Challenging applications offered by direct analysis in real time (DART) in food-quality and safety analysis

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Direct analysis in real time (DART) is an ambient ionization technique undergoing rapid development. With minimal sample pretreatment, ionization of analyte molecules outside the mass spectrometry (MS) instrument in the ordinary atmosphere is feasible. This ionization approach relies upon the fundamental principles of atmospheric pressure chemical ionization.

The current review highlights and critically assesses application of DART (and some related desorption/ionization techniques) coupled to various types of MS analyzers for both target and non-target analysis of complex food matrices. Based on existing studies, DART-MS is presented as a simple, high-throughput tool for:

(i) qualitative confirmation of chemical identity;
(ii) metabolomic fingerprinting/profiling; and,
(iii) quantification of low-molecular-weight food components, including some trace organic contaminants.

With regard to regulatory requirements, we mention practical aspects of DART-MS use, as well as performance characteristics that can be attained.

Keywords: Ambient ionization; Atmospheric pressure chemical ionization; Contaminant; DART; Direct analysis in real time; Fingerprinting; Food quality; Food safety; Mass spectrometry; Profiling

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1. Introduction

Moving the ionization process from vacuum into the atmospheric environment was undoubtedly a development breakthrough in mass spectrometry (MS). Since their commercialization about two decades ago, systems employing electrospray ionization (ESI) and/or atmospheric pressure chemical ionization (APCI) have found an enormously wide scope of applications, namely in the areas employing liquid chromatography (LC)-based separation. The successful transfer of the ionization process into the open air (i.e. external to the mass spectrometer) resulted in significantly increased flexibility, and thus enabled further explosive expansion of applications. It has to be emphasized that ambient MS (also referred to as "direct ionization MS") allows examination of untreated samples or objects in the open environment, so sample integrity can be maintained. Contrary to "traditional" atmospheric pressure ionization (API) techniques, ions (including analytes) derived from some molecules contained in the sample (i.e. not the entire sample) are introduced into the mass analyzer.

Since the pioneering introduction in 2004 [1], almost 30 ambient ionization techniques for MS have been reported [2]. Among them, namely desorption electrospray ionization (DESI) [1] and direct analysis in real time (DART) [3] have become the most established. DESI, making use of a pneumatically-assisted charged jet, shares the key characteristics with typical ESI in terms of enabling the analysis of substances over a large mass range without significant fragmentation (with a droplet pick-up process proposed as the probable mechanism) [2]. DART, relying upon formation of a (distal) plasma discharge in a heated gas stream, represents an APCI-related technique [4] – thus offering orthogonal ionization potential to DESI.

This up-to-date review presents the DART-MS technique as an emerging tool for diverse applications, not only for food quality control (QC) and safety control but

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0165-9936/$ - see front matter © 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.trac.2010.11.001

also in food authentication. Based on the critical assessment of literature data and our experience obtained in earlier experimental studies, we discuss both advantages and limitations of this ambient ionization approach. In addition to DART, we briefly mention other APCI-related techniques {e.g., desorption atmospheric pressure chemical ionization (DAPCI) [5], low-temperature plasma ionization (LTP), [6] and atmospheric solids analysis probe (ASAP) [7]}.

2. DART-ion source and key features of the mechanism

The key processes taking place in DART-ion source are:

(1) thermo-desorption of condensed-phase analytes by a stream of a hot gas, which carries active species derived from a plasma discharge; and,

(2) APCI-like ionization, enabling acquisition of respective mass spectra.

Fig. 1A shows the lay out of a DART-ion source. Fig. 1B shows the hardware set-up, employing a gas-ion separator (*Vapur* interface) installed between the ion-source exit and the atmospheric-pressure-interface inlet of the mass spectrometer. A membrane vacuum pump connected to the interface enables efficient transfer of the ions through the ceramic tube from the ionization region into the mass spectrometer and maintains stable vacuum within its operating pressure limits.

In DART, metastable species (excited-state atoms and/or molecules of gas) involved in ionization processes are formed *via* a glow discharge occurring in a compartment separated from the sample desorption/ionization area. Charged particles are removed from the gas stream carrying metastable species through the perforated electrode. Then, the gas is heated in order to support thermo-desorption of the analytes from the sample surface. The grid electrode at the exit of the DART gun serves as an ion repeller, which prevents ion-ion recombination, a process that might result in signal loss [3].

In the sampling region, gas metastables react with some ambient atmosphere components to form reactive species, ionizing the analytes together with other sample components. Although the DART-ionization mechanism has not yet been fully characterized, many compound-dependent processes occurring in this ion source have been already identified. As far as helium is used as an ionization gas (the most common case), production of long-lived 2^3S excited state helium atoms with an internal energy of 19.8 eV occurs. Their interaction with neutral analyte molecules may directly yield odd electron ions (cation radicals $M^{+\cdot}$) by the Penning process. The dominating mechanism of positive-ion formation involves:

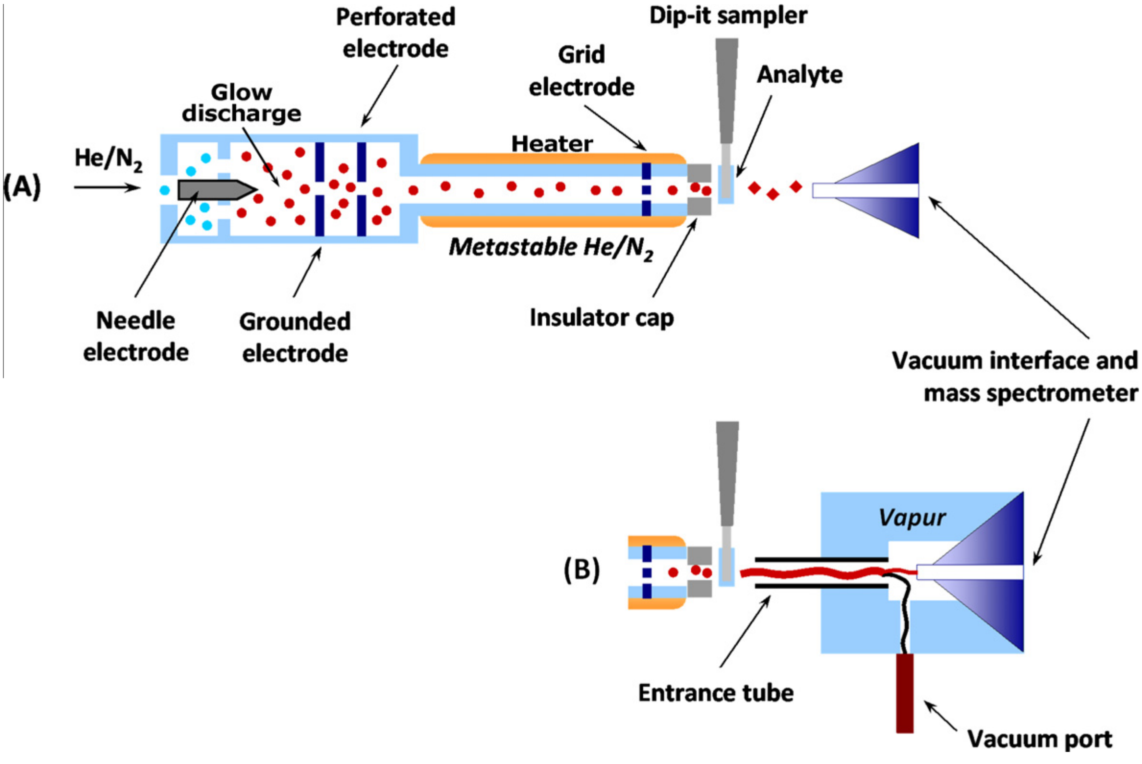

Figure 1. (A) Scheme of DART-ion source; and, (B) scheme of a gas-ion separator (*Vapur* interface) equipped with a vacuum pump.