

Thermally Assisted Vapour Introduction Atmospheric Pressure Photoionization MS/MS (TAVI APPI MS/MS)

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Thermally Assisted Vapour Introduction Atmospheric Pressure Photoionization Mass Spectrometry (TAVI APPI MS/MS) is presented as a versatile and rapid characterization technique for various solid and liquid organic and organometallic compounds. Using a Waters Quattro Premier LC MS/MS fitted with a Syagen PhotoMate photoionization lamp, samples of pure compounds and mixtures were heated to release vapours that were photoionized and introduced into a triple quadrupole mass spectrometer yielding exclusively molecular ions within seconds. In addition to observing pure molecular ion signals, Collision Induced Dissociation can be used to induce fragmentation to offer structural information.

This technique does not require a liquid sample solution and could easily determine the molecular weights of insoluble organometallic crystals with minimal sample preparation. Solid samples were tapped into a glass melting point capillary tube which was resistively heated directly below the photoionization lamp. Liquid samples could be either injected in a heated glass capillary tube or spotted onto a Lithium Fluoride plate that was held directly in front of the PI lamp. TAVI APPI MS/MS offers simple mass spectra dominated by molecular ion, $[M]^+$, signals compared to solvent based APPI which generally leads to $[M+H]^+$ [1].

Since its introduction in 2000 [2], Atmospheric Pressure Photoionization has been proven to be a useful, complimentary ionization technique to standard Electrospray and Chemical Ionization techniques, allowing non-polar compounds such as PAH's and lipids to be ionized [2, 3, 4]. In general, photoionization spectra have far fewer confounding peaks as compared to ESI [5] and do not suffer from ion suppression in complex matrices to the same extent as CI [4]. Photons are produced from an electrical discharge in a rare gas. The photon energy is dependent on the gas used; Krypton discharge lamps release photons at 124 and 117 nm corresponding to 10.0 and 10.6 eV, respectively [3]. Photons may ionize molecules with ionization potentials less than the energy of the photons with little fragmentation, as the excess energy is transferred to the departing electron [3], forming molecular ions.

The impetus of this research grew from requests from inorganic chemists at our university who required confirmation of their synthetic reactions. Compound solubility and small sample size where two challenges presented. There have been various recent attempts to find an appropriate mass spectrometric techniques to analyze organometallic and coordination compounds. Previous work by Dorcier et al. using photoionization on organometallic compounds

dissolved in solvents produced mixed results; molecular ions were observed but significant toluene substitution, analyte methylation and various unidentified peaks were also observed [6]. A “solvent-free” technique is desirable for insoluble compounds or compounds that may dissociate in solution. A recent paper by Hughes et al. reported success with the use of MALDI-TOFMS on organometallic and coordination compounds. For most of the compounds evaluated, strong molecular ions were observed, but sodium and potassium adducts were also observed [7].

To evaluate TAVI APPI MS/MS, a range of PAH and organometallic compounds were examined. For the majority of compounds pure molecular peak was observed. Mass spectra were extremely clean for PAH's, organometallic, polyphenolic compounds.

In positive mode naphthalene, biphenyl, anthracene, phenanthrene, pyrene, fluoroanthene, trans stilbene, rescorinol, salicylic acid, benzdiamine, ethyl-4-aminobenzoate all exhibited strong M^+ ion. Various novel inorganic compounds were found to be amenable with TAVI producing molecular ions.

Structural information could be rationalized with TAVI APPI CID MS/MS. While high energy electron impact ionization is distinct from CID fragmentation, comparisons between EI spectra and CID MS/MS showed general agreement to reference EI spectra. A compound with one of the strongest signals was ferrocene (molecular weight 186.04) with an impressively strong molecular ion at m/z 186. CID on the molecular ion gave nearly identical mass spectra as compared to reference EI spectra. The dominant peak was easily identifiable as loss of a cyclopentadienyl ring. Other organometallic compounds had similar results; $Cr(acac)_3$ had a strong molecular peak and when subjected to CID; readily produced expected daughter ions that corresponded to electron impact. Not all compounds gave pure molecular peak, $Fe(acac)_3$ for example had very strong peak assigned as $[M+H-acac]^+$ ($[M - acac]^+$ peaks were seen by Hughes et al.) and also $Fe(acac)_3$ produced an ion assigned as $[2M-acac]^+$.

Future work will focus on several aspects: the effect of reaction time in the ion source on ion distribution as controlled by path length, gas flows, cone and repeller voltages. Comparisons between solvent-free, dopant enhanced and traditional solvent based APPI may offer insight into ionization mechanisms. Future work will also focus on introduction methods for air sensitive compounds. Initial testing of using an inert sheath gas around the heated capillary tube has shown promise. Alternatives to Krypton discharge lamps for ionization will be examined with the aim of creating versatile ion sources.

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