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Selective pressurized liquid extraction as a sample-preparation technique for persistent organic pollutants and contaminants of emerging concern

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ABSTRACT

Sample preparation represents about two-thirds of the cost of analysis and often presents logistical bottlenecks in analytical and environmental chemistry laboratories, thus reducing our capacity and preparedness to quantify organic pollutants rapidly and accurately. Selective pressurized liquid extraction (SPLE) is an analytical technique that builds upon PLE by incorporating matrix-compound (i.e. interference) retainers into the extraction step, thereby reducing sample-preparation steps and increasing sample throughput. SPLE methods offer distinct advantages over traditional methods, namely reduction in the costs intrinsic to sample preparation (i.e. time, solvents, labor, laboratory space, training, and potential loss of analytes). The ability to analyze and to evaluate rapidly a large number of samples directly increases the analytical capacity and preparedness of a laboratory for certain situations (e.g. large-scale studies or environmental emergencies). We review the analytical improvements via SPLE and its wide-ranging applications.

Contents

Abbreviations: ACE, Acetone; ACN, Acetonitrile; ASE, Accelerated solvent extractor; CEC, Contaminant of emerging concern; CHEX, Cyclohexane; DCM, Dichloromethane; DEE, Diethyl ether; dl-PCB, dioxin-like polychlorinated biphenyl; EA, Ethyl acetate; EPLE, Enhanced pressurized liquid extraction; FFR, Fat-to-fat retainer ratio; GCB, Graphitized carbon black; GC-ECD, Gas chromatography-electron-capture detector; GC-MS^n, Gas chromatography-mass spectrometry; GPC, Gel-permeation chromatography; HEP, Heptane; HEX, Hexane; HPLC, High-performance liquid chromatography; HRGC-HRMS, High-resolution gas chromatography-high-resolution mass spectrometry; LC-MS^n, Liquid chromatography-mass spectrometry; MAE, Microwave-assisted extraction; MeOH, Methanol; PAH, Polyaromatic hydrocarbon; PBDE, Polybrominated diphenyl ether; PCB, Polychlorinated biphenyl; PCDD, Polychlorodibenzo-*p*-dioxin; PCDF, Polychlorodibenzofuran; PFE, Pressurized fluid extraction; PLE, Pressurized liquid extraction; POP, Persistent organic pollutant; PPCPs, Pharmaceutical and personal-care products; SFE, Supercritical fluid extraction; SPLE, Selective pressurized liquid extraction; TCDD, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin; TEQ, Toxic equivalency; TOL, Toluene; USEPA, United States Environmental Protection Agency.

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1. Introduction

The sample-preparation step is crucial in analytical protocols designed for the trace analysis of organic chemicals, including persistent organic pollutants (POPs) and many contaminants of emerging concern (CECs), in solid and semi-solid environmental samples. Typically, sample preparation is composed of several steps, including sample pre-treatment, extraction, and extract clean-up. Due to the many stages involved, sample preparation is the most error-prone, labor-intensive and time-determining step in an analytical protocol [1]. Additionally, inconsistencies in sample preparation limit the reliability, the accuracy and the validity of interlaboratory comparisons of POP measurements. Automation can help eliminate or reduce these inconsistencies, improve analytical throughput and reduce analyte loss [2].

In the past few decades, pressurized liquid extraction (PLE) became an increasingly popular approach to sample preparation and several recent reviews focused on PLE as an exhaustive extraction technique capable of extracting POPs and CECs from solid and semi-solid matrices [3]. The key advantages of PLE compared to traditional extraction techniques, such as Soxhlet, are that it uses less solvent, takes less time per sample and can be readily automated. However, as with other solvent-based extraction techniques, target analytes and some non-target analytes, including those that can interfere with quantification, are often co-extracted from the sample matrix. This means that post-extraction clean-up [e.g. with packed chromatographic columns or gel-permeation chromatography (GPC)] is generally needed before quantification of extracts produced with PLE.

In recent years, an advanced version of PLE was developed for use in simultaneously extracting target analytes and removing potential interfering matrix compounds by incorporating clean-up adsorbents (i.e. matrix-compound retainers) within the extraction cell. Selectivity for analytes over undesirable matrix compound is achieved by trapping or destroying the matrix compound. Several analytical terms, including selective PLE (SPLE), enhanced PLE (EPLE), in-cell clean-up, and *in-situ* clean-up have been used to describe this technique. Herein, the term SPLE is used when referring to these advanced PLE techniques.

This article mainly focuses on SPLE techniques developed for the analysis of POPs and selected CECs in solid environmental matrices, including biological tissues, soil, sediment, sludge and dust. We describe the significant analytical improvements associated with SPLE compared to traditional extraction methods. Specifically, this article builds on previous discussions on PLE that focused on extraction optimization and efficiency (i.e. analyte transport from the matrix and solubilized into the solvent) [3]. Method development for SPLE leads to an additional level of complexity compared to other methods, but, with this complexity, comes much opportunity.

Finally, this article addresses the analytical challenges and the potential research opportunities associated with the expanding applicability of SPLE.

2. Sample preparation

Sample preparation is a necessary step in most methods for the trace analysis of contaminants in environmental matrices. In the analysis of POPs and CECs, sample preparation represents about two-thirds of the analytical procedures and includes sample pre-treatment, extraction, extract clean-up or isolation, and analyte fractionation. These sample-preparation techniques are often considered bottlenecks in many analytical methods [2]. Efforts to reduce such bottlenecks have focused on the development of more high-throughput, high-efficiency methods [2]. Reducing the number of steps in the sample-preparation procedure also helps to reduce the overall uncertainty in final reported concentrations and therefore reduces interlaboratory discrepancies. Finally, reducing the number of steps in a sample-preparation procedure also makes it more environmentally friendly because less solvent and energy are used.

2.1. Sample pre-treatment

Runnqvist et al. published a detailed description of the key objectives and strategies associated with sample pre-treatment [3]. Pre-treatment typically involves sample homogenization followed by sample drying. The homogenization step serves to increase the surface area of the sample, potentially enhancing the accessibility of entrapped or bound analytes in sample matrices to the solvent(s) [3]. Sample drying can be achieved with air-drying, lyophilization, and/or mixing the sample with common dehydrating agents, such as anhydrous sodium sulfate, diatomaceous earth, or cellulose [3,16,32,33]. The pre-extraction removal of moisture from homogenized samples, particularly when non-polar extraction solvents are used, further enhances the extraction and helps to eliminate the extraction variability among samples with different moisture contents [9,34].

2.2. Sample extraction

During sample extraction, analytes are preferentially transferred from the environmental matrix to the extraction solvent [35]. Several reviews in the literature describe traditional methods, such as Soxhlet [1], supercritical fluid extraction (SFE) [32], and microwave-assisted extraction (MAE) [36], for extracting POPs from environmental samples [1,37–39]. Over the years, improvements in extraction techniques increase analyte solubility and solvent permeability, thus resulting in improved extraction efficiency and reproducibility, culminated with the development of pressurized liquid or fluid extraction (PLE or PFE) techniques [40]. Fig. 1 provides an overview of the general steps involved in the PLE of an analyte from a solid particle (as adapted and redrawn from reference [41]).

2.3. Extract clean-up and analyte fractionation

Environmental solids are often complex matrices, and improvements in the extraction efficiency of target analytes frequently also result in improved extraction of potentially interfering matrix compounds. The most common post-extraction clean-up strategies employ GPC and/or packed chromatographic columns. When using chromatographic columns, more than one type of column is often necessary and the eluent needs to be concentrated between each clean-up step. These clean-up steps are time consuming, increase personnel exposure to organic solvents, and increase the potential for analyte loss and sample contamination. Several clean-up sorbents