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Disk-based solid-phase extraction analysis of organic substances in water

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ABSTRACT

Solid-phase extraction (SPE) disks are used in many application fields as modified versions of the widespread SPE cartridges. Due to current trends in legislation and normalization in the context of implementation of the Water Framework Directive, their use will probably increase in the future. A particular reason is the better capability of SPE disks to deal with suspended particulate matter (SPM) compared with SPE cartridges. This overview focuses on the application of standard SPE disks for the analysis of priority pollutants in water. We discuss in detail the design and the characteristics of SPE disks and various general aspects of their application, such as the extraction, drying and desorption process, and the subsequent analytical method combined with SPE-disk-based sample preparation.

Contents

Abbreviations: ASE, Accelerated solvent extraction; CEN, European Committee for Standardization; DAD, Diode-array detector; DVB, Styrene divinylbenzene; FD, Fluorescence detection; FT-MS, Fourier transform mass spectrometry; GC, Gas chromatography; LC, Liquid chromatography; LLE, Liquid-liquid extraction; LOD, Limit of detection; log K_{OC}, Partition coefficients between organic carbon and water; MALDI, Matrix-assisted laser desorption ionization; MEKC, Micellar electrokinetic chromatography; MS, Mass spectrometry; OCP, Organic chlorinated pesticides; PAH, Polycyclic aromatic hydrocarbon; PBDE, Polybrominated diphenyl ether; PCB, Polychlorinated biphenyl; PMDS, Polydimethylsiloxane; PTFE, Polytetrafluoroethylene; SALDI, Surface-assisted laser desorption/ionization; SFE, Supercritical fluid extraction; SPE, Solid-phase extraction; SPM, Suspended particulate matter; SPME, Solid-phase microextraction; UV-VIS, Ultraviolet-visible; WFD, Water Framework Directive.

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1. Introduction

In the mid-1970s, the solid-phase extraction (SPE) technique was introduced [1,2] and has been commonly used since 1985 [1]. In 1989, particle-loaded membranes named extraction disks were brought on the market by 3M as an alternative to SPE particle-filled cartridges for the handling of large volumes of environmental samples and as solution for many drawbacks of SPE cartridges (see below) [3]. The first paper about SPE-disk use was published in 1990 by Hagen et al. for the analysis of environmental pollutants from aqueous matrices [4]. Since 1994, in addition to C_{18} phases, other materials, such as styrene divinylbenzene (DVB), and cation- and anion-exchange materials, have been used for disk SPE [5] (Fig. 1).

In the literature, different names and spellings are used for SPE disks, such as extraction discs (e.g. [6]) or membrane-extraction disks (e.g. [7]). “Membrane” in some names originates from the first construction principle of the particle-loaded membrane. In this overview, the term SPE disk covers all variants.

The SPE-disk procedure resembles the handling of SPE cartridges in water analysis (Fig. 2). In both approaches, the solid-phase material is activated by organic solvents and water to increase the effective surface area and to reduce interferences. Subsequently, the analytes are extracted from the water sample by passing a known sample volume over the phase material. The analytes are sorbed on the solid phase due to the released Gibbs free energy, consisting of cavity-energy and interaction-energy contributions from van der Waals and H-bond interactions [8,9]. Also, electronic interactions and ion-exchange processes may be relevant, depending on the nature of analyte and sorbent [9]. After drying the sorbent and possibly removing interferences, the analytes are desorbed from the phase material by small volumes of organic solvents. Thereby, the interactions between the analytes and the solid-phase material are disrupted. Eventually, following a further clean-up and concentration of the organic extract, the extract is analyzed.

Since 1978, the SPE technique has been commercially available, and today many manufacturers and suppliers offer SPE cartridges and disks with different phase materials and diameters [10]. In the literature, documented SPE-disk diameters vary in the range of 4–96 mm [3,10]. The dimension of SPE disks normally increases with the sample volume, so smaller disks are used for small sample volumes, as occur for example in biological and clinical applications [4]. The most frequently used standard SPE disks in water analysis have diameters of 47 mm and are normally used for sample volumes of 0.5–1 L [10]. For sample volumes of 5–20 L [2] and samples containing larger amounts of suspended particulate matter (SPM), SPE disks with diameters of 47–90 mm have been used. SPE disks with diameters of 4.6 mm were used in on-line SPE [10].

The most commonly used SPE sorbent is C_{18}-modified silica, mainly used for the extraction of non-polar compounds [1,11]. For the extraction of polar substances, such as phenols, DVB is more suitable [11]. It is the most commonly used polymeric resin [1]. Table 1 gives examples of applications of different sorbents in disk SPE for water analysis. Due to the great variety of available sorbents, selective extraction of substances is possible [11], so SPE disks have many fields of application in various analytical areas of interest [4].

SPE disks are widely used in water analysis for chemical substances [20]. This applies to analysis of emerging pollutants summarized in the Supplementary material, Table 2, as well as new sorbent types {e.g., carbon nanotube-based sorbents [15,16]}. However, SPE disk procedures for the analysis of the whole water sample are currently in the focus. The European Directive 2000/60/EC, the so-called Water Framework Directive (WFD), requires investigation of the whole water sample {i.e., the water sample including SPM [28,29]}. However, there are hardly any methods validated for water samples containing larger amounts of SPM [27], so the **European Committee for Standardization** (CEN) expressly requires disk SPE to be checked as alternative to existing methods (e.g., cartridge SPE and Soxhlet extraction) for the analysis of the whole water sample for several substance groups {e.g., polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and organic chlorinated pesticides (OCPs) [27]}. This is also reflected by the current establishment of standardized procedures by CEN. In turn, the number of SPE-disk users is likely to increase substantially in the future [30,31].

Table 1
Examples for sorbents used in disk SPE for the analysis of organic substances in water, without considering the different disk types

Sorbent	Extracted substances
C_8	Pesticides [12]
C_{18}	Pesticides [7], organochlorine pesticides (OCPs), organophosphorus pesticides, herbicides, insecticides, polychlorinated biphenyls, phthalate esters, polycyclic aromatic hydrocarbons (PAHs) [13]
Graphitized carbon black	Pesticides [14]
Single-walled carbon nanotubes	Nonpolar and polar analytes [15,16]
Styrene divinylbenzene (DVB)	Pesticides [7], phenols [11,17], phenylureas, organophosphorus compounds [7]
Sulfonated resin-loaded	Polar organic compounds such as phenols, alcohols, nitro-compounds, aldehydes, esters and haloalkanes [17]
Strong cation exchange (SCX)	Polar pesticides [18]
Strong anion exchange (SAX)	Polar pesticides [18], anionic pesticides [5], alkylphosphonic acids [19]

Nevertheless, there are no previous reviews in water analysis primarily dealing with SPE disks. If SPE disks are mentioned in reviews, the topic is covered only superficially, regardless of the review focus on (I) technical aspects or (II) substance groups (Supplementary material, Table A1). Only Thurman et al. treated in a detailed “introduction” and “general consideration” parts, different SPE-disk formats, including the construction principles of various SPE-disk designs and their practical use [32]. Consequently, this is the first overview focusing on disk SPE of organic substances in water analysis by using standard SPE disks considering different technical aspects to familiarize the reader with the different disk SPE options and general aspects of relevance in their application.

2. Characteristics and designs of SPE disks

2.1. Characteristics

All characteristics of SPE disks, such as high flow rates and reduced risk of plugging, are due to the large diameter compared to the thickness [33], independent of the SPE-disk designs. This property reduces the back pressure and leads to steady and high flow rates up to 200 mL/min [27], compared to SPE cartridges with typically 5–10 mL/min [17]. A doubling of disk radius leads to an increase of the flow rate by a factor of four [4]. Moreover, the high flow rates and the lower bed volume facilitate the drying of SPE disks compared to SPE cartridges [34].

In addition to the high flow rates, the high cross-sectional area of SPE disks reduces the chance of plugging by SPM contained in water samples [3], so SPE disks are more suitable for investigation of the whole water sample (i.e., the water sample including SPM), compared to SPE cartridges, because samples can be extracted without prior filtration and hence a further sample-preparation step