Quantitative Determination of Multi-Class Multi-Residue Pesticides in Edible Oil Using Captiva EMR-Lipid Cleanup by GC/MS/MS

Limian Zhao[1], Melissa Churley[2]

[1] Agilent Technologies Inc., 2850 Centerville Road, Wilmington, DE 19808, USA; limian_zhao8@agilent.com

[2] Agilent Technologies Inc., 5301 Stevens Creek Blvd, Santa Clara, CA 95051, USA; melissa_churley@agilent.com

NACRW 2018
P-66

Agilent Technologies

Introduction

The analysis of fat-soluble pesticides in edible oil at low levels remains a challenge where much effort is placed on the efficient cleanup on lipid interferences. Captiva Enhanced Matrix Removal—Lipid (EMR—Lipid) sorbent is a novel sorbent material that selectively removes major lipid classes from sample matrix without unwanted analytes loss. The lipid removal mechanism provided by EMR—Lipid sorbent is based on the combination of size exclusion and hydrophobic interaction between lipid compounds and the unique sorbent.

This study investigates the sample preparation using EMR-Lipid cartridge cleanup for the analysis of 46 representative and challenging pesticides by GC/MS/MS in edible oils; including olive oil, corn oil, soybean oil and canola oil. The fat-soluble pesticide recoveries were improved by using a more hydrophobic solvent mixture 20:80 ethyl acetate/ACN and a two-step extraction. The low water content (20%) required for EMR-Lipid cartridge use reduced the risk of hydrophobic analyte loss during sample cleanup.

The EMR-Lipid cartridge cleanup allows the use of a stronger solvent for sample extraction and provides efficient lipid cleanup despite higher co-extractive concentration with more providing significantly sample for GC/MS/MS analysis.

Experimental

Instrumental Parameters for GC/MS/MS

GC Parameters	QQQ Parameters
• Agilent 7980B GC • Agilent HP-5ms Ultra Inert, 0.25 mm x 15 m, 0.25 µm (two) • Helium, constant flow (1.0 mL/min column 1, 1.2 mL/min column 2) • Agilent Ultra Inert single taper splitless liner with wool • MMI inlet at pulsed cold splitless mode, 60ºC to 300ºC at 600ºC/min • Pulsed splitless injection • Oven: 60°C for 2.57 min, then to 150°C at 50°C/min, to 200°C at 6°C/min, to 300°C at 16°C/min, hold for 3 min; Post-run: 2 min at 300°C • 1 µL injection volume	• Agilent 7010C Triple Quadrupole GCMSMS, • Performance turbo pump • dMRM mode • Transfer line temp: 280°C • Source temp: 280°C • Quad temp: 150°C for Q1 • Solvent delay: 3 min • Collision gas flow: He quench gas at 2.35 mL/min, N_2 collision gas at 1.5 mL/min • MS resolution: MS1 and MS2 = 1.2u

Sample Preparation Workflow

Accurately transfer 2.5 mL of edible oil into a 15 mL centrifuge tube (tube 1)

↓

Add 5 mL of 20:80 EtOAc/ACN to the 15 mL tube.

↓

Vortex sample for 15 min, and then centrifuge @ 5000 rpm for 5 min

↓

Transfer supernatant to another 15 mL centrifuge tube (tube 2)

↓

Add 5 mL of 20:80 EtOAc/ACN to tube 1, vortex for 15 min, centrifuge @ 5000 rpm for 5 min.

↓

Transfer supernatant to tube 2

↓

Add 2.5 mL of water to tube 2, mix gently (no vortexing)

↓

Transfer 5 mL of supernatant to Captiva EMR-Lipid 6 mL cartridge, allow elution by gravity

↓

Add 1.25 mL of 80:20 ACN/water into the EMR-Lipid cartridge, gravity elution

↓

Gradually apply pressure to drain the cartridge when there is no visible liquid left in cartridge

↓

Transfer 5 mL of eluent to a new 15 mL tube (tube 3), add 3.5 g of anhydrous MgSO4 (EMR drying salt pouch)

↓

Vortex vigorously for 3 min, centrifuge @ 5000 rpm for 5 min, Transfer supernatant for GC/MS/MS analysis

Results and Discussion

Pesticides and Edible Oil Matrix

Classification	Pesticides	Classification	Pesticides	Classification	Pesticides
Organophosphate	Dichlorvos	Organochlorine	Lindane	Sulphamide	Dichlorfluanid
	Trichlorfon		Aldrin		Tolylfluanid
	Sulfotep		Endrin	Phthalimide	Captan
	Diazinon		Endosulfan		Folpet
	Chlorpyriphos-Me		DDT		Captafol
	Phosmet		Oxychlordane	Dicarbosimide	Procymidone
	Coumaphos		Mirex	Pyrimidinol	Bupirimate
	Malathion	Pheonl	2-Phenylphenol	Dicarboximide	Iprodione
	Parathion	Dinitroaniline	Ethalfluralin		Permethrin
	Dimethoate	Chloronitrile	Chlorothalonil		Deltamethrin
	Fenamiphos	Pyridazinone	Norflurazon	Pyrethroid	Esfenvalerate
	Terbufos sulfone	Pyridine	Thiazopyr		Fenvalerate
	Chlorpyriphos	Triazine	Atrazin		Bifenthrin
Oxazole	Vinclozolin		Prometryne	Strobilurin	Pyraclostrobin
Uracil	Bromacil		Propazine	Carbamate	Thiobencarb
				Diphenyl ether	Nitrofen

Olive oil

Corn oil

Canola oil

Soybean oil

Representative Pesticides GC/MS/MS Chromatogram

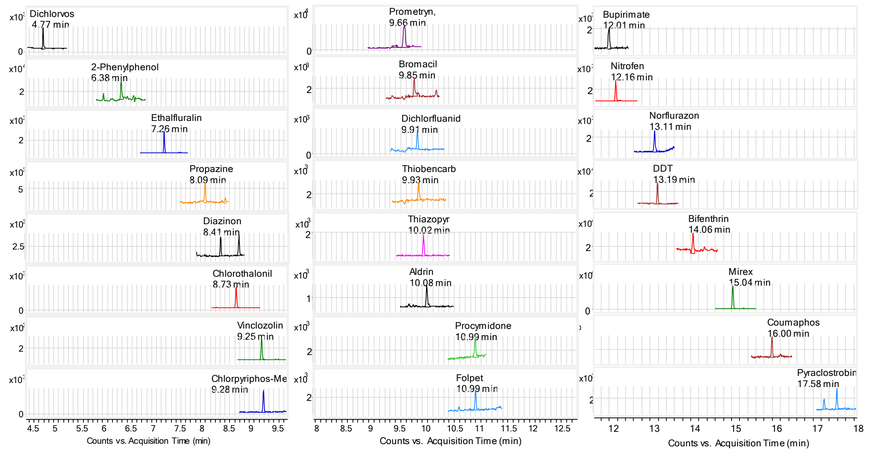

Figure 1. GC/MS/MS chromatogram of representative pesticides (1 compound from each class, except 3 and 4 compounds from OC and OP classes) in olive oil spiked with 1 ng/mL (LOQ).

Simplified Workflow

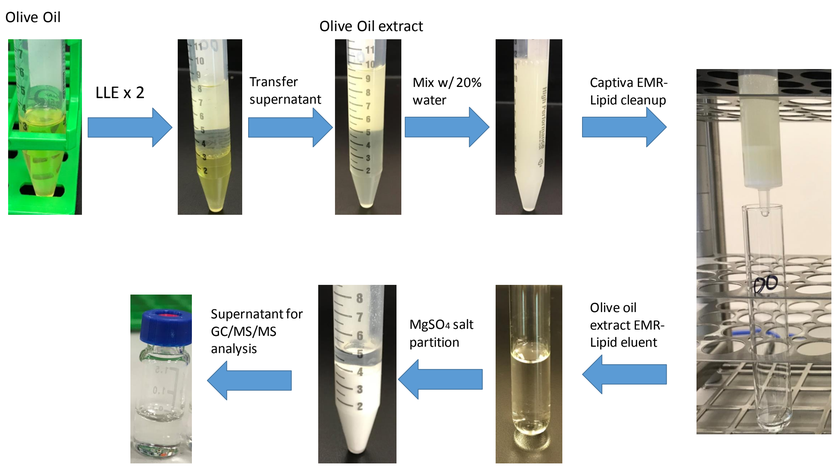

Figure 2. Olive oil sample appearance step by step prepared by LLE followed with Captiva EMR-Lipid cartridge cleanup.

Acceptable Analyte Recovery

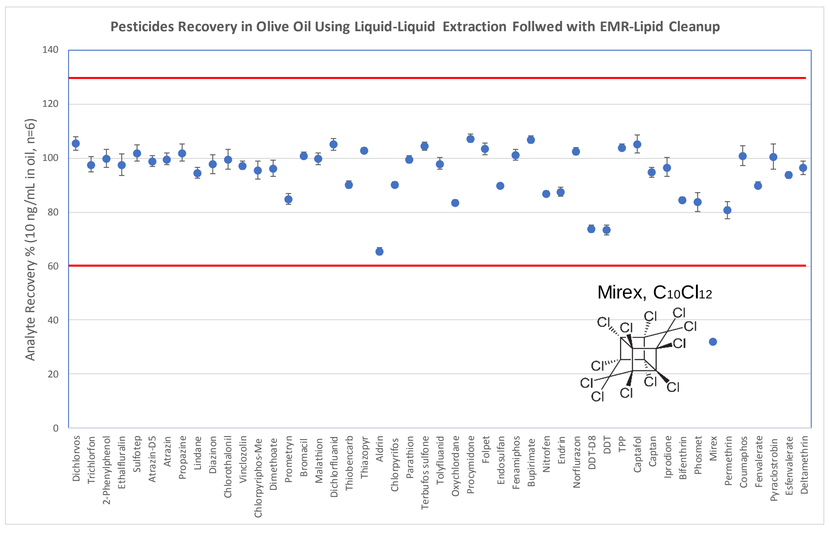

Figure 3. Pesticides absolute recovery (no IS correction) at spiking level of 10 ng/mL in olive oil.

Results and Discussion

Excellent Calibration Curve Linearity

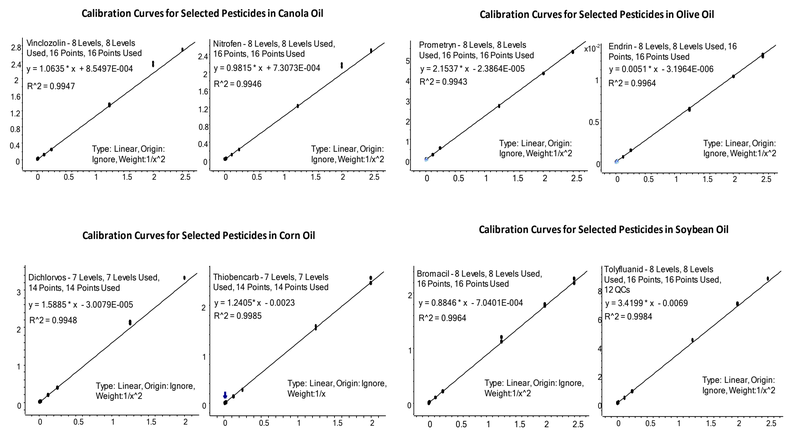

Figure 4. Typical calibration curve linearity for pesticides oil at range of 1 – 500 ng/mL in edible oil.

Statistical Results for Method Validation in Four Oil Matrices

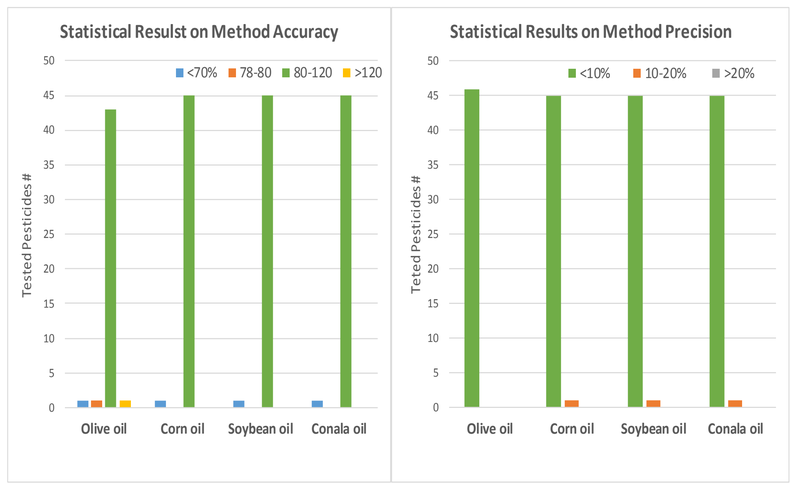

Figure 5. Statistical results on method accuracy and precision for method validation spiking at three levels, low level (1/5 ng/mL in oil), mid level (10 ng/mL in oil) and high level (100 ng/mL in oil), for total of n=18 in four edible oil matrices, respectively. Each column represents the analytes resulting in the corresponding range for accuracy or precision (RSD) category.

Efficient Oil Matrix Removal

		Olive oil	Corn oil	Soybean oil	Canola oil
No cleanup (mg/mL oil crude extract, n=2)		7.64	16.11	14.49	8.44
Captiva EMR-Lipid cleanup	Residue (mg/mL oil extract, n=2)	1.14	0.34	0.16	0.08
	Matrix removal (%)	85%	98%	99%	99%
QuEChERS dSPE C18 cleanup	Residue (mg/mL oil extract, n=2)	3.47	6.05	9.68	4.36
	Matrix removal (%)	55%	62%	33%	48%

Conclusions

A simple, rugged and reliable method using liquid-liquid extraction followed with EMR-Lipid cartridge cleanup was developed and validated for the multi-class, multi-residue analysis of pesticides in olive oil, corn oil, soybean oil and canola oil.

- ✓ Optimized liquid-liquid extraction improved extraction efficiency for fat soluble none-polar pesticides in oil.
- ✓ Captiva EMR-Lipid cartridge cleanup provides highly efficient lipids removal on oil extract.
- ✓ Acceptable analyte recoveries (60-120%) were obtained for > 95% pesticides.
- ✓ Simplified workflow and product easy use
- ✓ Excellent method accuracy, precision and linearity for reliable quantitation.
- ✓ Method validation in common edible oil matrices.

Check our website for more information:
www.agilent.com/chem/EMR-Lipid

Analytical Scientist Innovation Awards 2017