

**ION- AND PHOTON- INDUCED MASS
SPECTROMETRY OF NATURAL PRODUCTS:
ION FORMATION, MATRIX EFFECTS AND INSTRUMENTATION**



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Abstract

Ionization pathways and matrix-effects in plasma desorption (PD) and laser desorption (LD) time-of-flight (TOF) mass spectrometry (MS) of low-mass (0.1-1.0 kDa) natural products (alkaloids and compounds that are present in spicy plants) have been studied in this thesis.

The PD-TOF-MS results of natural products suggest that most of the target specific fragment ions are formed via uni-molecular dissociation of M^+ and MH^+ ions probably in the selvedge (gas) phase. The low-mass (i.e. less than m/z 70) positive ions, formed under PD conditions are found to be mostly unspecific in nature. These ions could originate either from the hot core of the infra-track or from the surrounding area of the track and the 'entropic breakup model' best describes the formation of these ions. In contrast, a universal hydrocarbon negative ion series independent of the target compound is observed for negative ions and the 'adiabatic expansion model' best describes the formation of these ions.

Probable explosive matrix-assistance in PD-TOF-MS, via the explosive energy flow through explosive decomposition under the action of ^{252}Cf fission fragment impact, has been demonstrated using a matrix (HMX)/analyte (insulin) as a model. Probable intermediate products that result from explosive decomposition (e.g. NO, NO₂, HNO₂, HCN), which are in highly vibrationally excited states are assumed to transfer their "excess" vibrational energy to analyte (e.g. proteins) molecules for their efficient desorption/ionization. Furthermore, an enhanced protonation of the analyte is explained through collisions with chemically decomposed products of explosives and due to their electron scavenging effect.

The LD-TOF-MS results of natural products indicate dominant ion-molecular reactions in the laser plume (i.e. in the gas phase). However, in matrix-assisted laser desorption/ionization (MALDI) conditions, ion-molecular reactions are considerably reduced. The ionization step is likely to take place at the very early stages of the development of the MALDI plume, where the excited-state matrix molecules are likely to act as precursors to produce protonated analyte species via matrix to analyte proton transfer mechanism.

Different mass spectrometric techniques such as PD, delayed extraction-MALDI and electrospray ionization (ESI) coupled to either TOF with an electrostatic ion reflector or Fourier transform ion cyclotron resonance mass analyzer with MS/MS are used to detect, isolate and characterize the individual components present in a mixture of alkaloids and curcuminoids in a curcumin sample.

Thesis also describes the construction details and preliminary results of the performance of a MALDI-TOF mass spectrometer that has been constructed at the Department of Physics, University of Colombo for the first time. As the initial results, the protonated molecular ions of try⁸-bradykinin (1077.2 Da) and N-acetyl renin substrate (1802.1 Da) have been obtained.