

NEW Custom “Dispersive” SPE Products for Pesticide and Acrylamide Analysis

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The multi-residue surveillance of pesticides in agricultural products (fruits, vegetables, meat, shellfish, grains, and dairy products) is an ongoing project for regulatory agencies, contract laboratories, and industrial laboratories worldwide. Hundreds of thousands of samples are analyzed annually to meet a variety of purposes including regulatory enforcement and surveillance monitoring (1).

In previous issues of the Supelco Reporter (Vol. 23.2 and 23.3), we discussed the use of dual-layer SPE technology (ENVI-Carb™-II/PSA SPE) to provide the necessary sample cleanup for analyzing pesticides in agricultural matrices for subsequent GC-MS analysis.

In this report, we discuss the utility of a new custom service Supelco offers to support an emerging sample prep technique called “Dispersive SPE”.

Dispersive SPE for Multi Residue Pesticide Analysis

In recent years, a number of SPE procedures have been published. Most of them involve an initial liquid-liquid extraction step, and/or solid-liquid extraction step using a water miscible solvent such as acetonitrile or acetone. Subsequent analysis is conducted via GC-MS, GC-fluorescence, GC-ESD, and other detection techniques. Further cleanup using SPE technology prior to GC analysis is necessary to decrease background levels for trace level pesticide detection, reduce matrix-induced signal enhancement, and relieve stress and reduce downtime on the GC system (2).

Most of the published SPE procedures for multi-residue monitoring (MRM) involved the use of SPE tubes to conduct sample cleanup. In 2003, Anastasiades et al. introduced a novel approach to SPE sample prep called “dispersive SPE” (3). In this method 10-20 g of a food sample is initially extracted with acetonitrile. Gram levels of salt (magnesium sulfate, sodium chloride, and/or sodium sulfate) are then added to drive partitioning between the aqueous residues and the acetonitrile layer. A small aliquot of the acetonitrile layer is removed for further SPE cleanup. Unlike most methods using conventional SPE tubes, in dispersive SPE, residual water and cleanup are performed simultaneously by mixing bulk SPE and magnesium sulfate with the acetonitrile extract. The bulk SPE

sorbent adsorbs matrix interferences, and after a simple vortex and centrifugation step, the supernatant is ready for further analysis using GC-MS or LC-MS.

In a follow-up study, Lehotay et al. demonstrated the method's effectiveness by extracting over 200 pesticides in a variety of matrices including lettuce and oranges for both GC-MS and LC-MS-MS analysis (4), and the use of buffering during the initial pre-SPE extraction process to stabilize base-sensitive pesticides (5). The final method (Table 1) was further validated in an inter-laboratory trial involving 15 laboratories in 7 countries (6). The method was termed the QuEChERS method which is short for “quick, easy, cheap, effective, rugged, and safe”.

Table 1. Inter-Laboratory Dispersive SPE Procedure for Pesticide Residues in Fruits and Vegetables

Solid-Liquid Extraction

1. Transfer 15 homogenized food sample to 50 mL PTFE tube
2. Add 15 mL 1% acetic acid in acetonitrile + 1.5 g anhydrous NaAc + 6 g anhydrous magnesium sulfate + 75 µL I.S. solution
3. Shake vigorously 1 min.; Centrifuge > 1500 rcf 1 min.

Dispersive SPE

1. Transfer 1-8 mL of acetonitrile layer to clean tube with 150 mg anhydrous magnesium sulfate + 50 mg PSA per mL extract and shake for 30 sec.
2. Centrifuge > 1500 rcf for 1 min.
3. Transfer supernatant to GC vial or LC vial for concurrent LC-MS and GC-MS analysis. Note that further processing may be necessary prior to chromatographic analysis (e.g. addition of formic acid for LC-MS analysis; or evaporation of supernatant and reconstitute with toluene for GC-MS analysis).

Dispersive SPE-Acrylamide Analysis in Starchy Foods

Numerous reports have been published for the extraction and analysis of acrylamide in starchy foods (e.g. potato chips). Most of which require a combination of SPE tubes of varying chemistries to provide adequate sample cleanup, and/or sample bromination to decrease acrylamide's polarity for improved chromatographic retention. In 2004, Mastovska et al. (7) introduced a fast and easy dispersive SPE method for the analysis of acrylamide in foods. In this protocol, food samples are initially extracted with a combination of hexane, water, acetonitrile, and high levels of salts (magnesium sulfate + sodium chloride). Most of the problematic fats in fried foods migrate to the hexane layer which is discarded. The high salt environment aids separation between the acetonitrile and water layers, and also drives acrylamide to the acetonitrile layer. An aliquot of the acetonitrile layer is further cleaned

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up with PSA (primary secondary amine) SPE under dispersive conditions. PSA removes residual fatty acids and other interferences remaining in the extract. The detailed protocol is described in Table 2.

Table 2. Dispersive SPE Procedure for Acrylamide Analysis**Solid-Liquid Extraction**

1. Add d3-acrylamide at 500 ng/g to 1 g of homogenized sample
2. Add 5 mL hexane and vortex
3. Add 10 mL DI water + 10 mL acetonitrile + 4 g magnesium sulfate + 0.5 g sodium chloride
4. Vortex 1 min. and centrifuge at 3450 rcf for 5 min.
5. Discard hexane layer

Dispersive SPE

1. Combine 1 mL of acetonitrile layer with 50 mg PSA + 150 mg magnesium sulfate
2. Vortex for 30 sec.
3. Centrifuge at 3450 rcf for 1 min.
4. Analyze supernatant via LC-MS-MS or GC-MS analysis

Custom SPE Products for Dispersive SPE

Described above are just a few application examples of dispersive SPE. Although the technique offers some advantages over conventional methods, it requires the analyst to weigh a pre-determined amount of salts and SPE sorbent(s) for each sample. The weighing process could be a time consuming bottleneck for larger studies when greater throughput is required.

To address this issue, Supelco now offers a new custom product service to support this emerging sample prep technique. In this service, we can provide the necessary pre-weighed SPE sorbents and salts for a given method in a convenient screw top vial format(s). The analyst can either perform the extraction in the vials itself, or combine the contents with the sample at the appropriate step during the procedure. For example, to support the method described in Table 1, we can provide two vials (e.g. 10-50/pk) containing the following contents:

**Vial 1: 6 g anhydrous magnesium sulfate +
1.5 g anhydrous sodium acetate**

**Vial 2: 150 mg anhydrous magnesium sulfate +
50 mg PSA**

Table 3 lists the available sorbents and salts commonly used in dispersive SPE. Figure 1 is a visual depiction of custom pre-weighed sorbents and salts for dispersive SPE.

Table 3. Available SPE Sorbents and Salts Commonly used in Dispersive SPE¹

Florisol (57209)	C18 SPE (52600-U)
NH2 SPE (57212-U)	PSA SPE (52738-U)
SAX SPE (57214-U)	ENVI-Carb (graphitized carbon black) (57210-U)
Sodium acetate (24,124-5)	Magnesium sulfate (23,039-1)
Sodium sulfate (23,859-7)	Sodium chloride (S 9888)

¹ Catalog numbers in parentheses are for bulk quantities of 100 g or greater.

Figure 1. Example of Custom Pre-Weighed Salt/Sorbent Vials for Dispersive SPE**References**

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**Related Information**

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