MgSO_4$, 1.5 g NaCl)
ECQUEU1115CT (1.2 grams $MgSO_4$, 0.4 g PSA, 0.4 g GCB)
ECMSC1850CT (1500 mg $MgSO_4$, 500 mg endcapped C18)
ECMAG00D (organic free magnesium sulfate anhydrous)

October 12, 2010

This modified QuEChERS procedure uses GC-MS/MS for analysis of organohalogen, organophosphorus, and pyrethroid pesticides in produce. It is an improvement over the traditional QuEChERS procedure since the sample extracts are in toluene instead of acetonitrile and cleaner due to additional cleanup procedures. In addition, the method uses smaller sample sizes and less solvent than standard multiresidue procedures, and the solid-phase dispersive steps involving GCB/PSA/C18 provide sufficient cleanup for GC-MS/MS analysis.

1) Sample Extraction

a) Combine 15 g of cryo-ground sample with 15 mLs acetonitrile
b) Add contents of **ECMSSC50CTFS-MP**
c) Shake by hand for 2 minutes
d) Add IS (500 µL of 3.4 µg/mL solution of tris(1,3-dichloroisopropyl) phosphate
e) Centrifuge 4500 rpm for 5 minutes

2) Clean-Up

a) Transfer upper layer (12 mLs) to a clean centrifuge tube **ECMSC1850CT** containing 0.5 grams C_{18} and 1.2 g $MgSO_4$
b) Shake for 1 minute and centrifuge @ 4500 rpm for 5 minutes
c) Transfer 9 mL of supernatant to extraction tube containing **ECQUEU1115CT**
d) Vortex 15 seconds
e) Add 3 mL toluene
f) Shake the centrifuge tube for 2 minutes
g) Centrifuge @ 4500 rpm for 5 minutes
h) Transfer extract to clean tube
i) Reduce 6 mL volume to < 100 µL using N_2 in an evaporator (35°C)
j) Add 1.0 mL toluene and QC standard (20 µg/mL deuterated polycyclic hydrocarbons) along with 50 mg anhydrous $MgSO_4$
k) Centrifuge @ 1500 rpm for 5 minutes
l) Transfer 1.0 mL of extract to ALS vials for analysis

Note:

- Use matrix-matched calibration standards in toluene rather than standards prepared in solvent. This will compensate for matrix enhancement effects
- Coextractives in the sample matrix have been shown to cause an enhancement of the pesticide peak response in the matrix compared to that of the same amount of the pesticide in the matrix-free solvent

GC-MS/MS Tandem Mass Spectrometry

- Varian CP-3800 series gas chromatograph coupled with a Varian 1200 L triple-quadrupole mass spectrometer with a CTCCOMBI PAL autosampler (Varian Inc., Palo Alto, CA)

    - Column: Deactivated guard column (5 m x 0.25 mm i.d., Restek Corp.) Varian 30 m x 0.25 mm x 0.25 µm, VF-5 fused silica capillary analytical column
    - Head pressure 13.2 psi with 1.2 mL/min flow rate
    - He carrier gas
    - Column temperature programmed as follows:
        - initial temperature 105° C for 6 min
        - increased to 130° C at 10° C/min
        - ramp to 230° C at 4° C/min and to 290° C at 1° C/min
        - Hold for 5.5 min.
        - Total run time 45 min.
    - Injector temperature: 280° C
    - injection volume: 1.0 µL in splitless mode
    - Ion source and transfer line temperatures are 240° and 300° C, respectively
    - Set Electron multiplier voltage to 1400V by automatic tuning
    - Use argon collision gas for all MS/MS
    - Pressure in the collision cell 1.8 mTorr

Table of Analytes Covered in this Method

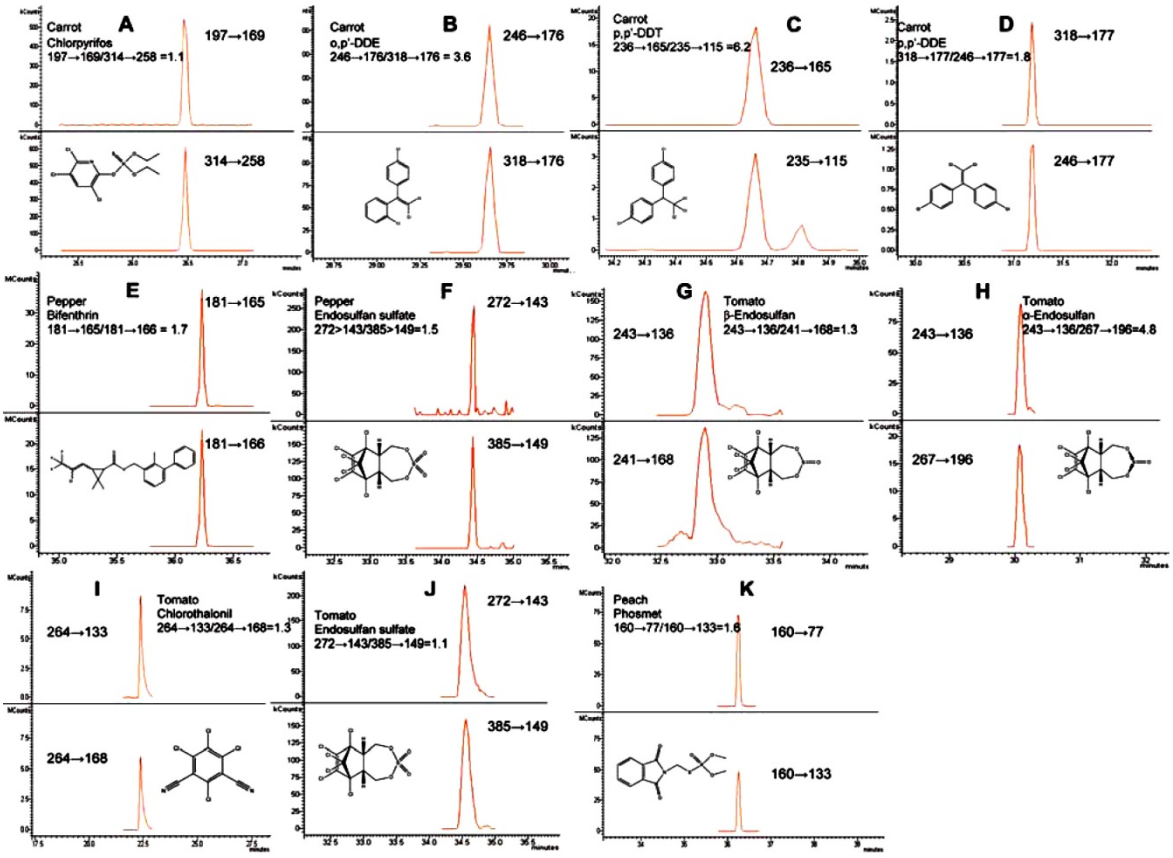
Analytes		
acenaphthene-d_{10}	Diamidafos (nellite)	*p,p'*-methoxychlor
acrinathrin	diazinon	metolachlor
akton	Dibutyl chlorenate	mevinphos
alachlor	dicapthon	mirex
aldrin	dichlobenil	naphthalene-d_8
allethrin	dichlofenthion	*cis*-nonachlor
atrazine	dichlofluanid	*trans*-nonachlor
azamethiophos	3,4'-dichloroaniline	parathion
azinphos-ethyl	4,4'-dichlorobenzophenone	parathion-methyl
azinphos-methyl	dichlorvos	pentachloroaniline
α-BHC	dicloran	pentachlorobenzene
β-BHC	dieldrin	pentachlorobenzonitrile
δ-BHC	dimethachlor	Pentachlorphenyl methyl ester
benfluralin	dioxabenzofos	pentachlorothioanisole
bifenthrin	dioxathion	*cis*-permethrin
bromophos	disulfoton	*trans*-permethrin
bromophos-ethyl	ditalimfos	phenanthrene-d_{10}
bromopropylate	edifenphos	phenothrin
captafol	α-endosulfan	phorate
captan	β-endosulfan	phosalone
carbophenothion	Endosulfan ether	phosmet
cis-chlordane	Endosulfan sulfate	phenthoate
trans-chlordane	endrin	pirimiphos-ethyl
α-chlordene	Endrin aldehyde	pirimiphos-methyl
β-chlordene	Endrin ketone	procymidone
γ-chlordene	EPN	profenofos
β-chlorfenvinphos	ethalfluralin	propachlor
chlorobenzilate	ethion	propazine
chloroneb	ethoprop	propetamphos
chlorothalonil	etridazole	propyzamide
chlorpyrifos	famphur	prothiophos
chlorpyrifos-methyl	Fenamiphos (ronnel)	pyraclofos
chlorthiophos	fenarimol	pyrazophos
chrysene-d_{12}	fenchlorphos	pyridaphenthion
coumaphos	fenitrothion	quinalphos
cyanazine	fensulfothion	quintozene
cyanophos	fenthion	resmethrin
Cyfluthrin 1	Fenvalerate 1	simazine
Cyfluthrin 2	Fenvalerate 2	sulfotep-ethyl
Cyfluthrin 3	fluchloralin	sulprofos
Cyfluthrin 4	Flucythrinaten 1	tebupirimfos
λ-cyhalothrin	Flucythrinate 2	propachlor
Cypermethrin 1	fluridone	propazine
Cypermethrin 2	Fluvalinate 1	Tecnazene (TCNB)
Cypermethrin 3	Fluvalinate 2	tefluthrin
Cypermethrin 4	folpet	temephos
Dacthal (DCPA)	fonophos	terbufos
o,p'-DDD	heptachlor	terbuthylazine
p,p'-DDD	Heptachlor epoxide	2,3,5,6-tetrachloroaniline
o,p'-DDE	hexachlorobenzene	tetrachlorvinphos
p,p'-DDE	Iprobenfos (IBP)	tetramethrin
o,p'-DDT	iprodione	thiometon
p,p'-DDT	isazophos	tolclofos-methyl
DEF (tribufos)	isofenfos	tolyfluanid
deltamethrin	Jodfenphos (iodofenphos)	triallate
demeton-S	leptophos	triazophos
demeton-S-methyl	Lindane (BHC)	trifluralin
dialifor	malathion	triphenyl
Diallate 1	methidathion	tris(1,3-dichloroisopropyl) phosphate
Diallate 2	*o,p'*-methoxychlor	vinclozolin

Problems with pesticides with low (<70%) recoveries or large variances (SD > 20%) may be attributed to the following issues:

- early eluting analytes
- sensitivity to pH changes
- prone to volatility loss (i.e., 3,4'-dichloroaniline, dichlorvos, diclobenil, and etridazole),
- strongly adsorbed to the PSA or GCB sorbents (i.e., chlorothalonil, endrin aldehyde, hexachlorobenzene, pentachlorobenzene, pentachlorobenzonitrile, and tachlorothioanisole)
- difficult to ionize by mass spectrometric detection (i.e., captafol, captan, dichlofluanid, folpet, and tolylfluanid).
- Highly nonpolar or late-eluting pesticides such as temephos and fluridone may also be problematic

For recovery data, target, qualifier and transition ions please reference original paper*

Reconstructed GC-MS/MS chromatograms of various commodities containing various pesticides including chlorpyrifos (A), o,p′-DDE (B), p,p′-DDT (C), and p,p′-DDE (D) present in carrot; bifenthrin (E) and endosulfan sulfate (F) present in bell pepper; β- (G) and R- (H) endosulfan, endosulfan sulfate (I) and chlorothalonil (J) present in tomato; and phosmet (K) in peach. Included are the transitions from precursor to product ions and the relative ion ratios between the two transitions, primary (top) and secondary (bottom), which are used for pesticide identification



Reagents and Materials

Obtain pesticide standards from:

- U.S. Environmental Protection Agency National Pesticide Standard Repository (U.S. EPA, Ft. Meade, MD)
- ChemServices (West Chester, PA), Sigma/Aldrich/Fluka Chemicals (St. Louis, MO),
- Crescent Chemicals (Islandia, NY)
- tris(1,3-dichloroisopropyl) phosphate from TCI America (Portland, OR)
- Quality control standards, naphthalene-d8, acenaphthalened10, phenanthrene-d10, and chrysene-d12 (Sigma/Aldrich/Fluka Chemicals (Milwaukee, WI).

*Adapted and used by permission from Jon W. Wong, Kai Zhang, "Multiresidue Pesticide Analysis In Fresh Produce By Capillary Gas Chromatography-Mass Spectrometry/Selective Ion Monitoring (GC-MS/SIM) and -Tandem Mass Spectrometry", (GC-MS/MS), J Agric. Food Sci., DOI: 10.1021/Jf903854n

Listing of instrument manufacturers and standards suppliers does not constitute endorsement by UCT. Equivalent systems may be used

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