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Evaluation of the SciK9 Training Aid Delivery Device for Containment of Powders

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The SciK9 Training Aid Delivery Device (TADD) was invented by the U.S. Army Combat Capabilities Development Command Chemical Biological Center (Aberdeen Proving Ground, MD) to contain solid, powder, or liquid training substances. The TADD is designed to enable free gas/vapor exchange and simultaneously prevent escape of a training aid substance into the environment. This study demonstrates that the SciK9 TADD wholly contains powdered substances in the form of fine particulates and does not allow release of any trace material into the surrounding environment. Experiments were designed to evaluate short and long term stationary and dynamic containment of substances with a dry or wet membrane. In addition, formation of condensation within the lid of the TADD was determined. Caffeine and benzylfentanyl were used as surrogates for hazardous powdered narcotics and exposed to various experimental conditions. After analysis by mass spectrometry, no traces of these substances were found on the outer surfaces of the TADD. The results demonstrate that SciK9 TADDs can be used to safely train canines in the detection of powders such as narcotics after exposure to various experimental conditions.

15. SUBJECT TERMS

SciK9	Fentanyl	Benzylfentanyl	Hazardous training aid
Canine	Fentanyl analogue	Mass spectrometry (MS)	Training Aid Delivery Device (TADD)
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PREFACE

The work described in this report was authorized under contract number 70OS0319K00006217. The work was started in October 2019 and completed in July 2020.

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EVALUATION OF THE SCIK9 TRAINING AID DELIVERY DEVICE FOR CONTAINMENT OF POWDERS

1. INTRODUCTION

Canine trainers use a variety of containment methods to house target materials of interest in canine odor detection training. Cotton scent bags, modified film canisters, and metal sniffer tins are widely used containment modalities, but these are not the most suitable containment methods for training odor detection canines for a variety of reasons. When these modes of containment are used to house powders, the porosity of cotton scent bags and the lack of a barrier in film canisters and metal sniffer tins allow powders to easily exit the container and leave residue on hide sites. As a result, handlers and canines can come into direct contact with potentially harmful substances. Not only do these containment approaches allow for contamination of surfaces with target materials, they also prevent trainers from using liquid substances and necessitate the removal of residual odors from the surfaces of training aids before reuse.

The SciK9 Training Aid Delivery Device (TADD) was invented by members of the U.S. Army Combat Capabilities Development Command Chemical Biological Center (Aberdeen Proving Ground, MD) to contain solid, powder, or liquid training substances. The SciK9 TADD is designed to enable free gas/vapor exchange and simultaneously prevent escape of training aid substances into the environment. The overall design (Figure 1) allows the TADD exterior to undergo cleaning processes to remove unwanted surface odors, thereby allowing reuse of the training aid. The TADD lid enables selective release of the training aid odor, which increases the longevity of target materials. These improvements provide significant cost savings. Trainers can now purchase fewer training aids because of the reusable nature of the TADD and the increased shelf life of the materials it houses. In addition, these changes have improved the training process. The TADD can house solid, liquid, or powder materials without leaving behind visible residues in hide sites, and a trainer can thoroughly remove any interfering odors from the TADD exterior. Thus, canines are presented with an unadulterated source of target odor for imprinting.

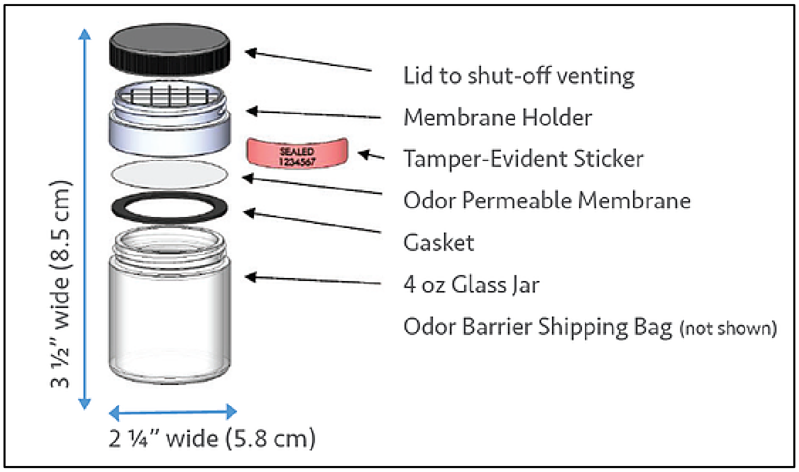
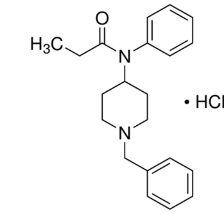
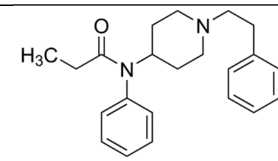
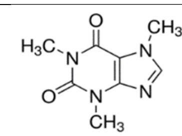


Figure 1. SciK9 TADD diagram.

The purpose of this study was to demonstrate that TADDs are able to contain powdered substances in the form of fine particulate without allowing release of any trace material into the surrounding environment. Experiments were designed to evaluate (1) short and long term stationary containment and (2) short and long term dynamic containment, both with a moist and dry filter barrier under ambient conditions.

Benzylfentanyl and caffeine were chosen for this study to simulate the chemical, physical, and bulk properties of powdered narcotics (such as fentanyl) contained within the TADD. The physical characteristics of each chemical are summarized in Table 1. Caffeine was used in the first set of experiments because it is a well characterized material in mass spectrometry (MS), can be procured in bulk, and is supplied as a fine powder. Benzylfentanyl was chosen as a fentanyl surrogate due to its similarity to the chemical structure of fentanyl. Benzylfentanyl was used alongside caffeine in the second set of experiments to validate the inability of powder to be released from the TADD during exposure to condensation-inducing conditions.

Table 1. Physical Characteristics of Chemicals

Trade Name	**CAS Number**	**Molar Mass (g/mol)**	**Molecular Formula**	**Chemical Structure**
Benzylfentanyl (hydrochloride)	5156-58-1	358.9	$C_{21}H_{26}N_2O \bullet HCl$	
Fentanyl	437-38-7	336.5	$C_{22}H_{28}N_2O$	
Caffeine	58-08-2	194.19	$C_8H_{10}N_4O_2$	

CAS, Chemical Abstracts Service.

The average particle size of synthetic opioids is between 0.2 and 2.0 µm.[*] Because the polytetrafluoroethylene (PTFE) membrane filter within the TADD has a pore size of 0.2 µm, it was hypothesized that the TADD would be able to wholly contain these types of chemicals. Narcotic detection dogs would then be able to safely train with the materials housed in the TADD in a way they could not with previously used containment devices such as cotton scent bags, film canisters, and sniffer tins.

[*] The InterAgency Board. *Recommendations on Selection and Use of Personal Protective Equipment and Decontamination Products for First Responders against Exposure Hazards to Synthetic Opioids, Including Fentanyl and Fentanyl Analogues*. [Online] https://www.interagencyboard.org/sites/default/files/publications/IAB%20First%20Responder%20PPE%20and%20Decontamination%20Recommendations%20for%20Fentanyl.pdf (accessed April 5, 2021), The InterAgency Board: Arlington, VA, 2017.

2. MATERIALS

The chemicals summarized in Table 2 were used in this study.

Table 2. Chemical Manufacturer Information

Chemical	Supplier	Catalog Number
Caffeine	Sigma Aldrich (St. Louis, MO)	C0750
Benzylfentanyl (hydrochloride)	Cayman Chemical (Ann Arbor, MI)	19883
Methanol	Fisher Scientific (Waltham, MA)	A456
Water	Fisher Scientific	W6500
Formic Acid	Sigma Aldrich	5438040100

3. EXPERIMENTAL CONDITIONS

Caffeine- or benzylfentanyl-filled TADDs were subjected to several experimental conditions in triplicate. First, the TADDs filled with caffeine were subjected to static and dynamic storage conditions for 24 and 168 h time periods before being tested for substance release. For static storage conditions, filled TADDs were placed in either "upside down" or "right side up" positions and stored for the allotted time periods before they were tested for substance release (Figure 2). For dynamic storage conditions, the filled TADDs were rotated at 15° inclines for the allotted storage time periods (Figure 3).

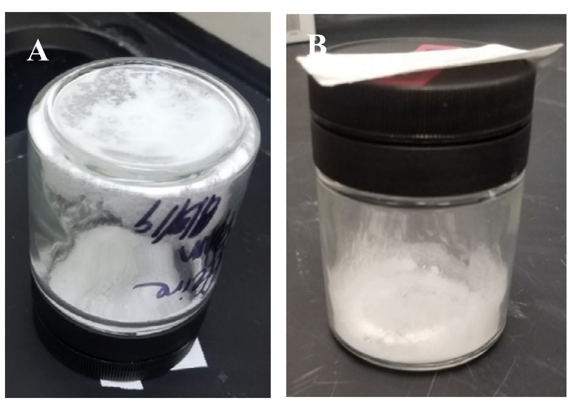


Figure 2. Static TADD storage conditions:
(A) upside down storage and (B) right side up storage.

Figure 3. Dynamic TADD storage setup.

Powdered caffeine was placed inside the TADDs, and testing was also performed in triplicate to determine if the substance could escape during storage in wet or dry conditions. For the dry experimental setup, 1.88882 g of powdered caffeine was added to the TADDs and stored under a static or dynamic condition for the allotted storage time period. For the wet experimental setup, 1.2250 g of powdered caffeine was added to the TADDs, 1 mL of water was added to the surface of each PTFE membrane, and the venting lid was screwed back on to maintain the water level between the surface of the PTFE membrane and the venting lid (Figure 4). For the TADDs subjected to the wet membrane, the hydrophobic PTFE membrane material caused the added water to pool on the surface on the membrane, and the added water remained on the surface of the membrane for the duration of the experiment. No absorption was observed, and the powder did not dissolve through the membrane into the liquid.

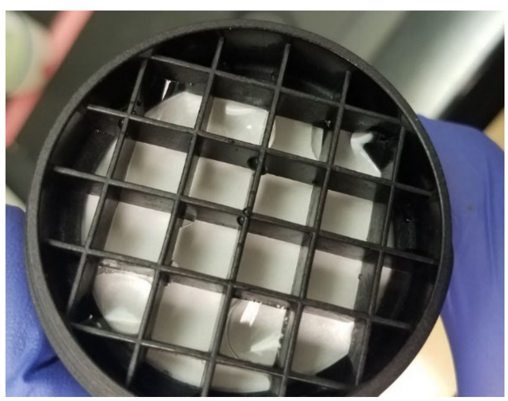


Figure 4. Wet membrane experimental setup.

Finally, lidded TADDs containing either 1 g of powdered caffeine or 10 mg of powdered benzylfentanyl were subjected to temperature cycling to encourage condensation to form between the lids and membranes during storage. Filled TADDs were subjected to temperature cycling at 4 °C for a time period from a minimum of 4 to a maximum of 48 h.

Temperature cycling was scheduled so that the temperature was 4 °C overnight. TADDs were stored statically right side up and were not inverted.

4. RESULTS

The results from the storage of TADDs filled with powdered caffeine under various membrane conditions, storage methods, and time periods are summarized in Table 3. For both dry and wet conditions, stored statically or dynamically for a time period of 168 h, no caffeine was detected beyond the outer surface of the PTFE membrane. Each experimental condition was repeated three times, and each replicate was analyzed three times. Both the surface of the PTFE membrane and the lid were sampled and analyzed, as described in Section 5.

Table 3. Detection Results for TADDs Containing Powdered Caffeine Stored Statically or Dynamically with either a Dry or Wet PTFE Membrane

Chemical	**Mass (g)**	**Membrane Condition** (3 replicates each)	**Storage Method**	**Time (h)**	**MS Detection***
Caffeine	1.88882	Dry	Static	24	None
				168	
			Dynamic	24	
				168	
	1.2250	Wet	Static	24	
				168	
			Dynamic	24	
				168	

*No detection was observed from triplicate sampling of each TADD replicate.

The results from the TADDs that underwent temperature cycling to form condensation inside the TADD lid are summarized in Table 4. For each filled TADD, 10 uL of condensate was sampled from the lid and tested for the presence of the stored substance. Sampling took place in triplicate from a single TADD. The collected condensate was analyzed as described in Section 5. For both benzylfentanyl- and caffeine-filled TADDs, neither chemical was detected beyond the outer surface of the PTFE membrane.

Table 4. Detection Results for TADDs Containing either Powdered Benzylfentanyl or Caffeine to Determine Condensation Formation on the Insides of TADD Lids

Chemical	**Mass (g)** (3 replicates each)	**MS Detection***
Benzylfentanyl	0.01	None
Caffeine	1	

*No detection observed from triplicate sampling of each TADD replicate.

5. METHODS

5.1 Sampling

Collection of transferred material was performed with a sterile cotton swab. The swab was wiped on the sample surface for approximately 1 min, as shown in Figure 5. The cotton swab was then eluted for 30 min in 190 µL of methanol. Methanol eluent was prepared as treated 95:5 methanol/water with 0.1% formic acid for mass analysis. Other collected liquids were acidified to 0.1% and analyzed neat.

Figure 5. Sample collection method.

5.2 Detection Methods

Experiments were carried out using an Orbitrap Elite mass spectrometer (Thermo Fisher Scientific; San Jose, CA) in positive mode with an ionization voltage of 3.5 kV on a Heated Electrospray Ionization source (Thermo Fisher Scientific; Waltham, MA). The [M +H]+ ions of the targeted benzylfentanyl and caffeine were fragmented with a normalized collision energy of 30 and 32, respectively. The transitions of the monitored [M +H]+ ions were the same as previously indicated. The solvent utilized an aliquot of 95:5 methanol/water with 0.1% formic acid. Successive dilutions were made until fragment ions were no longer quantifiable. The limit of detection for benzylfentanyl was 10.4 ± 0.1 ng, and the limit of detection for caffeine was 1.8 ± 0.2 ng. The limit of detection was quantified as any statistically significant ion signal garnered from precursor masses (323 and 195 *m/z* [M +H]+, respectively). The plots for the precursor mass and product mass for benzylfentanyl can be found in Figures A-1 and A-2 in Appendix A.

6. CONCLUSION

Filled SciK9 TADDs were subjected to various experimental conditions to determine whether any contained powders were released into the surrounding environment. Caffeine-filled TADDs were outfitted with dry or wet membranes and stored statically or dynamically for a period of up to 168 h before being analyzed. Samples from the membranes and lids were then tested by MS to determine whether the contained chemical was present on the outer surface of the PTFE membrane or the inner surface of the lid. TADDs containing powdered benzylfentanyl or caffeine were subjected to temperature cycling to induce condensation formation between the TADD lid and membrane. Samples of the condensate were gathered and analyzed by MS for the presence of the contained chemical. In all the experimental conditions, neither caffeine nor benzylfentanyl was found to contaminate the TADD exterior. These results indicate that the SciK9 TADD containment method is sufficient to wholly contain powdered training aid substances. The SciK9 TADD is recommended for use in containing hazardous training aid materials, so canines can be safely trained to detect the odors emitted by these substances.

APPENDIX A:
BENZYLFENTANYL PRECURSOR AND PRODUCT MASS SPECTRA

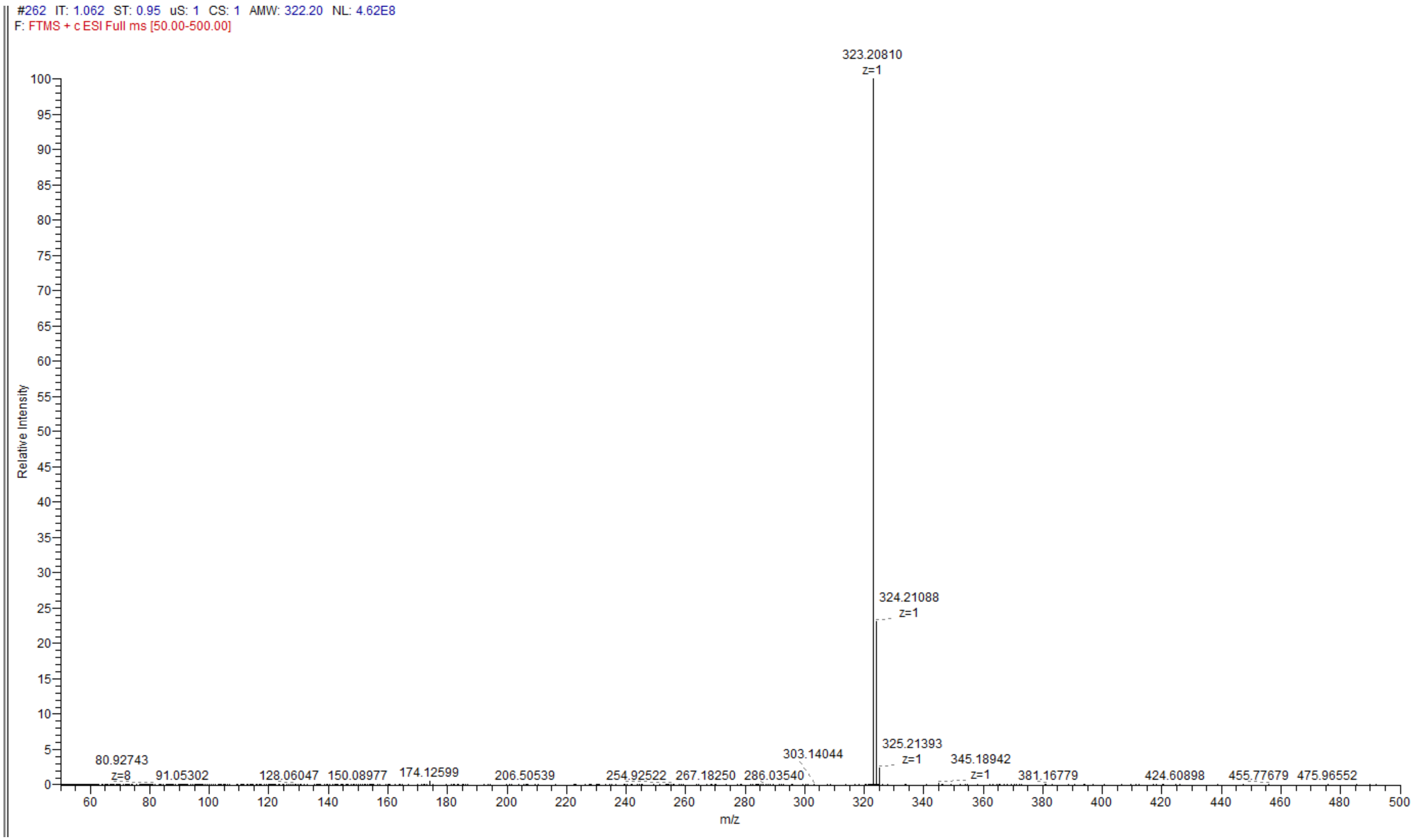


Figure A-1. Benzylfentanyl precursor mass.

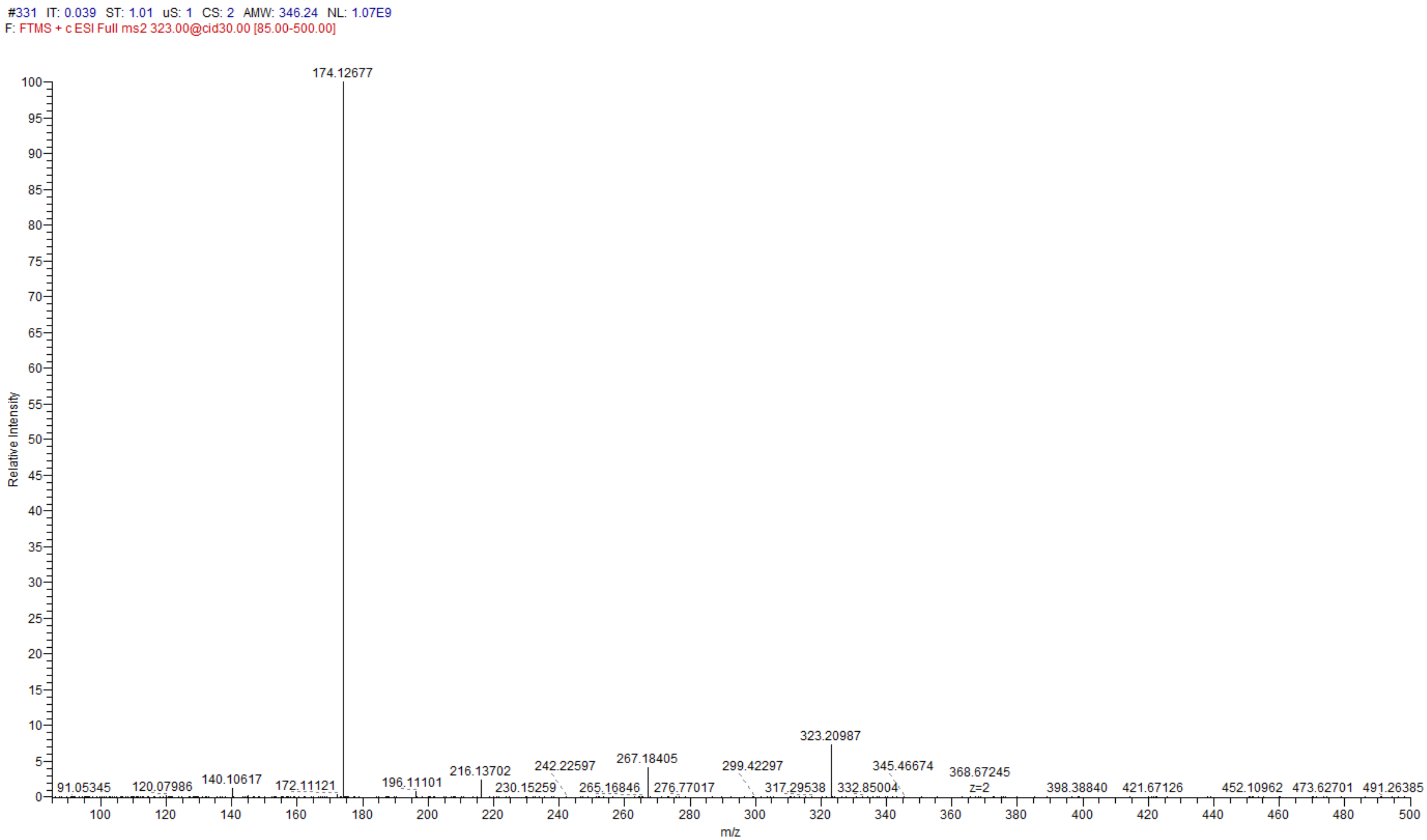


Figure A-2. Benzylfentanyl product mass.

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