

# QuEChERS Sample Preparation For The Analysis Of Pesticide Residues In Olives



## UCT Part Numbers

### **CUMPSC1875CB2CT**

For better recovery of  
planar pesticides  
2 mL centrifuge tube, 150 mg  
MgSO<sub>4</sub>, 50 mg PSA, 50 mg C18,  
7.5 mg GCB

### **ECQUEU122CT**

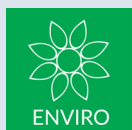
2 mL centrifuge tube, 150 mg  
MgSO<sub>4</sub>, 50 mg PSA, 50 mg C18  
and 50 mg GCB

### **ECMSSC50CT-MP**

4 g MgSO<sub>4</sub>, 1.0 g NaCl

## Summary:

This application is a summary of the original paper "Evaluation of the QuEChERS sample preparation approach for the analysis for pesticide residues in olives"\*. It describes the use of QuEChERS for the extraction and cleanup of 16 pesticide residues contained in olives. LC-MS/MS with positive ESI was used for pesticides that are difficult to detect by GC-MS. Matrix matched calibration standards were used to compensate for matrix effects. The method achieves acceptable quantitative recoveries of 70–109% with RSDs <20% for DSI-GC-MS and 88–130% with RSDs <10% for LCMS/MS, and LOQ at or below the regulatory maximum residue limits. Analyte protectants were used with DSI to improve analyte peak shapes and intensities.



### Analytes Covered in this Method

| Analyte             | CASRN       |
|---------------------|-------------|
| Ometholate          | 1113-02-6   |
| Dimethoate          | 60-51-5     |
| Simazine            | 122-34-9    |
| Diazinon            | 65863-03-8  |
| p,p'-DDE            | 82413-20-5  |
| Diuron              | 56449-18-4  |
| Carbaryl            | 63-25-2     |
| Malathion           | 121-75-5    |
| Fenthion            | 55-38-9     |
| Methidathion        | 950-37-8    |
| Napropamide         | 15299-99-7  |
| Oxyfluorfen         | 42874-03-3  |
| Carfentrazone-ethyl | 128639-02-1 |
| Phosmet             | 732-11-6    |
| Pyriproxyfen        | 95737-68-1  |
| Deltamethrin        | 64121-95-5  |

## Procedure:

### 1. Sample Extraction

- Weigh 10 g of homogenized sample into a 50 mL centrifuge tube
- Add 10 mL of acetonitrile (MeCN)
- Add contents of **ECMSSC50CT-MP**
- Shake vigorously by hand for 1 minute
- Centrifuge @ 3450 rcf for 1 minute

### 2. Dispersive Cleanup

- Transfer 1 mL the supernatant to a micro-centrifuge tube **ECQUEU122CT** or **CUMPSC1875CB2CT**
- Mix for 20 seconds
- Centrifuge @ 3450 rcf for 1 minute
- Transfer 400µL of supernatant to an autosampler vial
- Add 25 µL of TPP solution (10 g/mL triphenylphosphate on MeCN with 1.6% formic acid)
- Shake for 5 seconds
- Extract is ready for analysis

### 3. Automated DSI-GC-MS Analysis

GC-MS was performed using an Agilent (Little Falls, DE, USA) 5890 Series II GC and 5972 MS instrument. Injection was performed using a Combi-PAL autosampler (CTC Analytics, Zwingen, Switzerland) using second generation automated DSI accessory (Linex) in combination with an Optic 3 PTV (Atas-GL International BV, Veldhoven, NL)

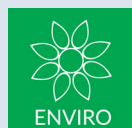
**Note:** Equivalent instrumentation and analytical columns can be used

#### Analyte Protectant Solution

(95% or better purity, prepare at 10:1:1 mg/mL in 7:3 water/MeCN, Sigma or Fluka)

- 3-ethoxy-1,2-propanediol
- D-sorbitol
- L-gulonic acid
- c-lactone

A quality check standard solution of 16 µg/mL triphenylphosphate (TPP) is prepared in MeCN containing 1.6% formic acid (FA)



For analysis by DSI-GC-MS, 20 µL of the analyte protectant solution was added to all the final extracts and matrix-matched calibration standards by transfer of 400 µL of extract into an autosampler vial and adding 25 µL of TPP solution

## Conditions:

- Injection volume 10 µL
- 100° C (held 3.5 min with 50:1 split ratio)
- Ramp at 5°C/s to 280°C (use splitless for 3.5 min, then 50:1 split until 9 min, then change split flow to 20:1 and cool injector temperature to 150°C)

## GC Separation:

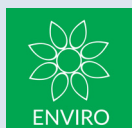
- Varian VF-5 EZ-guard column (30 m x 0.25 mm id x 0.25 µm film thickness) with an integrated retention gap (5 m x 0.25 mm) at the inlet and an additional 1 m of uncoated capillary at the MS entrance
- He carrier gas @ 1 mL/ min

## Oven temperature program:

- Start at 3.5 min (after sample introduction)
- 80°C hold for 3.5 min
- Ramp to 230°C at 108°C/min
- Then ramp to 300°C at 45°C/min, hold for 10 min.
- MS transfer line temperature at 290°C
- Electron ionization (EI) at –70 eV in SIM and full-scan (50–600 m/z) modes in different experiments

Agilent Chemstation for data acquisition/processing and GC-MS control, and Cycle Composer and Atas Evolution software are used to control the automated DSI process and PTV. The pesticide analytes in GC-MS and SIM ions are shown in the table below:

| GC-MS SIM Conditions for the Monitored Pesticides |                  |                      |                            |                               |
|---|------------------|----------------------|----------------------------|-------------------------------|
| Pesticide   | Start time (min) | t <sub>R</sub> (min) | m/z (% relative abundance) |                               |
|   |                  |                      | Quantitation ion           | Qualifier ions                |
| Dimethoate  | 4.5              | 15.89                | 87 (100)                   | 125 (45), 93 (54), 58 (19)    |
| Simazine  |                  | 16.00                | 201 (78)                   | 173 (41), 186 (51), 158 (25)  |
| Diazinon  | 16.09            | 16.18                | 179 (100)                  | 137 (98), 304 (47), 152 (70)  |
| Diuron  |                  | 16.52                | 72 (100)                   | 232 (38), 234 (26), 187 (11)  |
| Carbaryl  | 17.49            | 17.70                | 144 (100)                  | 115 (33), 116 (26), 145 (15)  |
| Malathion   |                  | 18.03                | 173 (94)                   | 125 (100), 93 (93), 127 (75)  |
| Fenthion  | 18.1             | 18.27                | 278 (100)                  | 125 (37), 109 (33), 79 (19)   |
| Methidathion                                      | 19.05            | 19.29                | 145 (88)                   | 93 (40), 125 (27), 302 (19)   |
| Napropamide                                       | 13.39            | 19.58                | 271 (26)                   | 72 (100), 128 (63)            |
| p,p'-DDE  |                  | 19.367               | 318 (64)                   | 246 (100), 248 (64), 316 (56) |
| Oxyfluorfen                                       |                  | 19.71                | 361 (38)                   | 252 (100), 300 (35), 280 (14) |
| Carfentrazonethyl                                 | 20               | 20.28                | 312 (100)                  | 330 (65), 340 (63), 376 (31)  |
| TPP   | 20.38            | 20.96                | 326 (100)                  | 325 (87), 77 (88), 215 (20)   |
| Phosmet   |                  | 21.17                | 160 (100)                  | 133 (15), 104 (15), 193 (4)   |
| Pyriproxyfen                                      | 21.30            | 21.50                | 136 (100)                  | 226 (12), 185 (6)             |
| Deltamethrin                                      | 22.8             | 23.59                | 253 (85)                   | 181 (100), 251 (44), 152 (20) |



#### 4. LC-MS/MS Analysis

**Suggested Instrumentation:** Agilent 1100 HPLC (consisting of vacuum degasser, autosampler Model WPALS, and a binary pump) equipped with a Prodigy ODS-3 (150 mm x 3 mm) and 5  $\mu$  particle size analytical column coupled to a ODS-C18 (4 mm x 2 mm and 5  $\mu$  particle size) guard column from Phenomenex (Torrance, CA, USA).

| LC-MS/MS   |                                    |
|--|------------------------------------|
| Column Temperature   | 30°C                               |
| Injection Volume   | 5 $\mu$ L                          |
| Mobile Phase   | A water, B MeCN, both with 0.1% FA |
| Flow Rate  | 0.3 mL/min                         |
| Gradient Program   |                                    |
| 25% solvent B linear gradient to 100% over the first 5 min |                                    |
| Hold for 7 min until 12 min                                |                                    |
| 11-min postrun column wash                                 |                                    |

The LC system is connected to an API 3000 triple-quadrupole mass spectrometer (Applied Biosystems, Toronto, Canada) operated in ESI positive mode. Optimizations of the mass analyzer parameters were done by infusion of 1  $\mu$ g/mL analyte solutions at 10  $\mu$ L/min with a syringe pump (Harvard Apparatus, Holliston, MA, USA) using the autotune function.

**Note:** Equivalent instrumentation and analytical columns can be used

#### Final MS/MS conditions include:

- N<sub>2</sub> pressure 55 psi
- nebulizer gas setting 14
- curtain gas setting 11
- collision gas setting 12
- 4200 V ionspray voltage
- ESI temperature 525°C
- focusing potential 100 V
- entrance potential 10 V
- 0.15 s dwell time

The pesticide analytes by LC-MS/MS are shown in the table below with respective analytical ions

| LC-MS/MS Conditions for the Monitored Pesticides<br>(Quantitation ion is shown as first mass) |                  |          |                     |                    |
|---|------------------|----------|---------------------|--------------------|
| Pesticide   | Start time (min) | tR (min) | Precursor ion (m/z) | Product ions (m/z) |
| Omethoate   | 2.5              | 2.68     | 214.0               | 183.2, 125.2       |
| Dimethoate  | 5                | 6.83     | 230.0               | 199.1, 125.1       |
| Simazine  | 7.6              | 7.98     | 202.0               | 124.2, 132.2       |
| Carbaryl  |                  | 8.48     | 202.2               | 145.1, 127.1       |
| Diuron  |                  | 8.67     | 233.1               | 72.2, 160.1        |
| Phosmet   | 9                | 9.27     | 318.0               | 160.2, 133.2       |
| Methidathion  |                  | 9.28     | 303.0               | 145.1, 85.1        |
| Malathion   |                  | 9.64     | 331.0               | 127.2, 285.2       |
| TPP   | 9.8              | 10.18    | 327.0               | 77.2, 152.0        |



## References:

- [1] \*Adapted and used by permission from Cunha, Sara C., Lehotay, Steven J., Mastovska, Katerina, Fernandes, Jos O., Beatriz, Maria, Oliveira, P. P., Sep. Sci. 2007, 30, 620 – 632, DOI 10.1002/jssc.200600410

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

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