# Structural Content in Field Induced Fragmentation Spectra from Tandem Ion Mobility Spectrometry toward Molecular Identification

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Ion mobility spectrometry (IMS) has been widely accepted as a selective detector for volatile and semi-volatile organic compounds particularly in commercial aviation security and military preparedness. The selectivity and detection limits needed in these applications have been satisfied by IMS through a combination of atmospheric pressure chemical ionization (with charge concentrated in one or two product ions of analytes) and the selectivity provided by mobility coefficients with resolving powers of 30 to 60 in air at ambient pressure. The simple profiles in mobility spectra for volatile organic compounds (VOCs) at ambient pressure do not contain seemingly the structural information necessary to provide a capability for molecular identification. Consequently, ion mobility analyzers at ambient pressure have been considered sensitive and selective detectors, only. Tandem embodiments of mobility spectrometers have been developed recently with a reactive region where an ion can be mobility-selected in a first mobility stage, fragmented using electric fields > 100 Td in a middle reactive stage, and resulting fragment ions mobility characterized in a subsequent mobility stage, all at ambient pressure. These field induced fragmentation (FIF) spectra have been analysed using back-propagation neural networks to assign of spectra by chemical class as a first step towards molecular identification. Classification rates for FIF spectra are >98% for compounds within a spectral library and as much as 70% for unfamiliar compounds never seen by the neural network (i.e., true unknowns). The concept of spectral classification by chemical family using FIF spectra with tandem ion mobility spectrometers has been demonstrated with small yet conventional drift tubes and with planar differential mobility spectrometers. Results from neural network analyses of FIF spectra, of mobility-selected spectra for protonated monomers, and of whole spectra demonstrate that structural information is introduced into mobility spectra through middle stage fragmentation of mobility-selected ions. Both the classification and the mis-classification of spectra can be explored using graphic tools based on radar charts to analyze neural network findings. The significance of these developments will be described toward molecular identification using mobility based technologies.