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Review

Gas chromatography coupled to atmospheric pressure ionization mass spectrometry (GC-API-MS): Review

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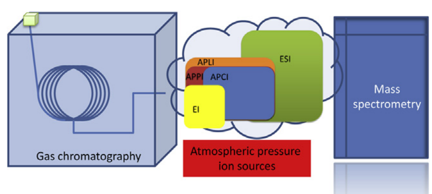
HIGHLIGHTS

- Atmospheric pressure ion sources (APCI, ESI, APPI, APLC etc) enable the coupling of LC-based high-end MS to GC.
- APIs show advantages in selectivity and sensitivity compared with EI in GC-MS.
- Accurate mass database in GC-APCI/MS is emerging as an alternative to GC-EI/MS database.

GRAPHICAL ABSTRACT



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ABSTRACT

Although the coupling of GC/MS with atmospheric pressure ionization (API) has been reported in 1970s, the interest in coupling GC with atmospheric pressure ion source was expanded in the last decade. The demand of a “soft” ion source for preserving highly diagnostic molecular ion is desirable, as compared to the “hard” ionization technique such as electron ionization (EI) in traditional GC/MS, which fragments the molecule in an extensive way. These API sources include atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI), atmospheric pressure laser ionization (APLI), electrospray ionization (ESI) and low temperature plasma (LTP). This review discusses the advantages and drawbacks of this analytical platform. After an introduction in atmospheric pressure ionization the review gives an overview about the history and explains the mechanisms of various atmospheric pressure ionization techniques used in combination with GC such as APCI, APPI, APLI, ESI and LTP. Also new developments made in ion source geometry, ion source miniaturization and multipurpose ion source constructions are discussed and a comparison between GC-FID, GC-EI-MS and GC-API-MS shows the advantages and drawbacks of these techniques. The review ends with an overview of applications realized with GC-API-MS.

Contents

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1. Introduction

Gas chromatography interfaced to mass spectrometry (GC/MS) is a well-established and powerful method for the analysis of volatile and thermally stable analytes. A great number of applications could be found in the areas e.g. environment, food and toxicology [1]. The technique of GC/MS combines the efficient GC separation with the spectral information and satisfactory sensitivity provided by MS. In comparison to liquid chromatography interfaced to mass spectrometry (LC/MS), GC/MS presented several advantages, namely higher chromatographic resolution and higher peak capacity, a single mobile phase (helium or hydrogen), fewer issues with solubility, and separations that can be optimized by electronic controls such as temperature programming [2].

The effluent from the GC is introduced into the vacuum system of mass spectrometer [2]. The separated analytes are traditionally ionized in a vacuum system prior to detection by MS. Electron ionization (EI) is the most adopted ionization technique for GC/MS because of its capability to ionize a broad range of organic compounds and availability to search against an EI-MS spectral library [3].

Typically, the molecule is extensively fragmented during ionization process. For many compounds, characteristic mass spectra are obtained. But in other cases, fragment ions are less specific, or fragmentation is too extensive, which reduces the sensitivity [4]. Furthermore, the highly diagnostic molecular ion is often absent, which hinders the identification of co-eluting low abundance molecules. Positive and negative ion chemical ionization (CI) are also commonly used in GC/MS, particularly in determination of molecular weights. CI has considerably less fragmentation but with reduced sensitivity in comparison with EI. Therefore, other soft ionization technique for GC are necessary. On the other hand, soft ionization techniques were often applied in LC/MS (Fig. 1), in which ionization process occurs at atmospheric pressure and then the ions are swept into the vacuum system through differentially pumped regions.

The ionization mechanisms occurring in atmospheric pressure ionization (API) sources are of low-energy (soft), which generate spectral data typically rich in molecular or protonated molecule information. Ionization in LC/MS can be realized by electrospray ionization (ESI) [5], atmospheric pressure chemical ionization (APCI) [6], photoionization (APPI) [7,8], atmospheric pressure laser ionization (APLI) [9,10] and others [11,12]. In GC-MS and LC-MS different instruments are used, since in GC-MS compounds are ionized at vacuum (EI and CI) and in LC/MS at atmospheric pressure [13]. But GC/MS can also be used under atmospheric pressure ionization conditions. In 1970s Horning and coworkers and in 1980s Korfmacher and coworkers have shown straightforward interfacing GC to MS by using APCI. However, in the later 15 years, GC-API-MS has been reported occasionally [14–16]. In 2005,

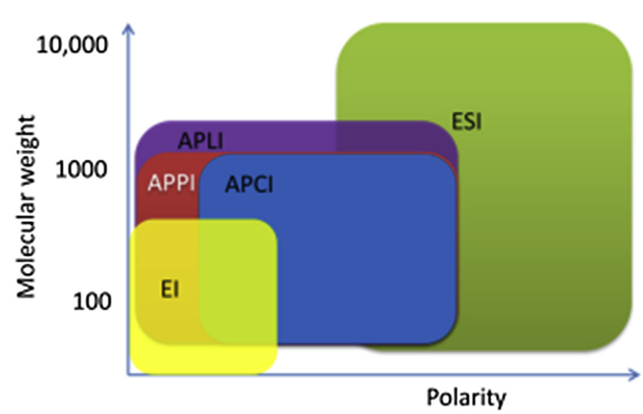

Fig. 1. Ionization ability of different ion sources.