



## Fast, Simple Sample Cleanup

### Using QuEChERS SPE Tubes

By Julie Kowalski, Innovations Chemist, Lydia Nolan, Innovations Chemist, Jack Cochran, Director of New Business and Technology, and Irene DeGraff, Product Marketing Manager



- Achieve a four-fold increase in sample throughput.
- Significantly reduce material costs.
- Convenient, ready to use centrifuge tubes with ultra pure, pre-weighed adsorbent mixtures.

**Quick, Easy, Cheap, Effective, Rugged, and Safe**, the QuEChERS (“catchers”) method for extracting pesticides from food is based on research by the US Department of Agriculture.<sup>1</sup> In addition to using less solvent and materials versus conventional SPE methods, QuEChERS employs a novel and much quicker dispersive solid phase extraction cleanup (dSPE). QuEChERS methods, including an AOAC Official Method<sup>2</sup> and modifications to the methods, have been posted on the Internet.<sup>3</sup> These methods have several basic steps in common:

**Step 1:** Sample preparation and extraction—Commodities are uniformly comminuted. Acetonitrile solvent is added for a shake extraction. Salts, acids and buffers may be added to enhance extraction efficiency and protect sensitive analytes. Surrogate standards can be added to monitor extraction efficiencies.

**Step 2:** Extract cleanup – A subsample of solvent extract is cleaned up using dSPE, a key improvement incorporated in the QuEChERS technique. Small polypropylene centrifuge tubes are prefilled with precise weights of MgSO<sub>4</sub> and SPE adsorbents to remove excess water and unwanted contaminants from the extracted samples. After agitation and centrifugation, the cleaned extracts are ready for analysis.

**Step 3:** Sample analysis – Samples may be pH adjusted to protect sensitive pesticides and/or solvent-exchanged to improve analysis by either GC/MS or LC/MS. Internal standards can be added.

**Table I** Modified mini-multiresidue QuEChERS for pesticides from strawberries.

#### Sample preparation and extraction

<b>Sample:</b>	10g of strawberries were homogenized and placed in a 50mL PTFE centrifuge tube
<b>Solvent:</b>	10mL of acetonitrile were added to homogenate Shake for 1 minute, until uniform
<b>Salts:</b>	4.0g MgSO <sub>4</sub> (powder or granular) 1.1.0g NaCl 1.0g trisodium citrate dihydrate 0.5g disodium hydrogencitrate sesquihydrate Salts were added and vigorously shaken for 1 minute. Sample was centrifuged and the supernatant removed for cleanup. Pesticides standards (200ng/mL) were spiked in at this point.

#### Sample extract cleanup

<b>QuEChERS tubes:</b>	1mL of supernatant from the previous step was placed into several 2mL polypropylene centrifuge tubes, each containing one of the following adsorbent mixes: A. 50mg PSA + 150mg MgSO <sub>4</sub> (cat.# 26124) B. 50mg PSA + 150mg MgSO <sub>4</sub> + 50mg C18 (cat.# 26125) C. 50mg PSA + 150mg MgSO <sub>4</sub> + 50mg GCB (cat.# 26123)
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**Cleanup:** Samples were shaken with the adsorbents for 30 seconds (carbon for 2 minutes), then centrifuged to produce a clear supernatant for GC/MS analysis.

**Internal standard:** Pentachloronitrobenzene in a formic acid solution, pH 5.

PSA—primary and secondary amine exchange material.

GCB—graphitized carbon black

**Table II** Instrument conditions.

<b>Column:</b>	Rtx®-CLPesticides2 20m, 0.18mm ID, 0.14µm (cat.# 42302)
<b>Sample:</b>	custom pesticide mix 200µg/mL each pesticide, internal standards: 8140-8141 ISTD, 1000µg/mL (cat.# 32279), 508.1 ISTD 100µg/mL (cat.# 32091), triphenylphosphate 1000µg/mL (cat.# 32281)
<b>Inj.:</b>	1.0µL splitless (hold 1 min.)
<b>Inj. temp.:</b>	250°C
<b>Carrier gas:</b>	helium
<b>Flow rate:</b>	constant linear velocity @ 40cm/sec
<b>Oven temp.:</b>	40°C (hold 1 min.) to 320°C @ 12°C/min.
<b>Det:</b>	Shimadzu GCMS-QP2010 Plus
<b>Transfer line temp.:</b>	300°C
<b>Ionization:</b>	Electron ionization
<b>Mode:</b>	Selected ion monitoring



QuEChERS methods are convenient, rugged methods that simplify extract cleanup, reduce material costs, and improve sample throughput. Here we demonstrate the effectiveness of QuEChERS sample cleanup using a multiresidue analysis of pesticides on strawberries.

### Experimental

Strawberry extracts were prepared, spiked, and dSPE treated according to Table I. Analytical conditions are presented in Table II.

One microliter splitless injections of the extracts were performed by a Shimadzu AOC-20i autosampler using “mid” injection speed into a Shimadzu QP-2010 Plus GC-MS system operated under the conditions in Table II.

#### Rtx®-CLPesticides2 Columns (fused silica)

ID	df (µm)	temp. limits	length	cat. #
0.18mm	0.14	-60 to 310/330°C	20-Meter	42302

## Results and Discussion

Primary and secondary amine exchange material (PSA) is the base sorbent used for dSPE cleanup of QuEChERS fruit and vegetable extracts because it removes many organic acids and sugars that might act as instrumental interferences.

A pesticide-spiked strawberry extract (200ng/mL) subjected to dSPE with PSA was used to generate one-point calibration curves. Spiked strawberry extracts subjected to additional dSPE sorbents were analyzed and the results versus PSA dSPE are shown as percent recoveries in Table III. C18 is suggested for use when samples might contain fats; not an issue for a strawberry extract, but it was important to verify that gross losses of more hydrophobic pesticides (e.g. Endrin and DDT) would not occur. GCB is used to remove pigments, and when treated, the pink/red strawberry extract became clear. However, GCB can also have a negative effect on certain pesticides, especially those that can assume a planar shape like chlorothalonil and thiabendazole.

Restek dSPE products in a variety of standard sizes and formats make QuEChERS even simpler. The centrifuge tube format, available in 2mL and 15mL sizes, contains magnesium sulfate (to partition water from organic solvent) and a choice of SPE sorbents, including PSA (to remove sugars and fatty acids), C18 (to remove nonpolar interferences such as fats), and GCB (to remove pigments and sterols). Custom products also are available by request. If you are frustrated by the time and cost involved with your current approach to pesticide sample cleanup, we suggest you try this simple and economical new method.

### References

1. Michelangelo Anastassiades, Steven J. Lehota, Darinka Štajnbaher, Frank J. Schenck. "Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and Dispersive Solid-Phase Extraction for the Determination of Pesticide Residues in Produce." *J. AOAC International*, 2003, vol. 86(22), pp.412-431.
2. AOAC Official Method 2007.01, "Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate."
3. <http://www.quechers.com/>

References not available from Restek

**Table III** Pesticide percent recoveries in strawberry extracts treated with C18 or GCB dSPE, relative to PSA only.

Rt (min.)	pesticide	CAS Number	action/Use	classification	C18*	GCB**
9.50	Dichlorvos	62-73-7	Insecticide	Organophosphorus	111	116
9.67	Methamidophos	10265-92-6	Insecticide	Organophosphorus	105	107
11.75	Mevinphos	7786-34-7	Insecticide	Organophosphorus	112	130
12.02	<i>o</i> -Phenylphenol	90-43-7	Fungicide	Unclassified	106	97
12.14	Acephate	30560-19-1	Insecticide	Organophosphorus	128	147
13.89	Omethoate	1113-02-6	Insecticide	Organophosphorus	120	119
14.74	Diazinon	333-41-5	Insecticide	Organophosphorus	108	127
14.98	Dimethoate	60-51-5	Insecticide	Organophosphorus	124	151
15.69	Chlorothalonil	1897-45-6	Fungicide	Organochlorine	125	13
15.86	Vinclozolin	50471-44-8	Fungicide	Organochlorine	102	98
16.21	Metalaxyl	57837-19-1	Fungicide	Organonitrogen	105	117
16.28	Carbaryl	63-25-2	Insecticide	Carbamate	114	111
16.60	Malathion	121-75-5	Insecticide	Organophosphorus	124	160
16.67	Dichlofluanid	1085-98-9	Fungicide	Organohalogen	122	103
17.51	Thiabendazole	148-79-8	Fungicide	Organonitrogen	88	14
17.70	Captan	133-06-2	Fungicide	Organochlorine	88	91
17.76	Folpet	133-07-3	Fungicide	Organochlorine	108	63
18.23	Imazalil	35554-44-0	Fungicide	Organonitrogen	115	95
18.39	Endrin	72-20-8	Insecticide	Organochlorine	104	101
18.62	Myclobutanil	88671-89-0	Fungicide	Organonitrogen	119	114
19.07	4,4-DDT	50-29-3	Insecticide	Organochlorine	102	95
19.22	Fenhexamid	126833-17-8	Fungicide	Organochlorine	118	77
19.40	Propargite 1	2312-35-8	Acaricide	Organosulfur	110	95
19.43	Propargite 2	2312-35-8	Acaricide	Organosulfur	121	114
19.75	Bifenthrin	82657-04-3	Insecticide	Pyrethroid	106	81
20.04	Dicofol	115-32-2	Acaricide	Organochlorine	98	54
20.05	Iprodione	36734-19-7	Fungicide	Organonitrogen	118	90
20.21	Fenpropathrin	39515-41-8	Insecticide	Pyrethroid	113	96
21.32	<i>cis</i> -Permethrin	52645-53-1	Insecticide	Pyrethroid	106	65
21.47	<i>trans</i> -Permethrin	51877-74-8	Insecticide	Pyrethroid	109	71
23.74	Deltamethrin	52918-63-5	Insecticide	Pyrethroid	97	52

\*50mg PSA, 50mg C18, \*\*50mg PSA, 50mg GCB

$$\% \text{ recovery} = \frac{\text{RRF C18 or GCB}}{\text{RRF PSA}} \times 100$$

### QuEChERS SPE Tubes

AOAC Method 2007.1	Benefits/Uses	qty.	cat#
2mL QuEChERS SPE Micro-Centrifuge Tube Contains 150mg Magnesium Sulfate and 50mg PSA	Cleanup of agricultural produce extracts, 1mL sample volume.	100-pk.	26124
2mL QuEChERS SPE Micro-Centrifuge Tube Contains 150mg Magnesium Sulfate, 50mg PSA, and 50mg Graphitized Carbon	Cleanup of 1mL sample extract with residual pigments and sterols.	100-pk.	26123
2mL QuEChERS SPE Micro-Centrifuge Tube Contains 150mg Magnesium Sulfate, 50mg PSA, and 50mg C18	Cleanup of 1mL sample extract with residual fat.	100-pk.	26125
15mL QuEChERS SPE Centrifuge Tube Contains 900mg Magnesium Sulfate, 300mg PSA, and 150mg Graphitized Carbon	Cleanup of 6mL sample extract with residual pigments and sterols.	50-pk.	26126

PSA—primary and secondary amine exchange material.



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