



Review

Direct ionization methods in mass spectrometry: An overview



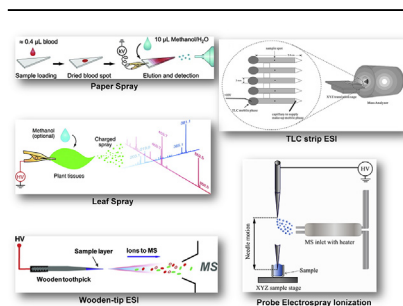
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HIGHLIGHTS

- Positioning of direct spray mass spectrometric techniques as a sub-group of ambient ionization mass spectrometry.
- Comprehensive overview of paper spray mass spectrometry applications published so far.
- Comprehensive overview of tissue spray mass spectrometry applications published so far.
- Comprehensive overview of other direct spray mass spectrometry applications published so far.

GRAPHICAL ABSTRACT



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ABSTRACT

Within this paper a sub-group of ambient ionization mass spectrometry namely direct ionization mass spectrometry techniques are reviewed. They are characterized by the generation of an electrospray directly from the sample investigated. Prominent representatives include paper spray mass spectrometry, tissue spray mass spectrometry, probe electrospray ionization or thin-layer chromatography mass spectrometry. Applications of all major direct ionization techniques within different fields such as biomedical analysis, analysis of natural products, analysis of technical products and food analysis, just to name a few, are discussed and relevant parameters are listed in five Tables.

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Abbreviations: DART, Direct analysis in real time; DESI, Desorption electrospray ionization; ESI, Electrospray ionization; PS-MS, Paper spray mass spectrometry; APCI, Atmospheric pressure chemical ionization; CNT, Carbon nanotube; DEP, Direct electrospray probe; PCA, Principal component analysis; PESI, Probe electrospray ionization; TLC, Thin layer chromatography.

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1. Introduction

Ambient ionization mass spectrometry has faced substantial interest since the introduction of desorption electrospray (DESI) and direct analysis in real time (DART) in 2004 and 2005 respectively [1–3]. In the following years a series of new ionization techniques falling into this sub-group of mass spectrometry (MS) have been developed. Methodological categorization has been performed to allow an unambiguous classification of these ionization techniques with their numerous acronyms. In their excellent tutorial on ambient ionization MS Huang et al. present the following approach allowing the categorization based on basic principles of ionization [3]. Thereby the following groups are defined: i) direct ionization methods, ii) direct ionization/desorption methods, and iii) methods based on a two-step ionization process. Following this scheme prominent techniques like, DESI with its combined desorption and ionization mechanism, desorption atmospheric pressure chemical ionization (DAPCI) or plasma assisted desorption ionization (PADI) can be classified in the second group; DART, based on the interaction of excited gas molecules (mostly helium) either directly with the analyte or via ionization of solvent molecules with subsequent proton transfer, extractive electrospray ionization (EESI), or desorption atmospheric pressure photo ionization (DAPPI) just to name a few examples can be found in the third group. In all these cases dedicated instrumentation i.e. the DART ion source, a dedicated DESI source or an electrospray (ESI) source adapted for DESI has to be employed. The first group defined by Huang et al., based on direct ionization can be regarded as the simplest of these ambient ionization techniques. Thereby an ESI process is generated directly from a solid substrate [4]. Techniques belonging to this group will be covered in the present review paper. These direct ionization methods (mostly from solid-substrate ESI methods) show several distinct advantages. These include the, in most cases, extremely low sample preparation effort, the possibility to directly analyze trace amounts of substances deposited on surfaces without additional extraction step, the avoidance of any clogging problems often encountered in capillary based ESI [4], and the wide range of materials suitable for direct ionization analysis. Not to forget, direct ionization methods can also be seen as a low-cost option to obtain MS spectra from a variety of specimens.

Aim of the present paper is to provide a comprehensive overview of direct ionization MS techniques and their application in various fields of analytical chemistry. Several Tables are included, whereby the direct ionization MS techniques discussed are categorized according to the substrate (solid sample probes, cellulose based materials, plant materials, metal foil and so on) employed for the generation of an electrospray.

2. Paper spray mass spectrometry

Although Fenn, in his patent from 1998 [5], already anticipated paper spray mass spectrometry (PS-MS) by describing a direct ionization method employing cellulose based materials, the actual start of PS-MS is assumed with the paper from Cooks and Ouyang groups in 2010 [6]. Since then PS-MS has developed to the most popular direct ionization method described in this manuscript, a fact that is also represented in several review papers and book chapters published so far [4,7–9].

In the basic PS setup a triangular piece of paper is held by a metal clip and positioned in front of an MS orifice [6]. The sample is placed in the middle of the paper triangle and the metal clip is connected to a high-voltage power supply. Subsequently the paper substrate is wetted by a solvent and as soon as high voltage is applied charged droplets are emitted from the tip of the paper triangle leading to MS spectra typical for electrospray ionization. Representative PS-MS working parameters and conditions are as follows: 3–5 kV for high voltage, 0.4–20 μL of liquid sample or 1–10 mg of solid sample, and 10–30 μL of spray solvent [9]. The spray solvent must suit the application regarding the extraction of the analyte from the sample spot and subsequently the efficient ionization during spraying. In most cases methanol/water based mixtures were used but for best results an optimization depending on the application is needed.

PS is described as a three-step process [6] with the first step being the extraction of analytes from the sample spot by the spray solvent deposited on the paper substrate. In the second step the dissolved compounds are transported to the tip by the solvent wicking through the paper structure and consecutively (when high-voltage is applied) an ESI like process generates charged droplets and ionization occurs [10]. Already in the first publication PS was compared to nano-ESI and both ionization methods generate similar spray plumes and spectra [6], although PS-MS requires a higher spray voltage. In their paper on PS-MS spray mechanism, Espy et al. have particularly focused on the voltage applied for spraying and the correct positioning of the paper triangle in front of the inlet of the MS instrument, thereby defining two modes of operation, as can be seen from Fig. 1 [11]. After deposition of the solvent, mode 1 occurs with high solvent flow rates (in the positive ion mode), resulting in a stable multi-jet spray with a broad droplet-size distribution and spectra dominated by proton-transfer reactions; after significant solvent depletion the system switches to mode 2 with very small, mono-disperse droplets and spectra showing similarities to APCI (i.e. occurrence of electron transfer species). Investigations on the influence of the shape of the paper tip used for spraying [12], changes in analyte distribution by different analyte-to-paper transfer strategies [12], types of solvents used [13], and the positioning of the paper triangle

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