Novel Coiled Microextraction Sampling Device used for Field Sampling of Illicit Drugs of Abuse and Analysis by Micro Gas Chromatograph/Mass Spectrometer

by Ethan McBride and Guido Verbeck from University of North Texas, Denton TX
Tiffany Arbon and Zachary Lawton from PerkinElmer, Shelton, CT
Correspondence: Tiffany.arbon@perkinelmer.com or Zachary.lawton@perkinelmer.com

Abstract

Micro gas chromatography (GC) is often used in the field, due to its size, for fast analysis of suspected illicit drugs of abuse, where it is easily carried to the source of the sample. Having a field-portable GC is advantageous, especially when decisions need to be made quickly on-scene and one does not have the luxury of time to send samples to a laboratory for analysis. One of the largest challenges for field chromatography is sample preparation, whether the sample is a solid powder or needs to be extracted from the sample matrix prior to injection into the instrument. Typically, sample preparation is the biggest limitation of in-field analysis and is the step that largely affects detection limits. Here, we demonstrate the use of the novel coiled microextraction (CME) syringe and portable GC/MS as a fast and easy-to-use screening tool for drugs of abuse in the field. Data acquired was matched to the Wiley Designer Drug Library, providing results in approximately 8 minutes from sample collection to identification.

Introduction

Gas chromatography/mass spectrometry (GC/MS) has regularly been used by scientists in fixed-based laboratory settings to detect the presence of pain medication. Fortunately, miniaturisation of GC and GC/MS instrumentation has made this technique available for in-field investigators and researchers, and offers a simple, prompt, and onsite identification of drug substances, such as fentanyl. These opioids are frequently produced in clandestine laboratories across the world, and have been found in counterfeit medicines made to look like pharmaceutical products while containing fentanyl analogues, as well as non-opioid substances [1]. Counterfeit drugs and heroin seized after fatal overdoses have been found to include fentanyl analogues, such as acetyl fentanyl, 3-methylfentanyl and the highly potent opioid carfentanil, a veterinary painkiller used for large animals that is approximately 10,000 times as strong as morphine [2]. The variations in potency and quantity of active components in counterfeit pills and powders is a threat to users, as well as the first responders that are exposed to the drugs at clandestine laboratories and intercepted through drug trafficking efforts.

The severity of the opioid epidemic has prompted the need for an analytical solution capable of safely screening confiscated drugs of abuse and clandestine laboratories for the presence of fentanyl analogues. Typically, samples prepared for GC/MS are collected on-site and transported to a forensic laboratory for analysis, but this process can take months due to current case backlogs and lengthy analysis times (15 – 60 minutes) associated with traditional benchtop units [3,4]. An alternative approach, which reduces the time between collection and analysis, is to bring the laboratory to the scene by employing portable GC/MS technology with rapid sampling techniques to acquire actionable results. In this work, we detail the process for analysing samples utilising coiled microextraction and a field-portable GC/MS [5] for the analysis of fentanyl, acetyl fentanyl, and carfentanil.

Coiled Microextraction (CME)

Coiled microextraction (CME) is a novel technique that combines field sample collection and instrument sample injection into a single device for liquid and dissolved solid samples. In HAZMAT applications, such as clandestine drug laboratory searches and potential narcotic seizures, sample collection has often been both cumbersome and potentially dangerous. Working in full personal protective equipment a sample collector's dexterity is often hindered, making it difficult to perform traditional sample collection activities, which can include sharp syringes, small containers, and multiple solvents. To ease this burden and improve on-site safety, the Custodian® CME syringe was developed to allow for single-handed sampling and injection onto a portable GC/MS for analysis.

The CME technology is comprised of a wire that has been coated with Inertium (a surface coating that makes the wire chemically inactive) and finely coiled to capture liquid samples (Figure 1). The coiled wire is housed within the Custodion syringe and traps the solution and target analytes through capillary action. The coil radius and number of turns in the wire (i.e., length of the coil) determine the sampling volume [6]. The CME stays extended while the sample matrix is evaporated, thus eliminating the matrix and leaving the target compounds behind on the coil. The CME is attached to a retractable plunger (part of the Custodion syringe) such that it can be retracted inside a 19 G needle for insertion into a standard GC injection port. The Custodian's hardened plastic handle is as simple to use as a retractable ball-point pen, allowing users to deploy the CME wire with a single button press.

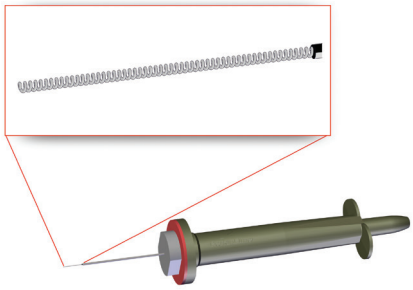

Figure 1. Custodion Coiled Microextraction (CME) syringe with an extended coiled wire.

A CME sampling technique is mostly useful for sampling powders, where the technician dissolves the power into a volatile solvent such as methanol. This is especially useful for identifying powders that are potentially drugs of abuse, or even explosive material. Sampling is easily performed when the wire is extended from the needle and is either dipped in a liquid sample (i.e., sample dissolved in a solvent), which draws up into the wire coil by capillary action, or by applying a specific volume of liquid sample onto the coiled wire using a micro-syringe. Analytes trapped in or on the coiled wire are introduced into the GC injection port before or after solvent evaporation [7] (Figure 2). The sampling and evaporation steps can be repeated several times to concentrate the target analytes onto the coiled wire prior to analysis. The device's design, and its flexible blunt tip, help avoid the safety concerns of a conventional sharp syringe. In addition, the Custodion's ball-point pen like design means users are free to collect samples with only one hand. The single-handed operation and ease of using CME syringes are ideal for first responders, HAZMAT teams and other forensic investigators wearing heavy personal protective equipment.

Table 1 GC/MS Parameters

Sampling	Coiled Microextraction (CME)
Injection Type	Splitless
GC Injector Temp.	270°C
GC Column	MXT-5, 5 m x 0.1 mm, 0.4 µm df
GC Column Temp.	50-300°C at 2°C/s, hold for 60 s
GC Carrier Gas	Helium, 0.2 mL/min.
Transfer Line Temp.	250°C
Ionisation Source	In-trap Electron Impact (EI)
Mass Analyser	Toroidal Ion Trap
Mass Range	41 - 500 Da
Detector	Electron Multiplier
Resolution	< 0.5 m/z at 300 amu, nominal unit mass at 500 amu

Portable GC/MS

Built for portability and rapid analysis, portable GC/MS instruments provide equivalent chromatographic performance to benchtop systems, but with a significantly shorter time to results. The portable GC/MS technology used in this work (Torion® T-9, PerkinElmer) integrates a low thermal mass (LTM) capillary gas chromatograph with a miniaturised toroidal ion trap mass spectrometer to provide a fast, reliable and easy-to-operate GC/MS while minimising power consumption to operate in the field. Weighing only 32 pounds (14.5 kg), the portable device is ideal for use in a wide range of HAZMAT situations where fast and accurate results are paramount.

The miniaturisation of the Torion T-9 GC/MS is achieved by replacing a conventional convectively heated column oven with a low thermal mass column bundle with direct-contact electrical resistive heating. LTM GC uses a small diameter, metal capillary GC column, which is bundled with resistive heating and temperature-sensing wires that are braided together with insulator strands. This design, as shown in Figure 3, provides for greater heating and cooling speeds and very low power consumption.

Experimental

Sample Preparation

Analytical grade standards of fentanyl, acetyl fentanyl, carfentanil, and heroin were obtained from Cerilliant Corp. (Round Rock, TX, USA) at 1.0 mg/mL concentrations. Mock clandestine laboratory samples of fentanyl, acetyl fentanyl and carfentanil were synthesised at University of North Texas (Denton, TX, USA).

Sample collection and injection was accomplished by a Custodion-CME syringe. For analytical standards, a gas-tight syringe was used to apply 5 µL of solution directly to the coiled wire and left to dry for 3-5 minutes

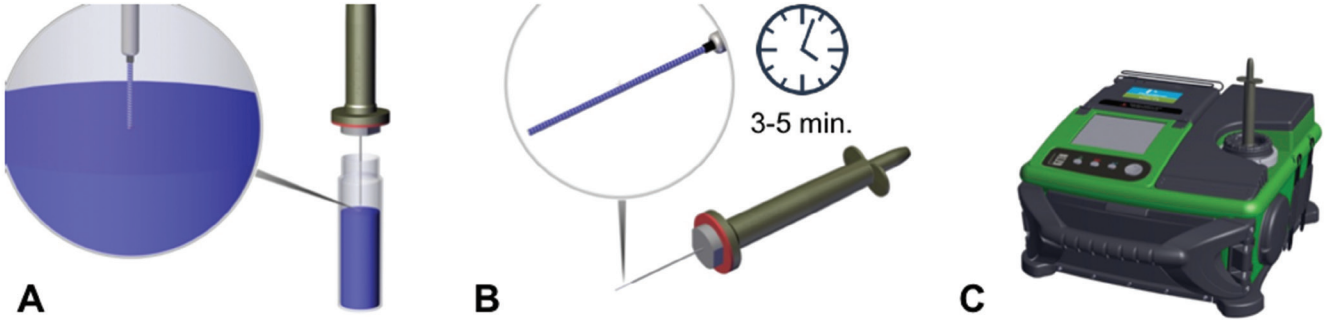

Figure 2. Representation of the sample collection and injection process using CME.

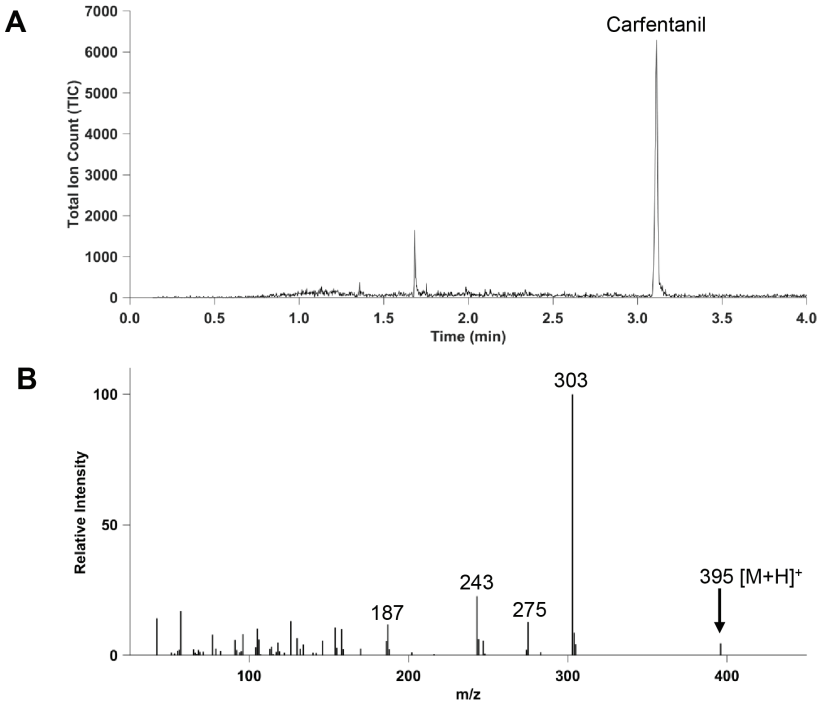

Figure 3: The Torion T-9 Low Thermal Mass Capillary GC design.

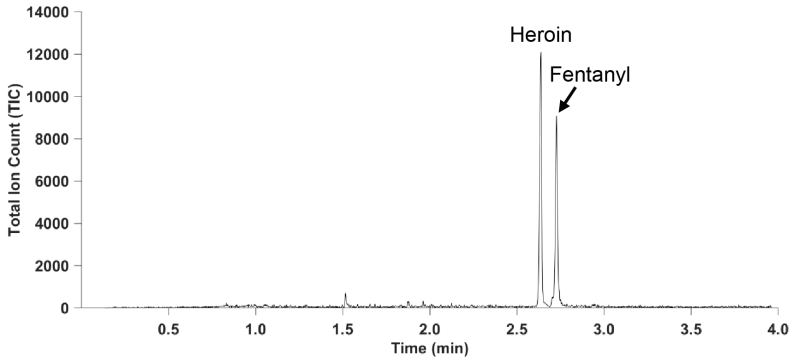

Figure 4. CME-GC/MS analysis of 100 mg/mL solution of carfentanil in methanol. (A) TIC of carfentanil. (B) Positive ion mass spectrum of carfentanil, showing the pseudomolecular ion at m/z 395.

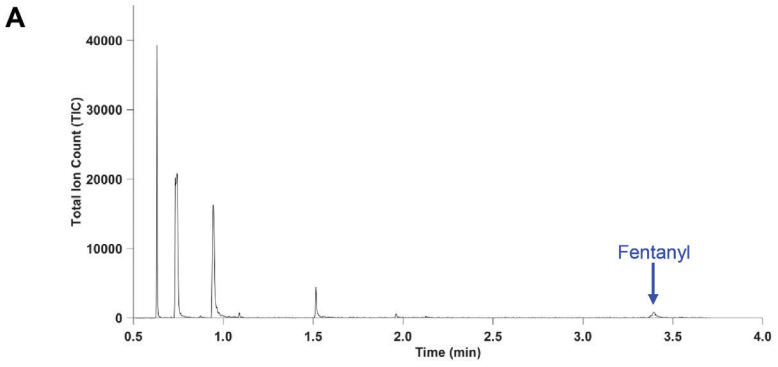

Figure 5. CME-GC/MS analysis of a heroin solution containing 5% fentanyl in acetonitrile.

to ensure repeatability. For on-site screening of laboratory synthesised materials, residual products from glassware were diluted in a suitable solvent (methanol or acetonitrile). Once fully dissolved, the tip of the coiled wire was extended, and submerged in the solution for 10 seconds, as shown in Figure 2. The coiled wire was removed from the solution and left to dry 3-5 minutes to minimise solvent entering the system, before direct injection into GC/MS for analysis.

Results and Discussion

Figure 4 shows the GC/MS analysis of carfentanil in methanol. All compounds were detected and positively identified by the Torion T-9 portable GC/MS. For identifying fentanyl analogues, an onboard deconvolution algorithm was able to positively identify and match MS data to the Wiley Designer Drug 2017 Library.

The Torion T-9 CME-GC/MS method successfully collected, analysed and identified the compounds of interest in relevant forensics scenarios involving adulterated heroin and synthesised fentanyl analogues. Figure 5 shows the CME-GC/MS analysis of a heroin solution containing 5% fentanyl diluted in methanol to demonstrate the capability of screening adulterated solutions. Figure 6A shows the CME-GC/MS analysis of residual products collected from glassware used in the synthesis of fentanyl analogues prepared at the University of North Texas. Post-processing and MS matching resulted in the identification of fentanyl collected directly from laboratory glassware. Figure 6B shows the MS data compared to a NIST reference to highlight the differences between the toroidal ion trap and quadrupole mass analysers. The differences in peak intensities and the presence of the pseudo-molecular ion [Fentanyl+H]+ at m/z 337 is due to collision-induced dissociations that occur in ion trap mass analysers.

Conclusions

Fentanyl, acetyl fentanyl, carfentanil, and heroin were collected and identified using Custodion Coiled Microextraction (CME) syringes with the Torion T-9 Portable GC/MS in relevant drug screening scenarios. The CME-GC/MS technique coupled with Wiley Designer Drug Library provided rapid identification of drugs of abuse and new psychoactive substances (NPS) in less than eight minutes, with a simplified approach to minimise user interaction from potentially harmful evidence and allow in-field screening.

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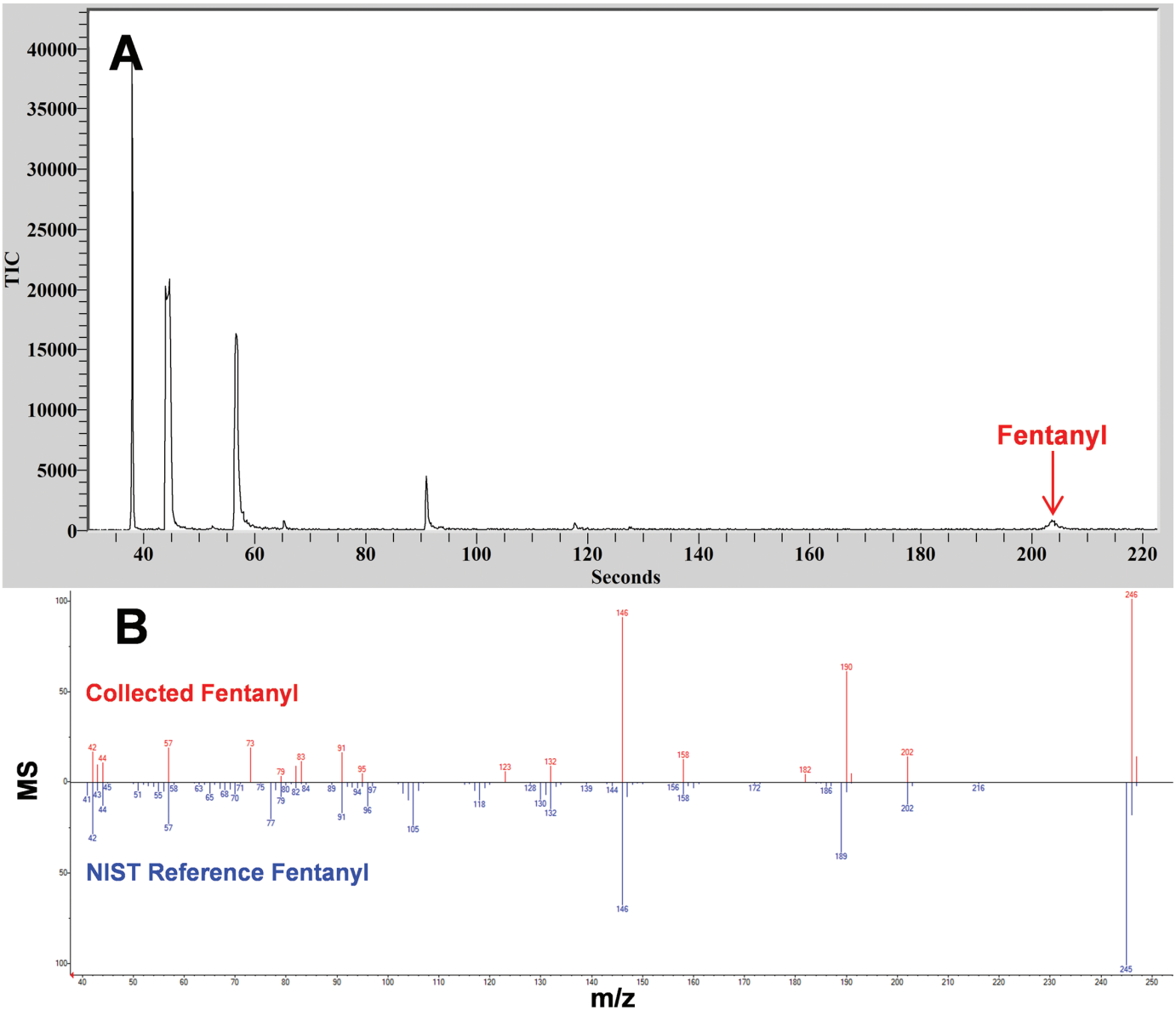

Figure 6. CME-GC/MS analysis of glassware used to synthesise fentanyl diluted in acetonitrile. (A) TIC of fentanyl and additional products from the fentanyl synthesis. (B) MS comparison between fentanyl collected with Torion T-9 (Blue) and NIST reference spectra (Red).

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