

Fast, Simple QuEChERS Extraction and Cleanup of Pesticide Residue Samples

- 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.¹ 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 Method² and modifications to the methods, have been posted on the internet.³ These methods have several basic steps in common:



Step 1: Sample preparation and extraction – Commodities are uniformly homogenized. 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 $MgSO_4$ 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 by a variety of techniques.⁴

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.

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. 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.

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

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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. Graphitized carbon black (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, available in a variety of standard sizes, make QuEChERS even simpler. The centrifuge tube format 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. Lehotay, 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/>
4. Schenck, F.J., *SPE Cleanup and Analysis of PPB Levels of Pesticides in Fruits and Vegetables*. Florida Pesticide Residue Workshop, 2002. References not available from Restek

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

Sample preparation and extraction

Sample:	10g of strawberries were homogenized and placed in a 50mL PTFE centrifuge tube (cat.# 26227)
Solvent:	10mL of acetonitrile were added to homogenate Shake for 1 minute, until uniform
Salts:	4.0g MgSO ₄ (powder or granular) 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.

(cat.# 26213)

Sample extract cleanup

QuEChERS tubes:	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 ₄ (cat.# 26124) B. 50mg PSA + 150mg MgSO ₄ + 50mg C18 (cat.# 26125) C. 50mg PSA + 150mg MgSO ₄ + 50mg GCB (cat.# 26123)
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.

Column:	Rtx®-CLPesticides2, 20m, 0.18mm ID, 0.14µm (cat.# 42302)
Sample:	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)
Inj.:	1.0µL splitless (hold 1 min.)
Inj. temp.:	250°C
Carrier gas:	helium
Flow rate:	constant linear velocity @ 40cm/sec
Oven temp.:	40°C (hold 1 min.) to 320°C @ 12°C/min.
Det:	Shimadzu GCMS-QP2010 Plus
Transfer line temp.:	300°C
Ionization:	Electron ionization
Mode:	Selected ion monitoring



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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

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

Rtx®-CLPesticides2 (proprietary Crossbond® phase)

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



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QuEChERS SPE Tubes

Quick, Easy, Cheap, Effective, Rugged, and Safe, the QuEChERS (“catchers”) method, developed by the USDA Eastern Regional Research Center, has become very popular for extraction and clean-up of pesticide residue samples. Our products are available in three centrifuge tube sizes to meet the needs of both extraction and clean-up of a wide variety of sample matrices following various methods.

The researchers developed a simple two-step procedure. First, the homogenized samples are extracted and partitioned, using an organic solvent and salt solution. Then, the supernatant is further extracted and cleaned, using a dispersive SPE technique. Multiple adsorbents are placed in a centrifuge tube, along with the 1mL of organic solvent and the extracted residues partitioned from step 1. The contents are thoroughly mixed, then centrifuged, producing a clean extract ready for a variety of GC or HPLC analytical techniques. Validation and proficiency data for the QuEChERS method are available for a wide variety of pesticides in several common food matrices at www.quechers.com

Free Sample Packs Available!

To receive your free sample pack, add -248 to the item number. (One sample per customer.)

Description	Material	Methods	qty.	cat#
50mL Centrifuge Tubes for Sample Extraction				
Resprep Q110	4g MgSO ₄ , 1g NaCl, 1g trisodium citrate dihydrate, .5g disodium hydrogencitrate sesquihydrate	Mini-Multiresidue, European prEN-15662	50-pk.	26213
Resprep Q150	6g MgSO ₄ , 1.5g NaOAc	AOAC 2007.1	50-pk.	26214
Empty 50mL Centrifuge Tube	—	Mini-Multiresidue, European prEN-15662, AOAC 2007.1	25-pk.	26227
2mL Micro-Centrifuge Tubes for dSPE (clean-up of 1mL extract)				
Resprep Q210	150mg MgSO ₄ , 25mg PSA	Mini-Multiresidue, European prEN-15662	100-pk.	26215
Resprep Q211	150mg MgSO ₄ , 25mg PSA, 25mg C18	Mini-Multiresidue	100-pk.	26216
Resprep Q212	150mg MgSO ₄ , 25mg PSA, 2.5mg GCB	Mini-Multiresidue, European prEN-15662	100-pk.	26217
Resprep Q213	150mg MgSO ₄ , 25mg PSA, 7.5mg GCB	European prEN-15662	100-pk.	26218
Resprep Q250	150mg MgSO ₄ , 50mg PSA	AOAC 2007.1	100-pk.	26124
Resprep Q251	150mg MgSO ₄ , 50mg PSA, 50mg C18	AOAC 2007.1	100-pk.	26125
Resprep Q253	150mg MgSO ₄ , 50mg PSA, 50mg GCB	—	100-pk.	26123
Resprep Q252	150mg MgSO ₄ , 50mg PSA, 50mg C18, 50mg GCB	AOAC 2007.1	100-pk.	26219
15mL Centrifuge Tubes for dSPE (clean-up of 6mL extract)				
Resprep Q350	1200mg MgSO ₄ , 400mg PSA	AOAC 2007.1	50-pk.	26220
Resprep Q351	1200mg MgSO ₄ , 400mg PSA, 400mg C18	AOAC 2007.1	50-pk.	26221
Resprep Q352	1200mg MgSO ₄ , 400mg PSA, 400mg C18, 400mg GCB	AOAC 2007.1	50-pk.	26222
Resprep Q370	900mg MgSO ₄ , 150mg PSA	European prEN-15662	50-pk.	26223
Resprep Q371	900mg MgSO ₄ , 150mg PSA, 15mg GCB	European prEN-15662	50-pk.	26224
Resprep Q372	900mg MgSO ₄ , 150mg PSA, 45mg GCB	European prEN-15662	50-pk.	26225
Resprep Q373	900mg MgSO ₄ , 150mg PSA, 150mg C18	—	50-pk.	26226
Resprep Q374	900mg MgSO ₄ , 300mg PSA, 150mg GCB	—	50-pk.	26126



cat. # 26123



cat. # 26124



cat. # 26227

cat. # 26214



cat. # 26125



cat. # 26126

did you know?

Multiple sorbents are used to extract different types of interferences.

MgSO ₄	removes excess water
PSA*	removes sugars, fatty acids, organic acids, and anthocyanine pigments
C18	removes nonpolar interferences
GCB**	removes pigments, sterols, and nonpolar interferences

*PSA—primary and secondary amine exchange material.

**GCB—graphitized carbon black

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