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Review

Strategies for coupling solid-phase microextraction with mass spectrometry

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ABSTRACT

Solid-phase microextraction (SPME) has experienced significant development since its introduction as a sample-pretreatment technique in the early 1990s. SPME is suitable for interfacing with chromatography and mass spectrometry (MS), but progress in coupling with chromatography has exceeded that with MS. In the past two decades, efforts have been made to couple SPME and MS with different applications in various research fields. Based on these previous studies, this review article summarizes historical developments, principles and operation, practical applications, and recent trends in SPME coupled with five types of MS: (1) electron-impact MS, (2) inductively-coupled plasma MS, (3) laser-desorption/ionization MS, (4) atmospheric-pressure ionization MS and (5) ambient MS (AMS). We particularly emphasize efforts on SPME coupled with AMS.

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1. Introduction

Solid-phase microextraction (SPME), a solvent-free sample-pretreatment technique that integrated sampling, isolation and enrichment of analytes into one step, was developed and implemented in analytical practice in the early 1990s by Professor Janusz Pawliszyn of University of Waterloo (Ontario, Canada) [1–3]. SPME provides significant advantages of simplicity, speed, sensitivity and ease of operation, when compared with conventional extraction techniques, such as liquid–liquid extraction and Soxhlet extraction. In an SPME-based analytical method, a fused-silica fiber coated with polymer is introduced directly into the sample or the headspace (HS) above the sample for enrichment and concentration of analytes, and then transferred to an analytical instrument for thermal/solvent/energy desorption and analysis of analytes [1–6]. The most commonly used analytical approach for desorption, separation, and detection of the analytes enriched on SPME fibers is chromatography. The combination of SPME with different chromatographic techniques has been investigated thoroughly by many research groups since the invention of the SPME technique [1,2,7–14]. SPME coupled with gas chromatography (GC) has been achieved by employing a GC-injection port as interface, in which analytes are released by thermal desorption and carried into GC column for separation and analysis [1,2]. Interfacing of SPME to liquid chromatography (LC) has been developed by applying an SPME desorption chamber as interface for solvent desorption of analytes and then introduction into LC column [10], and automated SPME-LC coupling has been successfully using in-tube SPME as interface [11]. The coupling of SPME with capillary electrophoresis (CE) was successfully realized by applying an adapter for connecting the SPME fiber and the capillary column [12], and in-tube SPME has also been introduced as another interface for on-line coupling of SPME and CE [13].

SPME is also capable of interfacing with mass spectrometry (MS) directly for detection of analytes without employing chromatographic separation. It is well known that MS allows high sensitivity and excellent specificity for rapid determination of compounds from complex matrices, and is a powerful tool for confirmation of targeted components, elucidation of non-targeted analytes, and identification of unknown compounds. However, direct introduction of complex samples into the mass spectrometer usually results in low sensitivity, high matrix effect, and rapid contamination of the instrument. By coupling SPME to MS, extraction, clean up, enrichment and detection of analytes are integrated into one single step. Thus, higher sensitivity and lower matrix-suppression effects can be achieved, and are extremely beneficial for detection of trace compounds from complex matrices. Moreover, the analytical time is greatly reduced because it eliminates the need for chromatographic separation.

The feasibility of SPME coupled with MS has been investigated since the late 1990s, but its progress is not nearly as good as that of SPME coupled with chromatographic techniques. In most cases, the interface of SPME to MS is complicated, requiring a series of modifications of the mass spectrometer. In the past two decades, sub-

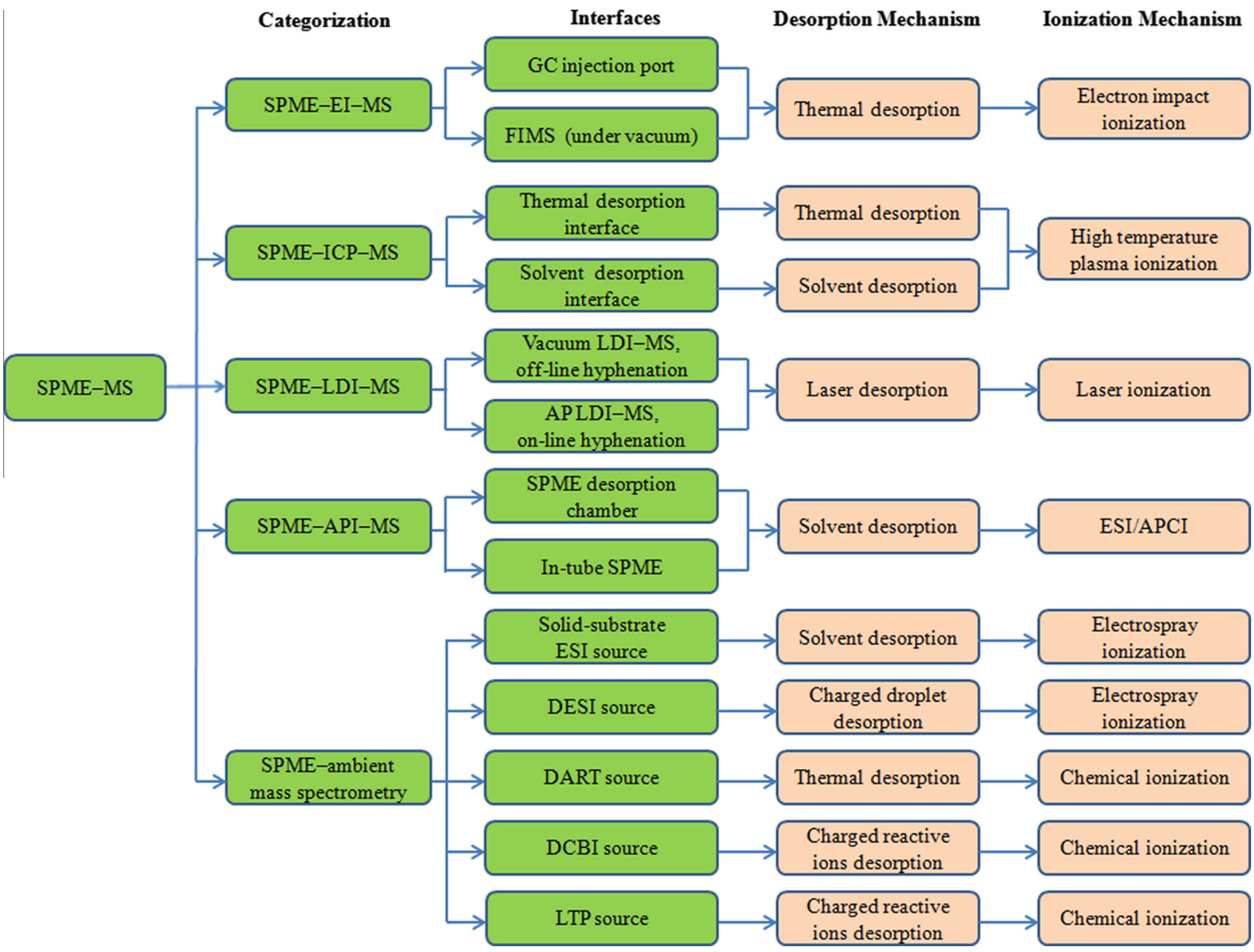

Fig. 1. Logical and methodological categorization of the schemes involved in solid-phase microextraction coupled with mass spectrometry.