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Ph.D. DISSERTATION DEFENSE

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Title:	Structural Dynamics of Tautomeric Forms and Artifacts of Aniline and Related Compounds under APCI (Atmospheric Pressure Chemical Ionization) Mass Spectrometry Conditions
Chairperson:	Dr.Athula Attygalle, Department of Chemistry and Chemical Biology, School of Engineering and Sciences
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ABSTRACT

Thermally desorbed aniline and 4-nitroaniline, upon atmospheric pressure chemical ionization (APCI), generate gaseous ions through protonation. In the case of 4-nitroaniline, the presence of both amine and nitro groups enables protonation to occur at different sites, resulting in the formation of multiple tautomeric species. Previous studies have demonstrated that ion source parameters and the nature of the spray solvent can significantly influence the formation of these tautomeric species under electrospray ionization (ESI) conditions.

Herein, we demonstrate that tautomers generated from thermally 4-nitroaniline by ASAP-APCI (atmospheric solids analysis probe – atmospheric pressure chemical ionization), without any solvent mediation, exhibit behavior similar to the ion mixtures generated by ESI technique. Moreover, we show that APCI source settings, such as corona current magnitude, sample placement location within the ion source, and desorption-gas temperature, significantly influence the rate of artifact formation from aniline. Recognizing and acknowledging the formation and presence of artifacts in an ion source is paramount for validated chemical analysis. Their existence can complicate mass spectral interpretation, potentially leading to erroneous conclusions and misinterpretations of both qualitative and quantitative data. Thus, understanding the intricacies of nonthermal plasma-driven artifact formation is critical for accurate analytical outcomes.