Prepare Samples in Half the Time Using a Fraction of the Solvent with dSPE

*Simplify and speed up sample preparation with **Resprep dSPE tubes**! Here we show the extraction and clean-up of pesticide residues from olive oil samples—twice as fast as GPC, with only a fraction of the solvent required for conventional SPE.*

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Olive oil is considered a healthy fat source and is a staple in many recommended diets. However, concerns about potentially negative health effects associated with pesticide residues have increased consumer interest in testing. While organophosporus pesticides are currently used in olive orchards to control pests, organochlorine pesticides are still tested for as persistent organic pollutants (residues), even though they are no longer in commercial use. There are several existing methods for measuring pesticide residues in olive oil, all of which involve sample extraction and clean-up.[1] The common goal of these methods is to remove lipids that are harmful to the analytical system.[2] Efficient sample clean-up procedures are critical to maximizing sample throughput and minimizing labor and material costs. Here we demonstrate the efficiency of a dSPE clean-up procedure, as well as the capabilities of both method-specific and general purpose analytical columns.

Simple Procedure Uses Half the Time and Minimal Solvent

Sample extraction and clean-up can be accomplished with gel permeation chromatography (GPC), solid phase extraction (SPE), or dispersive solid phase extraction (dSPE) methods. However the dSPE method shown here is much less expensive than GPC (which requires specialized equipment) and uses substantially less solvent than comparable GPC or SPE methods (Table I).[3] The method is simple to use and allows sample extraction and clean-up to be accomplished in half the time of other techniques (Table II).

Extraction and dSPE Clean-up for Pesticide Residues in Olive Oil

Test sample: A 1.5mL sample of commercially obtained virgin olive oil was spiked with a standard organochlorine pesticide mix. The spiked sample was processed as follows.

1. Dilute with 1.5mL hexane.
2. Add 6mL of acetonitrile (ACN).
3. Mix for 30 minutes on a shaker.
4. Allow layers to separate (approximately 20 minutes), then collect the top (ACN) layer.
5. Repeat the liquid-liquid extraction (steps 2-4) and combine both ACN extract layers.
6. Place 1mL of the combined ACN extract in a 1.5mL tube containing 150mg magnesium sulfate and 50mg PSA.
7. Shake the tube for 2 minutes.
8. Centrifuge at 3,000 U/min. for approximately 5 minutes.
9. Remove the top layer and inject directly into the gas chromatograph system.

Extracts were analyzed using both Rtx®-CLPesticides2 and Rxi®-5Sil MS columns (Figure 1). The Rtx®-CLPesticides2 column is a method specific column that resolves all compounds. The Rxi®-5Sil MS column is a general purpose column that has one coelution that can easily be extracted by a mass

Table I Resprep dSPE method uses 42% and 89% less solvent than SPE and GPC methods respectively.

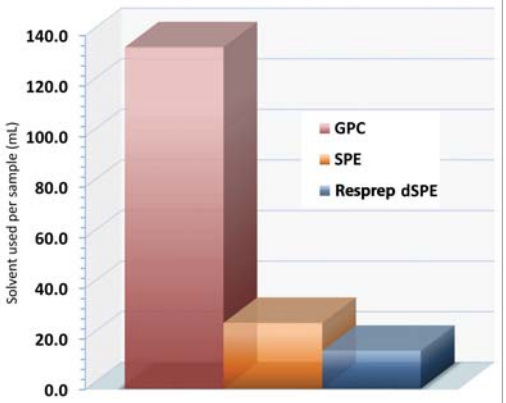


Table II Cut extraction/clean-up time by 50% using a Resprep dSPE method.

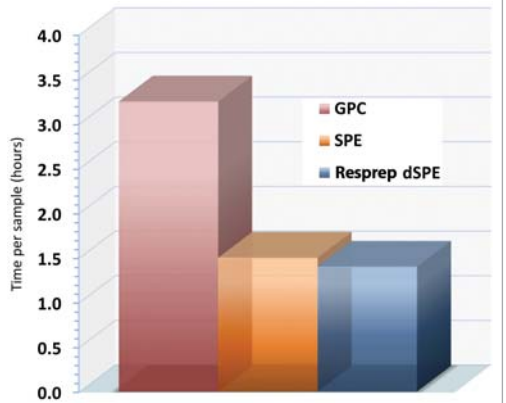
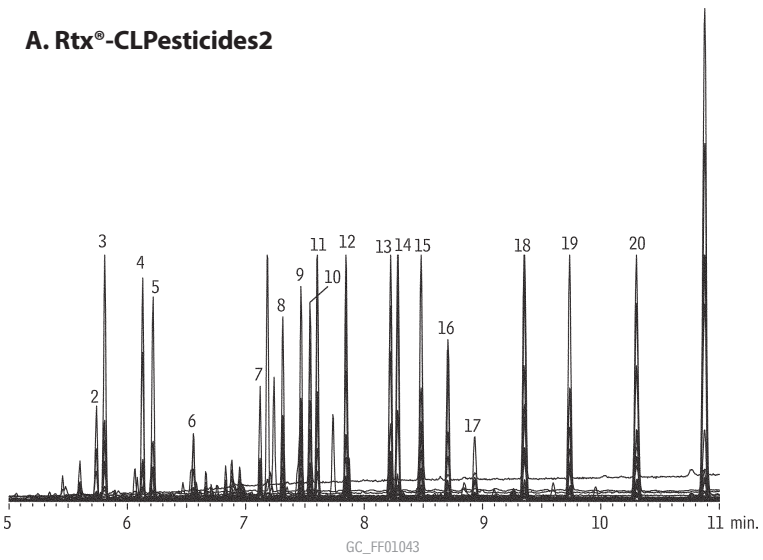
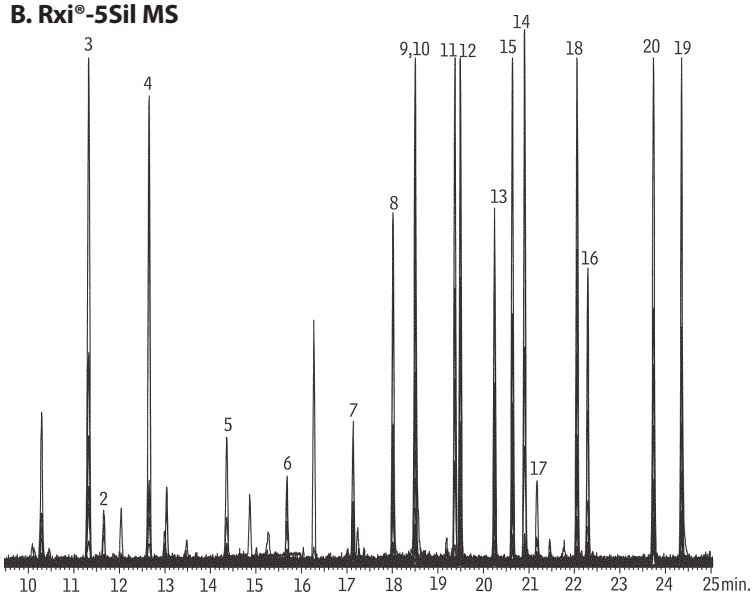


Figure 1 Chlorinated pesticide residues in olive oil are easily separated on either Rtx®-CLPesticides2 or Rxi®-5Sil MS columns.

A. Rtx®-CLPesticides2



B. Rxi®-5Sil MS



Column:	A. Rtx®-CLPesticides2, 30m, 0.25mm ID, 0.20µm (cat.# 11323) B. Rxi®-5Sil MS, 30m, 0.25mm ID, 0.25µm (cat.# 13623)
Sample:	10µg/mL Organochlorine Pesticide Mix AB # 3 (cat.# 32415) in olive oil
Inj.:	1µL, splitless (hold 0.5 min.), 3.5mm single gooseneck liner (cat.# 20962) packed with wool
Inj. temp.:	225°C
Carrier gas:	helium, constant flow
Flow rate:	1mL/min.
Oven temp.:	A. 140°C (hold 0.5 min.) to 268°C @ 20°C/min. to 290°C @ 3°C/min. to 330°C (hold 5 min.) @ 20°C/min. B. 130°C (hold 0.5 min.) to 330°C @ 5°C/min
Det:	MS
Transfer line temp.:	320°C
Ionization:	EI
Mode:	SIM

Compound	Quant. ion	Qual. ion 1	Qual. ion 2
*1. α-BHC	219	181	109
2. γ-BHC	219	181	109
3. β-BHC	219	181	109
4. δ-BHC	219	181	109
5. heptachlor	272	237	100
6. aldrin	263	293	220
7. heptachlor epoxide	263	237	81
8. δ-chlordane	272	237	65
9. α-chlordane	272	237	65
10. endosulfan I	195	207	241
11. 4,4'-DDE	246	318	176
12. dieldrin	79	263	277
13. endrin	263	281	81
14. 4,4'-DDD	235	165	199
15. endosulfan II	195	207	-
16. 4,4'-DDT	235	165	199
17. endrin aldehyde	67	250	345
18. endosulfan sulfate	272	229	239
19. methoxychlor	227	274	-
20. endrin ketone	67	317	281

* not present

spectrometer detector (MSD). Only α-BHC was not detected, a subject of further investigation, however either column can be used effectively. Recoveries of 70%-80% were obtained, levels comparable to conventional SPE—without the necessity of vacuum manifolds or high pressure systems. The GPC method attained recoveries of > 95%. However this method requires large amounts of solvent and takes over twice as long as other methods.

The dSPE method shown here is an efficient, cost-effective way to clean up chlorinated pesticide residues in olive oil. With good recoveries and minimal matrix interference, it is an easy way to reduce solvent usage, compared to conventional SPE, and is more cost-effective than GPC.

References
1. C. Lentza-Rizos, E.J. Avramides, Rev. Environ. Contam. Toxicol. 141 (1995) 111.
2. S. Cunha, S. Lehotay, K. Mastovska, J. Sep. Sci. 30 (2007) 620.
3. M. Crawford, M. Halvorson, J. Stevens, The Examination and Automation of GPC, SPE and QuEChERS Utilized in Extracting Pesticides from Olive Oil. HPLC 2008 poster presentation.

Product Listing

dSPE Tube for Clean-Up of Pesticide Residue Samples

Description	Material	Methods	qty.	cat#	price
2mL Microentrifuge Tubes for dSPE					
Resprep	150mg $MgSO_4$,	AOAC			
Q250	50mg PSA	2007.1	100-pk.	26124	

PSA—primary and secondary amine exchange material.

Organochlorine Pesticide Mix AB # 3

(20 components)

aldrin	dieldrin
α-BHC	endosulfan I
β-BHC	endosulfan II
δ-BHC	endosulfan sulfate
γ-BHC (lindane)	endrin
α-chlordane	endrin aldehyde
γ-chlordane	endrin ketone
4,4'-DDD	heptachlor
4,4'-DDE	heptachlor epoxide (isomer B)
4,4'-DDT	methoxychlor

2,000µg/mL each in hexane:toluene (1:1), 1mL/ampul
cat. # 32415 (ea.)

Rtx®-CLPesticides2 Columns (fused silica)

ID	df (µm)	temp. limits	length	cat. #	price
0.25mm	0.20	-60 to 320/340°C	30-Meter	11323	

Rxi®-5Sil MS Columns (fused silica)

(Crossbond®, selectivity close to 5% diphenyl/95% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #	price
0.25mm	0.25	-60 to 330/350°C	30-Meter	13623	