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Review

Photo-ionisation mass spectrometry as detection method for gas chromatography
Optical selectivity and multidimensional comprehensive separations

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Abstract

Mass spectrometry (MS) with soft ionisation techniques (i.e. ionisation without fragmentation of the analyte molecules) for gaseous samples exhibits interesting analytical properties for direct analysis applications (i.e. direct inlet mass spectrometric on-line monitoring) as well as mass spectrometric detection method for gas chromatography (GC–MS). Commonly either chemical ionisation (CI) or field ionisation (FI) is applied as soft ionisation technology for GC–MS. An interesting alternative to the CI and FI technologies methods are photo-ionisation (PI) methods. PI overcomes some of the limitations of CI and FI and furthermore add some unique analytical properties. The resonance enhanced multi-photon ionisation (REMPI) method uses intense UV-laser pulses (wavelength range ∼350–193 nm) for highly selective, sensitive and soft ionisation of predominately aromatic compounds. The single photon ionisation (SPI) method utilises VUV light (from lamps or laser sources, wavelengths range ∼150–110 nm) can be used for a universal soft ionisation of organic molecules. In this article the historical development as well as the current status and concepts of gas chromatography hyphenated to photo-ionisation mass spectrometry are reviewed.

Keywords: Gas chromatography; Photo-ionisation; Mass spectrometry; GC–MS; REMPI; SPI

Contents

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1. Introduction

For analysis of complex samples typically hyphenated analytical methods are applied, combining chromatographic separation and spectroscopic/spectrometric detection techniques such as mass spectrometry or IR-spectroscopy. Gas chromatography (GC) is a standard separation technique for volatile and semi-volatile organic compounds up to molecular masses of about 500 Da. Very polar compounds, such as e.g. poly-alcohols, need to be derivatised prior to GC separation. Mass spectrometry is the most commonly applied spectrometric detection method for GC (GC–MS). Often quadrupole (QMS) or ion trap (ITMS) mass spectrometers are used for this purpose. The standard ionisation technique in GC-MS is electron impact ionisation (EI) with electrons of 70 eV kinetic energy. EI is a universal ionisation method, since all organic compounds are ionised with a comparable efficiency. Organic compounds usually are heavily fragmented upon the ionisation process. The resulting fragmentation ion pattern in the mass spectrum represents a more or less specific fingerprint of the analyzed molecule. Thus compounds often can be identified using mass spectrometric libraries. Ideally the mass spectrum of a (separated) compound contains the molecular mass peak as well as several characteristic fragment peaks. However in many cases the interpretation is hampered because the molecule is too fragile and does not exhibit a molecular mass peak and/or the fragment pattern is not specific.

For complex samples even highly resolved capillary chromatograms gas often only can achieve a far beyond complete separation. Ultra complex samples, such as mineral oil fractions or ambient particular matter extracts, thus typically exhibit regions where multiple overlapping eluent peaks form broad congested areas in the chromatogram (UCM, unresolved complex mixture). An improved analysis of such highly complex mixtures can be achieved by further increasing the selectivity of hyphenated instrumental analytical technologies. In general two strategies are possible to increase the selectivity of hyphenated analytical methods:

(i) Enhancement of the separation power of the chromatographic technique.
(ii) Improvement of the selectivity of spectrometric detection technology.

The first possibility, the enhancement of the gas chromatographic resolution, is an active, current research field. In particular the technology of comprehensive two-dimensional gas chromatography (GC × GC) needs to be mentioned in this regard [1–7], which may be representing a similar step in the development of gas chromatography like the introduction of fused silica capillary columns was.

However, this review is focussing on the second optimisation strategy, namely the improvement of the selectivity of the spectrometric detection technology. In detail mass spectrometry is considered and here specifically the selectivity enhancement that can be gained by mass spectrometry using soft photo-ionisation techniques.

The selectivity of the mass spectrometric detector again can be increased by different approaches. Mass spectrometers with high or ultra-high mass resolution, e.g., allow the deduction of the elemental composition of the detected ions (i.e. via the exact mass numbers). Another possibility is the application of tandem mass spectrometry (MS/MS), where mass selected ions of a (first) mass spectral analysis are again excited, fragmented and analyzed in a further mass spectroscopic separation step. Finally soft and selective ionisation methods can be applied. Selective ionisation methods only ionise compounds with specific chemical or physical properties and typically do show no or little fragmentation (soft ionisation). The most common soft and selective ionisation methods for gaseous compounds are:

(i) Chemical ionisation (CI) [8–10], where the analyte molecules are ionised by chemical ion-molecule reactions,
(ii) Field ionisation (FI) [11–13], where molecules are ionised by very high electrical fields in the close proximity of emitter needles and finally
(iii) Photo-ionisation (PI), were analyte molecules are ionised by absorption of two or more ultraviolet (UV) or one single vacuum ultraviolet (VUV) photon.

The photo-ionisation mass spectrometry technique exhibits unique selectivity properties. Briefly, two principally different photo-ionisation methods can be applied: The resonance enhanced multi-photon ionisation technique (REMPI) uses intense UV-light laser pulses for a two photon absorption/ionisation process and is highly selective for aromatic molecules. The single photon ionisation method (SPI) on the other hand uses VUV-photons for the ionisation. Sufficiently intense VUV-light can be generated by a laser process (third harmonic generation, THG) or by high performance lamps such as special electron-beam pumped rare gas excimer lamps (EBEL, see [14–17]) or conventional discharge VUV-lamps [18–20]. This paper is structured as follows: Firstly the background of the REMPI- and SPI-MS methods is briefly highlighted. In the main section the application of photo-ionisation mass spectrometry as gas chromatographic detector is reviewed. This section consist of two parts, the first one deals with gas chromatography–REMPI photo-ionisation mass spectrometry methods and applications while the second part describes the newly upcoming gas chromatography–SPI photo-ionisation mass spectrometry technology. The review closes with a short conclusion.

2. Resonance enhanced multi-photon ionisation (REMPI) and single photon ionisation (SPI) as photo-ionisation methods for mass spectrometry

The laser based resonance enhanced multi-photon ionisation technique (REMPI) combined with mass spectrometry technique was introduced in 1978 for analysis of polyatomic molecular species [21]. In the REMPI process a simultaneous absorption of at least two UV-photons are used for photo-ionisation utilising an optical resonance absorption step. If the photon power density of the pulsed laser is adjusted in the