B16 Argon Direct Analysis in Real-Time Mass Spectrometry (Ar DART®-MS) for Forensic Analysis of Illicit Drugs

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After attending this presentation, attendees will understand a new mode of DART®/MS using Ar instead of the popularly used Helium (He) as the DART® ionization gas, its ionization mechanism toward polar compounds, its capability in positively identifying commonly abused drugs, and its application in successfully analyzing drug tablets.

This presentation will impact the forensic science community by introducing a novel Ar DART®/MS technique as an alternative to He DART®/MS for forensic analysis of illicit drugs, especially in consideration of the looming worldwide helium shortage.

Helium was originally selected as the DART® gas because its long-lived $^2S_3$ state has an Internal Energy (IE) of 19.8eV, which is the highest among inert gases; however, a helium shortage has been looming over the past ten years. Argon is the most abundant noble gas in the air at 9,340ppmv, third only to nitrogen and oxygen. To this point, dopant-assisted Ar DART®/MS has been investigated for the analysis of melamine, labile compounds, polycyclic aromatic hydrocarbons, diesel fuels, etc. In this study, Ar DART®/MS is explored as an alternative to He DART®/MS for the forensic analysis of illicit drugs, without the assistance of any dopant.

The ionization capability of Ar DART®/MS was first tested with polar solvents, including water, acetonitrile, methanol, ethanol, isopropanol, ethyl acetate, acetone, and tetrahydrofuran with respective ionization energy of 12.62eV, 12.20eV, 10.84eV, 10.50eV, 10.17eV, 10.01eV, 9.70eV and 9.40eV. It was found that Ar DART®/MS was unable to efficiently ionize water, acetonitrile, and methanol, but was able to ionize ethanol moderately and the rest of the polar solvents efficiently. Therefore, it was concluded that Ar DART®/MS was able to ionize all the organic compounds, including illicit drugs as they are molecularly larger and should have IE lower than ethanol.

Subsequently, ten commonly abused drugs (i.e., (±)-amphetamine, cocaine, diazepam, heroin, Lysergic Acid Diethylamide (LSD), (±)-3,4-Methylenedioxymethamphetamine (MDMA), Phencyclidine (PCP), psilocin, testosterone, and Δ^9-Tetrahydrocannabinol (THC)) were analyzed by Ar DART®/MS to test the ionizing capability of Ar DART® toward compounds with diverse functional groups, optimize the instrumental conditions for the analysis of illicit drugs, estimate the Limit Of Detection (LOD) of the analysis, and develop a general analytical protocol for the analysis. Under optimum conditions, the LOD of Ar DART®/MS was determined to be approximately 100μg/mL. Because the sampling volume was approximately 1μL, the LOD of Ar DART®/MS was approximately 100pg in quantities. The general analytical protocol took approximately three minutes in the analysis of each commonly abused drugs. All the commonly abused drugs were positively identified at 100μg/mL because the experimentally measured monoisotopic mass of the predominate $[M+H]^+$ ion, sometimes with the additional molecular ion, from each drug were within ±5mDa of the theoretically calculated monoisotopic mass. No time-consuming and labor-intensive sample preparation steps were required during the analysis.

Finally, the general analytical protocol was applied to tablet analysis of six prescriptions drugs (i.e., clonazepam 1mg, cyclobenzaprine 10mg, metaxalone 800mg, oxycodone/acetaminophen 5/325mg, tramadol/APAP 37.5/325mg, and zolpidem10 mg). It was found that while Ar DART® was able to efficiently ionize and subsequently identify the active ingredients, it practically omitted the inactive ingredients in the tablets.

The ionization mechanism of Ar DART® was likely the generation of protonated molecular ions through direct Penning ionization of polar compounds by metastable Ar followed by self-protonation of the analytes, which was also confirmed by the observation of molecular ions of some commonly abused drugs. In comparison with He DART®, Ar DART® generated much cleaner background mass spectrum and simpler mass spectra of tested drugs due to the lower IE of metastable Ar species, which was an advantage in data analysis; however, Ar DART® had an LOD approximately two orders of magnitude higher, though it should be still sensitive enough for the analysis of seized drug evidence.

Illicit Drugs, Ar DART®/MS, Tablet Analysis