Dielectric Barrier Discharge Microplasma-Ionization for Liquid Chromatography / Mass Spectrometry

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Introduction

The coupling of liquid chromatography and mass spectrometry (LC/MS) has been established as one of the most powerful tools in analytical chemistry and has resulted in important advances especially in biomedical and biochemical research. The predominantly used interfaces are electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). Non-polar compounds, however, are difficult to analyze with these atmospheric pressure ionization (API) techniques due to their soft ionization mechanism. It is therefore desirable to expand the applicability of LC/MS with API techniques to the determination of rather non-polar compounds. The presented API method is based on a dielectric barrier discharge microplasma-ionization, and provides superior ionization efficiency for non-polar analytes compared to ESI, APCI and atmospheric pressure photoionization (APPI).

Method

An atmospheric pressure microplasma-ionization source based on dielectric barrier discharge (DBD) has been developed for LC/MS. Therefore, a DBD discharge probe was implemented into a commercial API source (Ion Max source, Thermo Fisher Scientific). The coupling was realized to a linear ion trap and a hybrid ion trap-Fourier transform ion cyclotron resonance mass spectrometer. The latter instrument was used for elemental composition determinations of possible ionization artifacts, e.g. oxidation and degradation products by exact mass measurements. A small library of model compounds covering a wide range of polarities was investigated in order to evaluate the performance of the DBD microplasma-ionization.

Preliminary Data

The DBD microplasma had a helium plasma cone outside the electrode region [1]. This DBD microplasma ionization was compared to conventional ESI, APCI, APPI as well as a combined APCI/APPI source in the positive mode. Special emphasis was paid to ionization efficiency and the occurrence of possible oxidation and degradation products. Therefore, a heterogenous compound library was investigated covering polar compounds such as amino acids (lysine, tryptophan, threonine, glutamamic acid), water-soluble vitamins (biotin, riboflavin) and non-polar compounds like hydrocarbons (azulene, bipheneylene, anthracene, fluorene, phenanthrene, benzo[a]pyrene) and functionalized hydrocarbons (9-carboxyanthracene, 2-aminoanthracene, 9,10-anthraquinone). The ionization by DBD microplasma ionization was mainly dominated by the formation of protonated molecules and only little fragmentation was observed. Besides the protonated molecule, radical cations were detected for non-polar hydrocarbons. However, some oxidation due to ozone formation from residual oxygen in the ionization source was observed. In general, compounds covering a wider range of polarities can be ionized by DBD microplasma than by ESI. Furthermore, limits of detection compared to APCI, APPI and APCI/APPI are in most cases better or at least equal.

Novel Aspects

Dielectric barrier discharge microplasma as novel ionization method for LC/MS analysis of non-polar compounds

References