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Forensic Chemical Analysis of Synthetic Cathinones Using Portable Mass Spectrometric Instrumentation

Caitlin N. Cain
Virginia Commonwealth University

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Departments of Forensic Science and Chemistry

Introduction

Forensic laboratories are backlogged with evidence of suspected illicit drugs.

- The Virginia Department of Forensic Science receives over 30,000 controlled substances cases a year [1].
- The Virginia Department of Forensic Science's average turnaround time on these cases was 75 days [1].

The U.S. DEA reports that emerging "designer drugs" are the main contributor to the evidence backlogs [2].

"Designer Drugs"

Synthetic cathinone derivatives have become the drug of choice within the past decade due to their legality issues.

- Packages commonly labeled as "bath salts" or "plant food" with the notice that they are "not for human consumption" [3].
- By changing the synthesis process slightly, new derivatives can be made instantly that are not covered under current laws [4].

Synthetic Cathinones

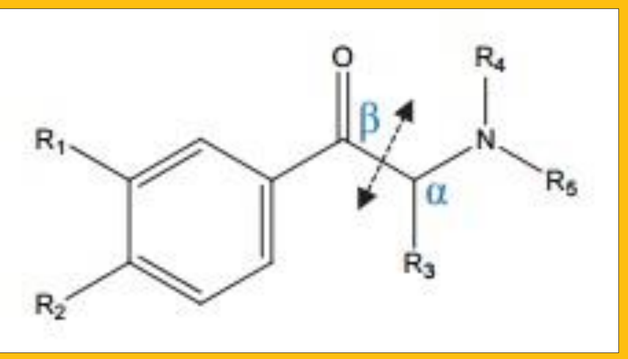

Figure 1: General structure of a synthetic cathinone derivative showing substitution patterns [4].

Objective

This study had two main objectives:

1. To understand the difficulties associated with identifying synthetic cathinones using current methods found in forensic chemistry laboratories.
2. To investigate portable mass spectrometric methods for on-site analysis of samples to reduce the strain of the evidence backlogs.

Methods

A comparison of research on gas chromatography-mass spectrometry (GC-MS), typically used in forensic laboratories, and ambient mass spectrometry, an upcoming method, was conducted to determine which technique would be more suitable for on-site analysis of synthetic cathinones.

Results

Finding #1: Problems with GC-MS

When analyzing synthetic cathinones with GC-MS, three main problems occur:

1. **Sample Preparation**: Because the typical evidence sample can contain multiple synthetic cathinone derivatives and other adulterants, an extensive acid-base combined extraction as outlined by Agilent Technologies is necessary before injection into the GC port [5].
2. **Stationary Phase Used**: Most forensic laboratories use phenyl columns that are slightly polar. However, due to the chirality and isomerism of synthetic cathinones, these columns are ineffective for separation of these samples [6].
3. **Thermal Degradation of the Sample**: These drugs are thermally instable. Therefore, when injected into the heated GC port for evaporation before analysis, the sample undergo an oxidative decomposition with loss of a hydrogen, causing spectral fragmentation [4].

Finding #2: Ambient Ionization Mass Spectrometry

With ionization of the sample occurring under ambient conditions outside of the mass spectrometer, forensic laboratories can analyze trace-level amounts of evidence with minimum sample preparation in a short amount of time when compared to GC-MS [7].

Due to these capabilities, two ambient ionization methods, desorption electrospray ionization (DESI) and direct analysis in real time (DART), can be coupled with portable mass spectrometers for on-site analysis [8].

DESI-MS

- DESI occurs when a charged species is introduced to a sample for desorption and ionization to occur [9].
- When the DESI spray hits the sample, it ionizes the sample and droplets of various sizes, speeds, and angles accelerate the mass spectrometer inlet [10].
- No sample preparation is needed because DESI-MS can directly analyze samples in the solid state [7].
- Analysis of synthetic cathinones takes approximately 35 seconds to complete [11].
- DESI-MS is able to tell the difference between synthetic cathinone derivatives because of the intense spectral signals given and lack of fragmentation [11].

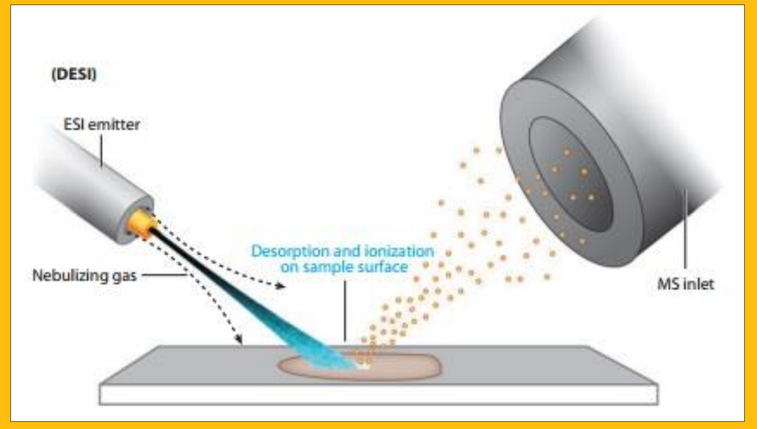

Figure 2: Schematic representation of DESI-MS on a sample [9].

DART-MS

- DART instantly ionizes samples due to atmospheric pressure [12].
- By exposing a sample to a constant stream of excited Helium atoms, the sample ionizes due to the energy transfer between the Helium gas species and the sample [6].
- The only sample preparation required is placing the sample on the closed end of a capillary melting tube to hold between the two instruments [13].
- DART-MS shows the characteristic molecular ion peak and key ion peaks of synthetic cathinone derivatives, even when in a complex mixture, for accurate identification [13].

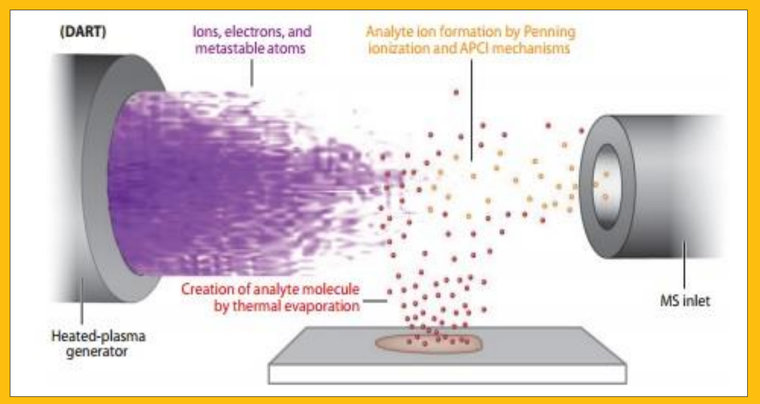

Figure 3: Schematic representation of DART-MS on a sample [9].

Conclusions

An improved stationary phase column and way of regulating temperature at the injection port and throughout the column would have to be created for GC-MS to be used in the field on synthetic cathinone samples. Research has shown that the use of:

- Polysiloxane-anchored cyclodextrin derivatives can be used as a stationary phase for GC separation on enantiomers and isomers of different organic compounds [14].
- Resistive heating systems, such as low thermal mass (LTM) GC, can be incorporated around the GC column to avoid sample degradation [15].

After spending the money on a portable GC-MS system and incorporating these solutions for synthetic cathinone analysis, the extensive sample preparation and amount of time needed for analysis would still make this method impractical for field use.

However, ambient ionization mass spectrometry methods can already be employed for on-site analysis of synthetic cathinones when coupled with a portable mass spectrometer. DESI-MS and DART-MS have been shown to be able to accurately identify synthetic cathinone derivatives, even when in complex mixtures with other adulterants, with minimal sample preparation. Additionally, these methods have the capability to be conducted by non-technical operators, especially when the mass spectrometer is paired with a mass spectral library search algorithm.

Therefore, with the use of portable ambient ionization mass spectrometry techniques, synthetic cathinones would be accurately identified in the field, reducing the controlled substances backlog in forensic laboratories.

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