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Streamlined sample cleanup using combined dispersive solid-phase extraction and in-vial filtration for analysis of pesticides and environmental pollutants in shrimp☆

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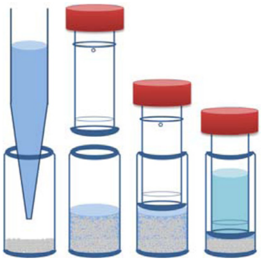
HIGHLIGHTS

- The first report that combines in-vial filtration and dispersive-SPE for sample cleanup.
- The unique application of ammonium formate for salting-out partitioning in QuEChERS.
- Evaluations of a new zirconium-based and a non-friable GCB sorbent for d-SPE cleanup.
- A new analytical method for 59 pesticides and environmental pollutants in shrimp.

GRAPHICAL ABSTRACT



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ABSTRACT

A new method of sample preparation was developed and is reported for the first time. The approach combines in-vial filtration with dispersive solid-phase extraction (d-SPE) in a fast and convenient cleanup of QuEChERS (quick, easy, cheap, effective, rugged, and safe) extracts. The method was applied to simultaneous analysis of 42 diverse pesticides and 17 environmental contaminants, including polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), and flame retardants, in shrimp as the sample matrix. Final extracts were analyzed by both low-pressure gas chromatography – triple quadrupole tandem mass spectrometry (LPGC-MS/MS), and high-performance liquid chromatography – triple quadrupole tandem mass spectrometry (HPLC-MS/MS) to provide a wide scope of analysis for targeted analytes. During method development, several different commercial sorbents for d-SPE were investigated and compared with respect to analyte recoveries. The method was validated at 10, 50, and 100 ng g^{-1} spiking levels (10-fold lower for PCBs), and the results for nearly all analytes were between 70 and 115% recoveries with $\leq$17% relative standard deviations. The method was shown to be simple, fast, and effective for multi-application analysis of chemical residues in the representative food and environmental marker matrix.

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Abbreviations: DPX, Disposable pipette extraction; d-SPE, Dispersive solid-phase extraction; FRs, Flame retardants; HPLC-MS/MS, High-performance liquid chromatography – tandem mass spectrometry; IS, Internal standard; LOD, Limit of detection; LOQ, Limit of quantification; LPGC-MS/MS, Low-pressure gas chromatography – tandem mass spectrometry; MRM, Multiple reaction monitoring; PAHs, Polycyclic aromatic hydrocarbons; PBDEs, Polybrominated diphenyl ethers; PCBs, Polychlorinated biphenyls; POPs, Persistent organic pollutants; PSA, Primary secondary amine; PVDF, Polyvinylidene fluoride; QuEChERS, Quick, easy, cheap, effective, rugged, and safe; TPP, Triphenylphosphate.

☆ *Disclaimer*: Mention of a brand or firm name does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

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1. Introduction

Monitoring of chemical residues in food and the environment is an important function of countless laboratories around the world. The monitoring results are used to help assess risks to the consumer and environment, contribute to fair trade and good agricultural practices, enforce laws, set regulatory limits, among other aspects in the food and environmental arenas. To best meet needs, efficient methods that yield high quality results for a wide scope of analytes at ultratrace concentrations in a variety of matrices should be used. Food is perishable and analyses add to consumer costs, thus high sample throughput with rapid sample turnaround time at low expense constitutes a major goal in method development research.

The "quick, easy, cheap, effective, rugged, and safe" (QuEChERS) approach to sample preparation for pesticides [1–3], veterinary drugs [4–6], environmental contaminants [7,8], mycotoxins [9,10], and other chemical components in a variety of matrices [11–13] is designed to help meet current monitoring needs. QuEChERS works well with both gas and liquid chromatography (GC and LC) coupled to mass spectrometry (MS) for analysis. At this time, more than 900 publications in the scientific literature have involved QuEChERS or its associated cleanup technique, dispersive solid-phase extraction (d-SPE).

In method development, any labor, time, and/or cost savings measure that can be achieved often yields significant benefits when the measure can be implemented in routine operations. For example, it is common practice currently to conduct d-SPE by shaking the extract with adsorbents followed by a centrifugation step [1–13]. Then, a portion of the final extract is either filtered into autosampler vials using a syringe filter or a commercial in-vial filter device [14–16]. It is possible to transfer the final extract directly without filtration, but the risks increase of clogged syringes or other instrumental problems due to the presence of injected particles. A simple and effective streamlining measure can be achieved by eliminating the centrifugation step and combining the d-SPE and in-vial filtration steps. This shaves several minutes of time and labor from each analysis, and can eliminate the need for a (mini-) centrifuge. Flow-through SPE with a syringe format [17,18] or disposable pipette extraction (DPX) [19,20] are other options to avoid centrifugation, but less filtration is provided using their screen mesh frits and transfer of consistent volumes are not ideal in those techniques.

The combined filter-vial d-SPE approach is currently patent pending [21], and the aim of this study was to evaluate this new approach for the first time in practice. We chose to apply it in a novel multiclass, multiresidue monitoring method that serves to analyze a wide range of pesticides and environmental contaminants which are traditionally monitored by separate methods. A combined approach for pesticides and persistent organic pollutants (POPs) has been validated previously in fish using only low-pressure gas chromatography – tandem mass spectrometry (LPGC-MS/MS) for analysis [8], and a further goal of this present study was to also extend the method to more polar analytes amenable to liquid chromatography (LC)–MS/MS analysis. Shrimp was selected as the model matrix which serves as both a common food and environmental marker tissue for exposure to contaminants (including veterinary drugs used in aquaculture).

2. Material and methods

2.1. Reagents and samples

To investigate the feasibility of the new approach, 59 representative analytes were chosen, including 42 diverse pesticides and 17 environmental pollutants. Pesticide standards were obtained from Chemservice (West Chester, PA, USA), Dr. Ehrenstorfer GmbH (Augsburg, Germany), and the Environmental Protection Agency's National Pesticide Repository (Fort Meade, MD, USA). Flame retardants (FRs), which include triphenyl phosphate (TPP), hexabromobenzene (HBB) and 3 polybrominated diphenyl ether (PBDE) congeners (#47, 99, 100), were purchased from Accustandard (New Haven, CT, USA), as were 9 polychlorinated biphenyl (PCB) congeners (#105, 114, 118, 123, 126, 156, 157, 167, 169) and 3 polycyclic aromatic hydrocarbons (PAHs), consisting of anthracene, pyrene, and phenanthrene. The internal standards, atrazine-d_5 and fenthion-d_6, were obtained from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). All standards were labeled as $\geq$98% purity.

HPLC-grade acetonitrile (MeCN) was from Fisher Scientific (Fair Lawn, NJ, USA). Deionized water of 18.2 Ω-cm was prepared with an E-Pure system from Barnstead/Thermolyne (Dubuque, IA, USA). ACS-grade ammonium formate (HCO_2NH_4) was obtained from Mallinckrodt (Paris, KY, USA), and formic acid (88% purity) was from Spectrum (New Brunswick, NJ, USA). Anhydrous magnesium sulfate (anh. $MgSO_4$), 99.5% purity, and primary secondary amine (PSA) sorbent were purchased from UCT (Bristol, PA, USA). C18 sorbent was from Thomas Scientific (Swedesboro, NJ, USA), and zirconium-based Supel^{TM} QuE Z-Sep sorbent was from Supelco (Bellefonte, PA, USA). Non-friable graphitized carbon black (CarbonX$^{®}$ Plus) sorbent was provided by United Science (Center City, MN, USA).

Stock solutions of each analyte were prepared in toluene or MeCN at concentrations of 1 mg mL^{-1} and stored at −18 °C. A standard working mixture containing the 17 environmental pollutant and 42 pesticide analytes was prepared at 2 ng μL^{-1} in MeCN, except the 9 PCB congeners had 0.2 ng μL^{-1} concentrations. A 10 ng μL^{-1} mixture of atrazine-d_5 and fenthion-d_6 was prepared in 0.05% formic acid in MeCN as the internal standard solution. Calibration standards of 0, 5, 10, 50, 100, and 150 ng g^{-1} equivalent concentrations (10-fold lower for the 9 PCBs) were prepared in MeCN (reagent-only calibration) and in shrimp blank extracts (matrix-matched calibration). Final extracts were 1 g mL^{-1} equivalent sample.

Approximately 2 kg frozen shrimp were purchased from local food stores. The shell was peeled and the shrimp tissue was homogenized with a probe blender homogenizer; ≈50 g portions were transferred into many plastic bags, which were stored in a −20 °C freezer until they were thawed prior to analysis.

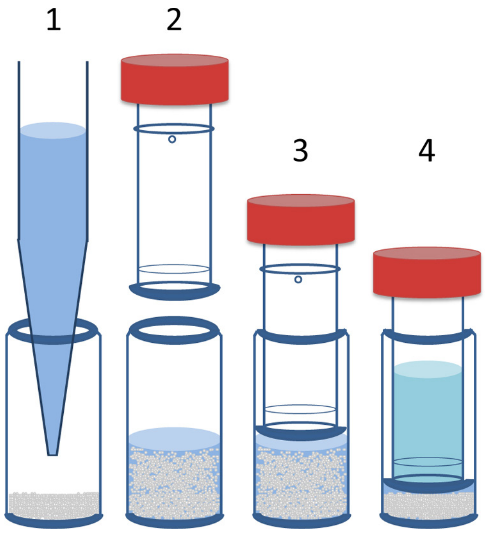

Fig. 1. Procedure for filter-vial d-SPE: (1) pipette 0.5 mL of initial QuEChERS extract into bottom piece containing sorbents; (2) press filter plunger half-way into bottom piece; (3) shake for 30 s; (4) depress filter plunger to filter extract for analysis.