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The persistence of illicit drug smoke residues and their recovery from common household surfaces

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Third-hand smoke is the residue remaining on surfaces during smoking events. It is composed of particles and vapours that form upon heating. The phrase 'third-hand smoke' is primarily used to describe nicotine and other chemicals from cigarettes, but any residues formed from the smoking of various substances could be classified similarly. There has been an increasing body of research on third-hand smoke from cigarettes in the last decade, but little has been done in regards to understanding the persistence of particles and vapours from illicit drugs. In this work, small samples of cocaine and methamphetamine were volatilized to produce an illicit drug smoke that was collected onto various surface materials and left exposed to ambient conditions over 672 h (four weeks). Chemical analyses by electrospray ionization-mass spectrometry of residues on silicon, plastic, laminate, and artificial leather surfaces indicated a rapid decrease in recovery of the parent molecule, with varied formation of decomposition products over the first 168 h of exposure. Measurable amounts of the parent molecule were still present after 672 h, exhibiting a strong persistence of these drugs on various household materials. This is important in a forensic science context, as third-hand smoke residues could provide a viable source of trace evidence previously not utilized. Published 2016. This article is a U.S. Government work and is in the public domain in the USA.

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Introduction

According to the 2013 National Survey on Drug Use and Health, an estimated 24.6 million Americans over the age of 12 are users of illicit drugs.[1] The illegal activity conducted for the creation, sale, purchase, and use of these drugs impacts our healthcare and criminal justice systems, the environment, and businesses. However, the negative effects of drug use affect not only persons directly involved with drug activity, but also others as a result of indirect contact with a variety of illicit drugs. Research attempting to measure these indirect impacts on the environment and public health aim to understand things such as how many people use or abuse drugs in a population, what concentrations of these toxic chemicals are released into water supplies or air, do they persist once they are there, and how do places that have been contaminated with such chemicals affect the average person? Studies by groups around the world have been undertaken to investigate licit (e.g. nicotine, caffeine) and illicit (e.g. cocaine, methamphetamine) drugs in the public drinking water,[2,3] waste water,[4–6] and air.[7–9]

An increasing body of research has focused on the human health and environmental implications of air quality inside the home associated with drug use.[10–19] Much has been learned about sorption and emission rates of semi-volatile organic chemicals (SVOCs) through cigarette chamber studies. When the tobacco in cigarettes undergoes combustion it creates aerosol particles, ranging in size from tens of nanometers to several microns, as well as SVOCs that can be inhaled. The thermal combustion products that adhere to clothing and surfaces are called third-hand smoke.[20] Nicotine poses the largest threat to indoor air quality from third-hand smoke, which can become more carcinogenic under exposure to oxygen,[15,17] and has the ability to re-emit from porous substrates like painted wallboard and clothing materials.[11,14,16] Researchers found that neither ventilation of, nor furnishings within, the room was enough to reduce the persistent indirect exposure of nicotine.[12] It was also observed that nicotine and other third-hand smoke chemicals persist in homes at least two months after smokers vacate a residence, and emission occurs even after homes have been cleaned and prepared for new non-smoking residents.[21] Dust also appears to be an efficient collection media for third-hand smoke chemicals.[22]

The established literature on nicotine presses the issue of passive or indirect exposure to similar thermal combustion products from illicit drugs. Pyrolysis of powdered drugs has been shown to produce aerosol particles,[23–25] and the resulting decomposition products can have vapour pressures equivalent to other SVOCs (vapour pressure range between 10^{-6} Pa and 10 Pa).[10] The products resulting from pyrolysis of cocaine and methamphetamine have been well documented by a variety of research groups. Although some thermally generated products are temperature dependent, the most common analytes observed for cocaine included cocaine,

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anhydroecgonine methylester (methylecgonidine), and benzoic acid.[24,26–30] Some other less frequently identified fragment ions were methyl cycloheptatriene carboxylates,[27,28] norcocaine, cocaethylene,[29] methyl benzoate, and N-methylbenzamide.[27] Methamphetamine, by nature of its chemical structure and lability, produces many thermal decomposition products besides methamphetamine. These analytes of interest include amphetamine-like structures (amphetamine, dimethylamphetamine, benzylethyltrimethylammonium),[31] various substituted benzenes (benzene, toluene, ethylbenzene, styrene, methylstyrene, cumene, propyl benzene, allylbenzene, 1-phenylpropene, and phenylacetone),[29–31] and multi-ring aromatics (bibenzyl[29] and 3-methylisoquinoline[31]).

Indirect exposure to these decomposition products is directly related to the presence and persistence of third-hand smoke residues remaining from smoking illicit drugs within occupied spaces. Work from the State Department[32] examined effects of opium abuse on women and children in homes in Afghanistan. Findings showed significantly high concentrations of morphine and codeine in biological samples, bedding, utensils, and toys. Researchers investigating methamphetamine have shown similar results to that of the opium study, where residues can accumulate on clothing, blankets, walls, and even the oils in skin just from coming into contact with the smoke and the residues it leaves behind.[33–35] Reemission of persistent methamphetamine contamination and similar chemicals from painted walls has been observed,[35] and would be a risk factor in places where smoking or manufacturing of methamphetamine have taken place.

The persistent nature that makes smoke residues an environmental concern also makes them a potentially useful source of trace evidence in forensic investigations. Trace detection of illicit drugs is a necessary part of many criminal investigations. Much research is done to aid forensic science as a discipline. Topics such as fragmentation pathways of molecules,[27,36,37] effects of adulterants and solvents,[38–40] and the ability to detect drugs in various media[41,42] increases understanding of how drugs react under different conditions while also improving detection during analysis in the laboratory. Some researchers are developing techniques that can be utilized for robust analysis of trace drugs in the near future including ambient ionization strategies[43–46] and Raman spectroscopy.[47,48] Both techniques exhibit plausibility for ease of use and eventual deployment in the field. Lastly, research on the practical use of current analysis techniques for examining real-world samples is vital to improving forensics. Studies that investigate samples confiscated from airports and border patrol locations,[49–51] or recovery methods to test the remediation of clandestine methamphetamine labs[52–54] would be examples of such practical uses.

The goal of this preliminary study was to begin understanding the chemical and physical characteristics of illicit smoke residues, and determine if recovery of these residues from surfaces was both practical and useful for forensic trace detection. Small deposits of cocaine freebase and methamphetamine hydrochloride were heated to volatilization and collected onto four different substrate materials with the intention of mimicking smoke depositing onto household surfaces. A persistence study was performed to evaluate and identify what chemicals were being produced after being thermally volatilized, how exposure to an ambient atmosphere affected the recovery of these smoke residues, and how the chemistry changed over a specified period of time. Samples were also examined to determine if there were any specific chemical or physical markers present that could determine any noteworthy differences from unsmoked powders. Though no specific markers were positively identified in this investigation, the persistence of drug residues on both model and realistic surfaces helped improve understanding on the relevance that these smoke residues may have as a form of trace evidence.

Materials and methods

Illicit drugs and standards

Powdered methamphetamine hydrochloride (Lot #: 098 K0693, purity 100%) and cocaine hydrochloride (Lot #: 028 K1165, purity 98.3%) were purchased from Sigma-Aldrich (St Louis, MO, USA). A known mass of the powdered drug was weighed out and dissolved in 1 mL of solvent (Optima liquid chromatography-mass spectrometry (LC-MS) grade water from Fisher Scientific (Pittsburgh, PA, USA) for methamphetamine, Photrex Reagent grade acetone from J. T. Baker for cocaine) to make drug standard solutions. The methamphetamine hydrochloride was used as received and without any further purification. The cocaine hydrochloride was first converted to its freebase form using a slight variation of a method described elsewhere.[55] Details of the method used in this work can be found in the Supporting Information.

Deuterated certified reference materials, methamphetamine-D_5 (1 mg/mL in methanol) and cocaine-D_3 (1 mg/mL in acetonitrile), were purchased from Cerilliant (Round Rock, TX, USA) and used as internal standards. Each deuterated standard was diluted to nominally 1 μg/mL using LC-MS grade methanol (Fisher Scientific, Pittsburgh, PA, USA). These were subsequently used to create approximately 250 mL of a 10 ng/mL deuterated internal standard in methanol, which was used for the extraction of all aerosol samples, as well as the creation of calibration curves.

Substrates

Four different substrates were used during the course of these experiments. Round, pre-cleaned silicon wafers (diameter 2.54 cm, single-sided polish) were purchased from Virginia Semiconductor, Inc. (Fredericksburg, VA, USA) and used as received. These wafers were chosen to represent an ideal smooth surface for their ease of imaging and removal of captured aerosols. Blue acrylonitrile butadiene styrene (ABS) plastic, green paper-backed plastic laminate, and tan artificial leather were used to simulate surfaces often found in homes and vehicles (e.g. credit cards, countertops, and car seats or sofas) to examine more realistic evidence collection. Round, 2.54 cm diameter tokens were cut from these three substrates in order to standardize surface area across all samples. The plastic, laminate, and artificial leather were all cleaned prior to use by sonication in a beaker with isopropanol (Certified ACS Plus, Fisher Scientific, Pittsburgh, PA, USA) to remove any adventitious carbon and excess dirt from the surfaces. In the case of the artificial leather, sonication in isopropanol also helped extract excess dye molecules from the leather backing that could have interfered with the mass spectrum signal.

Aerosol generation and collection

Drug samples for volatilization to aerosols were prepared by taking the stock drug standards and pipetting an aliquot onto a cleaned and heat pretreated aluminium dish to yield an approximate 500 μg total mass of drug to be sampled. Aerosol generation was performed inside an enclosed acrylic container within a biosafety cabinet with front downdraft flow to eliminate the escape of any drug vapours from the

experiment. Sampling was completed either passively or dynamically. Passive collection comprised the majority of samples collected during this study, where any vapours that were lifted through a condensing tube by convection were collected onto the various substrates. These samples were used to measure the persistence of drug residues on different substrates while being exposed to ambient environmental conditions (22 °C ± 1 °C, 1.01×10^5 Pa, and 16 % RH ± 2 %) over the course of four weeks (672 h). Dynamic aerosol collection was performed using an MSP Corporation Micro-Orifice Uniform Deposit Impactor (MOUDI) (Shoreview, MN, USA) to learn about the size of the aerosol particles being generated during volatilization. A detailed description of each sampling method, as well as results from dynamic particle sizing experiments, can be found in the Supporting Information.

Sample extraction

Each token was extracted using methanol containing 10 ng/mL of the appropriate deuterated internal standard (IS). Extraction of the hard substrate tokens (silicon, plastic, laminate) was completed by placing the token into a 25 mL beaker with 1 mL of IS. The tokens were then agitated by hand for 10 s to remove any drug particles/vapours collected on the surface. The solvent was then removed from the beaker and placed into a 1.5 mL amber glass screw cap vial for analysis. Since the artificial leather could not be submerged without the possibility of extracting any remaining loose dye molecules or losing solution to absorption by the leather, a glass fibre filter (Whatman, 47 mm, grade GF/A) was cut into 1.27 cm squares and wet with 100 μL of plain methanol. The leather was then wiped thoroughly and the filter placed into a 1.5 mL conical centrifuge tube with 0.5 mL of plain methanol. The tubes were centrifuged at 1047 rad/s for 3 min, after which the solvent was removed and placed into a 1.5 mL amber glass screw cap vial. The vials were left uncapped in the back of the fume hood to evaporate to dryness, usually overnight. A 1 mL aliquot of IS was then added to the vial. Extraction efficiency analyses were conducted by depositing a known amount of analyte onto the surface of each of the four substrate tokens and the glass vials used for collection and storage, then performing the same extraction procedures as with the volatilized samples (details in Supporting Information).

Electrospray ionization-mass spectrometry

Samples analyzed by mass spectrometry were diluted prior to injection by diluting 50 μL of the residue sample up to 500 μL total volume using IS. Chemical analysis was primarily performed using a JEOL AccuTOF JMS T100LP mass spectrometer (JEOL USA, Peabody, MA, USA) equipped with an electrospray ionization source (ESI-MS) operated in positive ionization mode. The protonated molecular ions, $[M+H]^+$, were selectively monitored for the drug and the internal standard (*m/z* 304 and *m/z* 307 for cocaine, and *m/z* 150 and *m/z* 155 for methamphetamine). In addition, major decomposition products such as benzoylecgonine (*m/z* 290) from cocaine, and the 1-phenylpropane and benzyl carbocations (*m/z* 119 and 91, respectively) from methamphetamine were identified. Calibration curves ranging from 0 ng/mL to 500 ng/mL were constructed from standard solutions made from the powdered drugs used for experiments, and diluted serially with 10 ng/mL IS. The extract from each sample token (three for each time point) was analyzed using 5 injections to yield 15 data points for each time point, from which averages and standard deviations/errors were obtained.

Infrared spectroscopy

Samples of drug smoke were also collected onto low emission MirrIR slides (Kevley, Chesterland, OH, USA) by volatilizing a small quantity of powder directly under the slide to produce a visible residue. These slides were examined immediately following collection, and then over the next 672 h to observe any changes that may corroborate the ESI-MS time study data. The residues were analyzed using a Smiths IlluminatIR II infrared microscope (Smiths Detection, Edgewood, MD, USA). An attenuated total reflectance (ATR) objective with a diamond crystal was used, averaging signal from a 100 μm × 100 μm scanned area 128 times with 8 cm^{-1} resolution. Images of the area to be scanned were also captured with a 10× objective in brightfield.

Scanning electron microscopy

Drug smoke deposits were collected onto silicon wafers, both passively and dynamically, for analysis by electron microscopy to identify the physical structures that compose the volatilized drug sample. Samples volatilized onto individual substrate tokens were exposed to the same ambient laboratory conditions as those for extraction (from 0 h to 168 h), but instead were examined using scanning electron microscopy (SEM). Individual tokens were used for each exposure time, and were not reused after imaging because interaction with the electron beam may induce damage to the sample. SEM was performed with an FEI Quanta 200 F environmental scanning electron microscope (Hillsboro, OR, USA) that uses a field emission gun operating in high vacuum mode. Secondary electron images were captured with a beam energy of 5 kV and spot size of 3, using an integrated capture mode.

Results and discussion

Cocaine and methamphetamine persistence on a model surface

Chemical analysis to obtain the mass of cocaine and methamphetamine from a sample of drug smoke residue was performed with ESI-MS. The *extracted mass* is that which was determined from each diluted sample, adjusted for dilution errors. These extracted masses were then back calculated using extraction efficiencies to reveal the actual *deposited mass* of drug on a given substrate. The calculated deposited masses from model silicon wafers are plotted in Figure 1. The inset plots in 1A (cocaine) and 1B (methamphetamine) magnifies the first 24 h of time spent exposed to the ambient atmosphere for each drug examined. Figure 1 exhibits, on average, a rapid decay in the recovered mass calculated from the observed signal beginning in the first 24 h. An almost steady state was reached after approximately 48 h to 72 h. Detection of the parent drug molecule for cocaine and methamphetamine was still viable after 672 h of exposure to ambient laboratory conditions, with some extracted masses measuring as low as 1.5 ng.

Some common decomposition products were also identified in all of the silicon samples examined. For cocaine, the protonated ion *m/z* 290 corresponding to benzoylecgonine (BE) exhibited a rise in integrated intensity with respect to the internal standard over the first 72 h of exposure (Figure 2A, red data points). The temporal data pointed to a formation and increase of BE even as the signal from *m/z* 304 decreased over the same time period. This suggests that the product was progressively formed as a result of exposure to the atmosphere, most likely undergoing hydrolysis of the methyl ester as is often seen in the metabolism of cocaine.[56] As the *m/z*

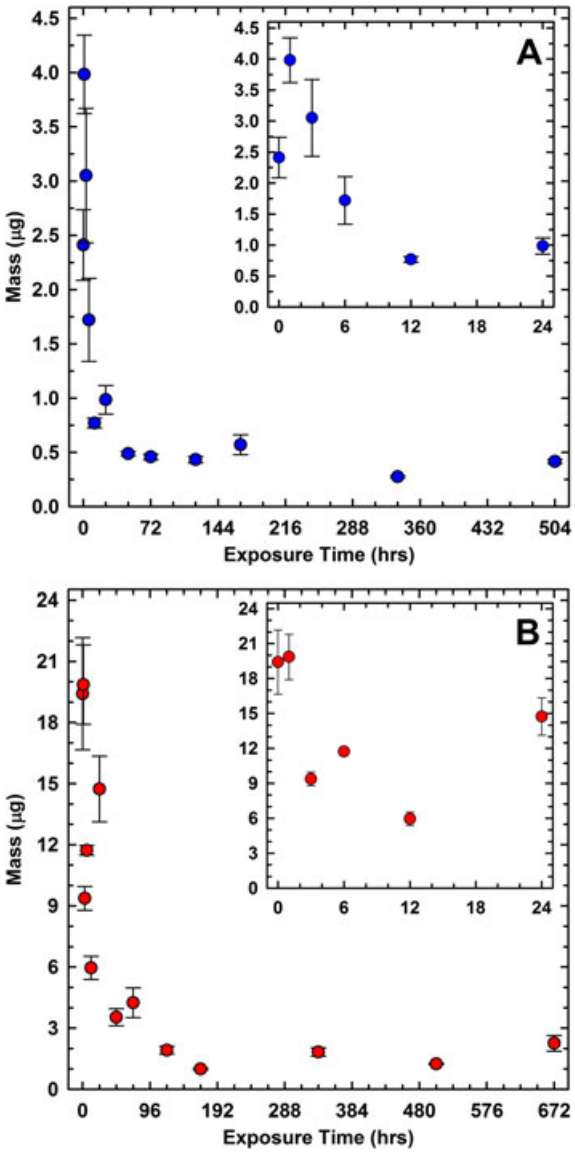

Figure 1. The calculated average masses of cocaine (A) and methamphetamine (B) recovered from silicon wafers, which were extracted and analyzed by ESI-MS. Each data point for a given exposure time is the resulting average from the extractions of three individual tokens. Each extraction was injected 5 times to produce a total of 15 measurements. The error bars represent the standard error of these 15 measurements. Inset is a plot illustrating in higher detail the first 24 h of exposure time.

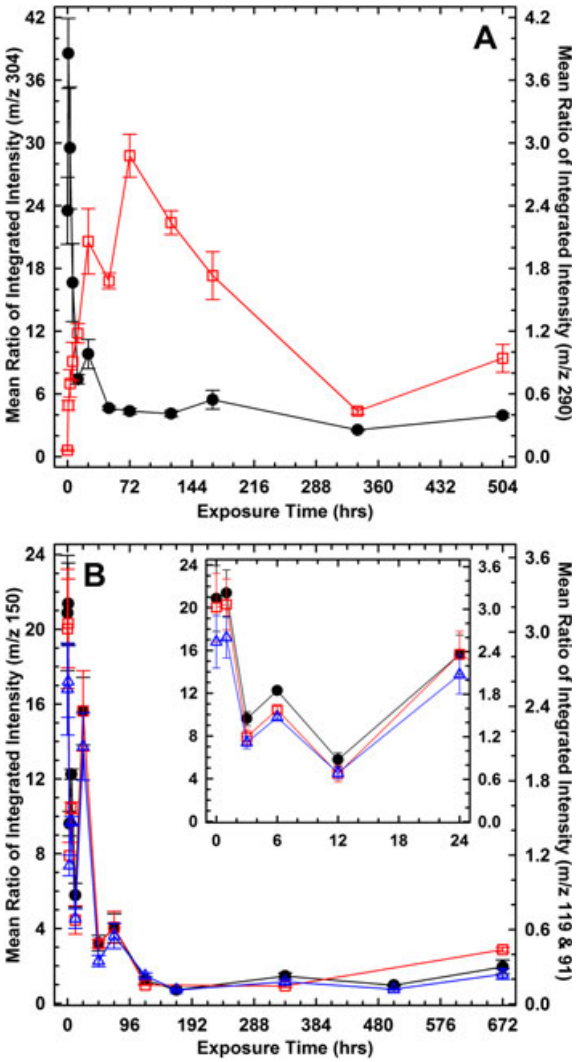

Figure 2. The averaged integrated intensity of the parent molecular ion is presented as a ratio to the internal standard (black-filled circles) on the left y-axis. This is compared to the averaged integrated intensity resulting from the decomposition product(s) presented as a ratio to the internal standard (red open squares and blue open triangles) on the right y-axis for cocaine (A) and methamphetamine (B) from 0 h to 672 h of exposure time. In (A) cocaine is compared to the major product benzoylecgonine, and in (B) methamphetamine is compared to the two products 1-phenylpropane (squares) and benzyl (triangles). Lines have been drawn connecting data points to assist the eye. The error bars represent the standard error of 15 measurements.

290 intensity began to decrease, ecgonidine, the major fragment and common metabolite of BE ($[M+H]^+$ *m/z* 168), was not detected in any of the samples. An interesting observation was that neither of the two most common fragment ions, anhydroecgonine methylester or benzoic acid,[24,26–30] were detected by this method. Competitive ionization between the cocaine molecules, internal standard molecules, and the various decomposition products was believed to be the main cause for not detecting their presence. This competition, as well as a constantly varying ratio of cocaine to BE in volatilized samples, prevented any attempts to quantify benzoylecgonine concentrations.

Methamphetamine exhibited two major decomposition product peaks at *m/z* 119 and *m/z* 91. Both of these ions were identified in experimental sample spectra as well as in the spectra from standard calibration curve solutions. The literature suggests that the *m/z* 119 ion originates from a protonated 1-phenylpropene, allylbenzene, or methylstyrene molecule.[29–31] However, since there is no chromatographic separation, the signal here could result from a contribution of all three fragments. The peak at *m/z* 91 is most likely a benzyl carbocation fragment remaining from toluene losing a hydrogen. Upon measuring these two fragment ions in the standards, *m/z* 91 exhibited a relatively constant integrated area equaling 3.5% of the *m/z* 150 area for concentrations of 5 ng/mL to 100 ng/mL, whereas *m/z* 119 was not detectable in the lower concentrations and did not trend in a similarly consistent manner. Like BE, competitive ionization prevented quantification of the decomposition products in experimental samples. Changes in the products' integrated intensity compared to that of *m/z* 150 from silicon experiments (Figure 2B) showed a marginally slower

decrease in the products. Upon examining the ratio of *m/z* 91 to *m/z* 150, a very slight increase with time could be seen, which could be the result of a small amount of product formation by exposure as well as by ionization. Aside from these fragments, no other characteristic peaks (e.g. benzene, amphetamine) were observed.

The decomposition products from cocaine and methamphetamine exhibited very different trends over the course of several weeks' exposure to ambient laboratory conditions. The exact reasoning for this is currently not known, but is most likely related to the chemical nature inherent to each compound. For example, the vapour pressure of cocaine, at 2.55×10^{-5} Pa, is much lower than that of methamphetamine, at 21.73 Pa,[57] indicating much stronger intermolecular forces in cocaine. Benzoylecgonine is predicted to have a higher boiling point and enthalpy of vaporization than cocaine,[58,59] suggesting an even more stable molecule. The small molecule fragments of methamphetamine are predicted to have lower boiling points and enthalpies[60–63] than the parent drug, signifying less stable molecules. The increased stability of the cocaine decomposition product compared to the parent molecule could be a reason for why an increase in BE was seen over a week of exposure time, but neither the substituted benzenes nor the benzyl carbocation showed an increase in the methamphetamine volatilizations.

Cocaine and methamphetamine persistence on realistic surfaces

Similar decreasing trends in the recovery of cocaine and methamphetamine with respect to exposure time were observed for the ABS plastic, laminate, and artificial leather substrates as shown in Figure 3. Of the four substrates, cocaine displayed the greatest persistence on ABS plastic over the longest period of time (Figure 3A). Though there was a large decline in the first 12 h, the mass recovered over the next 120 h remained relatively stable before exhibiting another sharp drop. With the cocaine molecule being hydrophobic, non-polar, and aromatic in nature one could posit that there may be a chemical affinity for the surface of the non-polar, hydrophobic ABS plastic. Artificial leather maintained a similar profile to silicon and laminate over time, but exhibited the lowest overall extracted mass of cocaine among the four substrates, possibly a result of physico-chemical interactions with the surface, penetration into the porous substrate, or the method of removal used (swipe versus submersion). Laminate, with very good extraction efficiency, surprisingly yielded the lowest deposited masses.

Normalizing the mass obtained at each time point to that at time zero enabled comparison between the four substrate data sets on a single scale. This process made apparent some variability in the experimental process. For instance, performing an individual volatilization for each substrate token could have produced small differences in the amount of residue collected, depending on how well heat was transferred to the aluminum dish and convection currents within the enclosed chamber. Figure 3A (inset) shows an increase in the amount of cocaine after 1 h to 6 h of equilibration with the ambient laboratory environment for three of the four substrates. Repeat experiments exhibited similar variations in extracted mass among the first few time points, suggesting inconsistencies in the amount of drug smoke collected during each volatilization. However, since the desired goal was more focused on observing the general trends upon exposure and less about measuring the absolute mass collected onto a given substrate, these variations do not greatly impact the overall result.

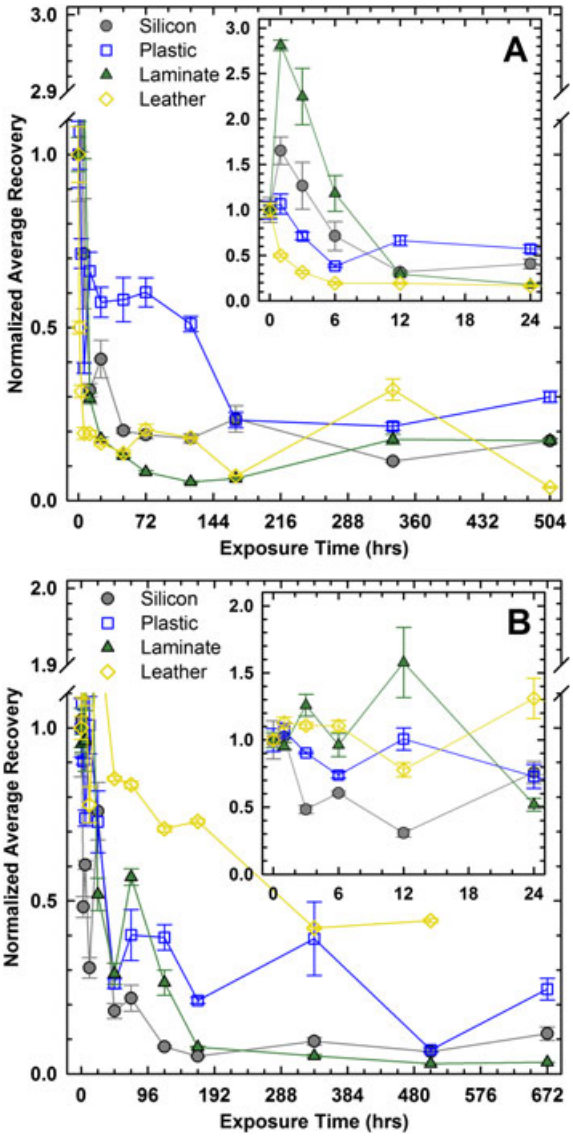

Figure 3. The normalized average recovery of cocaine (A) and methamphetamine (B) from all four of the substrates investigated calculated from the deposited masses. Values were obtained by normalizing the concentration calculated at each time point to that at time zero (i.e., time zero = 1.0). Inset is a plot illustrating in higher detail the first 24 h of exposure time. Lines have been drawn connecting data points to assist the eye. The error bars represent the normalized standard error of 15 measurements.

Methamphetamine trends from the four substrates exhibited some similarities to those of cocaine (Figure 3B). The silicon, plastic, and laminate substrates all showed an increase in the amount of methamphetamine recovered after 1 h to 6 h, but not to the same extent as was seen with cocaine (Table S3). In the case of artificial leather, the extracted recoveries were significantly lower than any of the other substrates, but maintained a relatively sustainable yield over the course of 168 h. Even corrected for extraction efficiency, the calculated deposited masses of methamphetamine on leather were very low. This is illustrated by the lowest efficiencies being recorded for leather, but all four substrates displayed significantly low extraction of methamphetamine compared to the glass vial (Table S1).

The low extraction of methamphetamine from all substrates could indicate a few possible scenarios: (1) that some form of

equilibrium between methamphetamine molecules partitioning to the air and the substrate was reached early on in the exposure process and only a small amount of drug was then left on the surface to recover; (2) methamphetamine may not have the chemical structure or properties that attracts it to these surfaces and very little drug actually adsorbed to the substrate to be recovered; or (3) the wipe technique and/or the solvent used was ineffective at removing all of the methamphetamine from the surface. Future investigation into the efficacy of different solvents is needed to better understand the best route to recovering various drug molecules from these surfaces. Examination of more soft and porous substrates, like the artificial leather, would also be beneficial to identify substrates that may require a different extraction protocol and the parameters needed for field recovery situations.

There are surprisingly few studies involving the recovery of volatilized drugs from surfaces. The majority of published literature has focused on liquid drug samples spotted onto surfaces and either analyzed directly or removed for analysis, but studies that have examined aging of drugs on various surfaces can be compared here.[52,54] Lim Abdullah and Miskelly[52] used enclosed versus open experiments to observe the desorption of pseudoephedrine and methamphetamine from different materials over two days' time. They determined that surface material and texture influences recovery, where only 50 % to 60 % of the deposited sample was recovered from clean impermeable materials and that recovery decreased with age primarily from volatilization of the two compounds. Other investigators researched the use of newer technologies to test sample recovery from fabrics,[43] smooth and painted surfaces,[45] and building materials.[53]

The results from this work are most comparable to those collected in Martyny *et al.*'s wipe experiment with methamphetamine, even though the experimental parameters vary significantly between the two studies. Their group performed simulated methamphetamine smoking and cooking in a hotel room using between 100 mg and 2000 mg,[33] whereas in this study only 0.5 mg was volatilized at a time. The levels extracted from laminate substrates here were slightly higher than Martyny *et al.* reported from the table surfaces they measured, 5.9×10^{-3} μg/cm^2 compared to 3.1×10^{-3} μg/cm^2 for the lowest fractions and 0.38 μg/cm^2 compared to 0.17 μg/cm^2 for the higher fractions. They also did not mention any measurement of extraction efficiency for the substrates they tested. In that regard, this work adds some context to the literature on how different volatilized drug molecules respond differently to the same non-wipe extraction treatment on a few common substrate materials.

The small masses detected on each substrate in this experiment may represent the trace quantities investigators may find adsorbed to various household or vehicular surfaces. Forensic investigators already look for the presence of smoked or unsmoked drugs in drug cases by swabbing or extracting empty packaging material and paraphernalia. They can also examine more complex surfaces for minute drug residues such as carpets or bodily fluids on clothing. The persistence of these drugs over the course of 504 h to 672 h, even after being left open to ambient room conditions, is significant for potential recovery of drug evidence. It should be noted that the experiments reported here only conducted a single volatilization per substrate token, which would deposit a small amount of residue compared to cases of multiple smoking sessions. In circumstances of habitual use within a given area, the concentrations and lifetime of cocaine and/or methamphetamine would be expected to increase.

Chemical and physical characteristics of residues

Attenuated total reflectance (ATR) was performed on aerosol residues in addition to mass spectrometry to corroborate findings. Macroscopic observation of cocaine residues showed two distinct areas: those that were more opaque in colour, usually around the edges of the residue; and those where the residue appeared more translucent, normally at the middle. Upon inspection with a light microscope, the more opaque areas tended to have a more structured crystalline appearance, whereas the translucent areas appeared less ordered with more amorphous features (Figure S3). Figure 4 illustrates the IR spectra obtained from areas of higher crystallinity over the course of 672 h exposure to ambient conditions. The initial spectra at time zero (gray) looks very similar to that for powdered cocaine freebase (black), which is consistent with the mass spectral results from ESI-MS. Some of those characteristic features were retained over the course of the next 672 h, though decreasing signal intensity and peak broadening was observed indicating a loss of crystallinity.[64] The more amorphous areas exhibited the same spectral features; however these areas displayed more heterogeneous broadening from the onset as well as slight shifts in peak position. These are most likely the result of the reduced crystallinity in these areas, but may also be a function of ATR operation.[64,65]

Methamphetamine aerosols also produced a white residue, visible to the eye, upon initial volatilization. However, analysis with

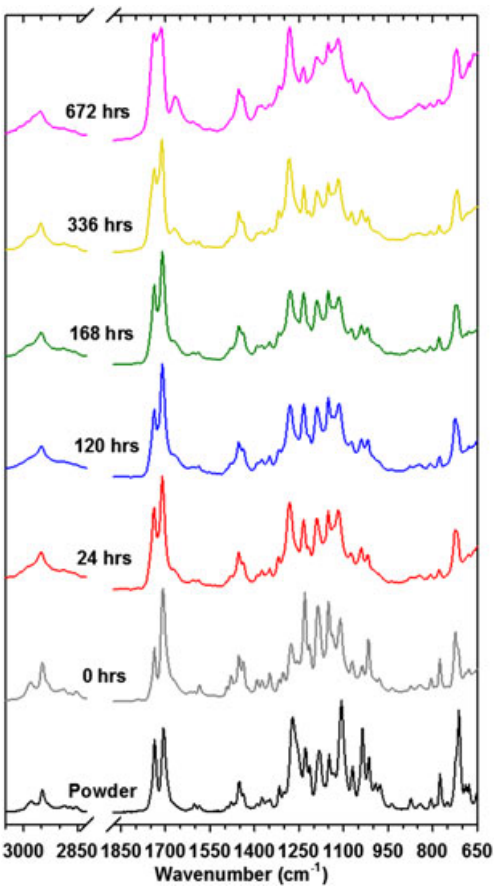

Figure 4. IR ATR spectra of cocaine freebase powder compared to that from the crystalline areas within the cocaine residue after volatilizing onto a slide and leaving it exposed to ambient laboratory conditions over the course of 672 h. Spectra are normalized to the tallest peak for each time point.

ATR did not yield the same quality spectra as with the cocaine residue. Macroscopically the methamphetamine residue was similar to the cocaine in that the outer edges appeared more opaque, but investigation with the 10× objective indicated a scattering of small amorphous particles at the edges sometimes clumped together. In the middle of the residue, finding anything resembling particles or crystals with the 10× objective was difficult, indicating much smaller sized particles and/or a thin film covering the surface. The spectra resulting from analysis of these two regions were mostly featureless at time zero and for readings through the next 168 h. However, between 24 h and 120 h crystals began to form in small clusters which began branching outward (Figure S4). These needle-like crystal formations gave the most recognizable spectra for methamphetamine.

The IR spectra of aerosol residues confirmed mass spectral results out through 672 h of exposure to ambient conditions. This is significant in that the crystalline structure remains well enough intact for chemical identification via matching through a spectral library. The different crystal formations observed, where cocaine formed crystals more rectangular in shape while methamphetamine exhibited longer more needle-like crystals that branched outward from a center point, could potentially be useful in their own right. If a residue was visible, light microscopy and IR spectroscopy could be used for identifying pure drug smoke residues captured on surfaces. This observation could allow forensic investigators to examine undisturbed, flat surfaces where drug vapours may settle for evidence of drug activity. However, it is noted that these structures change over time during exposure to environmental conditions. Adulterant or diluent chemicals may also alter the crystal structures and the resulting IR spectra formed by these aerosols, and a chromatographic technique coupled to a mass spectrometer would yield more identifiable information.

Identifying physical characteristics of drug aerosols

Since ESI-MS and IR did not indicate that there were any chemical differences between smoked and unsmoked drug samples, powdered drugs and aerosols that had been collected onto silicon wafers were examined by SEM to ascertain if there existed any distinguishing physical features of interest. Figure 5 shows images of pure cocaine (Figure 5A) and methamphetamine (Figure 5E) powders alongside smoke residues from three different time points spanning the first 168 h of ambient exposure. The pure powders were jagged and crystalline in appearance, with the cocaine freebase looking more amorphous than the salt. The cocaine (Figures 5B–5D) and methamphetamine (Figures 5F–5H) aerosols, volatilized from the dried deposits, exhibit some of the same particle characteristics of the powders, as well as some other interesting features such as amorphous rounded particles, spotting, and rings across the surface. Particles ranging in size from less than 250 nm to upwards of 10 μm were observed over the course of exposure to ambient conditions for both drugs examined. Clusters of these smaller particles were also seen as large as 80 μm across. Size distribution measurements were not attempted with the SEM, however more information on particle size as measured with an inertial impactor can be found in the Supporting Information.

The images from this time lapse study suggest that there are some small physical differences between the aerosols and the unsmoked powders. A number of possible reactions could happen during the volatilization process, including transformations that may occur once the aerosols and vapours deposit onto the surface. Solid aerosol particles were seen with characteristics very similar to that of the powder, which may indicate that small solid chunks are physically being ejected from the heated surfaces. It also could be the result of a melting and reformation process where volatile gas phase molecules condense from the air as they cool to form liquid droplets and subsequently very small particles.[66] These could deposit onto the substrate if there is sufficient time from when they begin to condense to the time they reach the substrate. The crystal growth and formation exhibited by methamphetamine suggests that this process can occur once the molecules are already on the surface. Some evidence of this was also seen with cocaine, where small square crystals formed at the center of small droplets or around the edges of rings (Figure S5). This migration of molecules to eventually form small crystals may account for a dearth of noticeable particles in the centers of the wafers at time zero, which showed some large particles scattered near the edge of the wafer more than anywhere else. Though interesting, these small physical differences may not be of any practical use in forensic investigations.

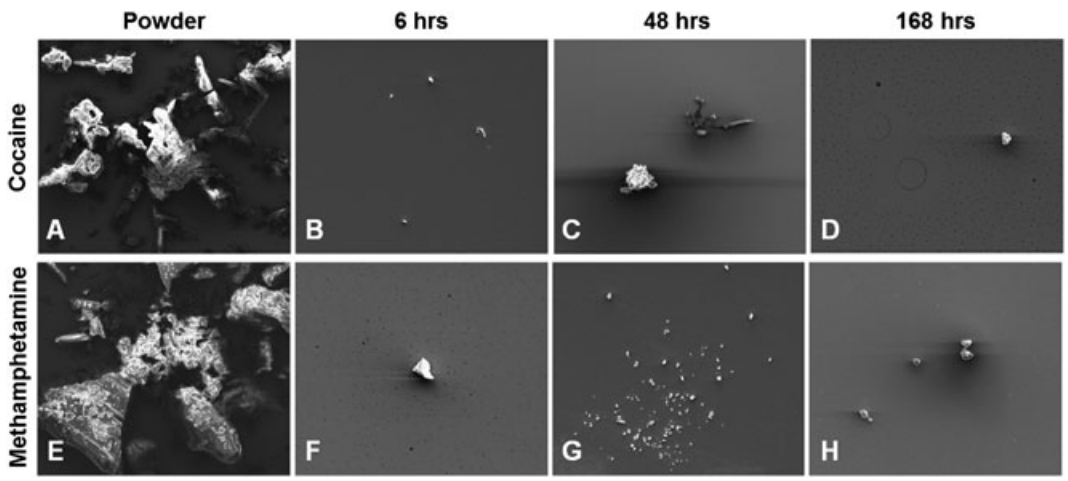

Figure 5. SEM images of cocaine (top) and methamphetamine (bottom) powders (A and E) shown alongside aerosols collected after volatilization at 200 °C, and after being exposed to ambient laboratory conditions for 6 h (B and F), 48 h (C and G), and 168 h (D and H). The horizontal field width of each image is 102 μm.

Conclusions

The goal of this work was to understand the chemical and physical characteristics of illicit drug smoke residues, as well as if their recovery and use was practical as trace evidence in forensic investigations. Immediately after volatilization at 200 °C, samples of cocaine extracted from the four different substrates and analyzed by ESI-MS were primarily composed of the characteristic molecular ion. Methamphetamine samples contained not only the molecular ion, but two major decomposition products as well. Different trends were observed for the decomposition products in relation to the parent molecule. Benzoylecgonine (*m/z* 290) showed an increase even while the parent cocaine molecule decreased over time, whereas the substituted benzenes (1-phenylpropene, allylbenzene, methylstyrene) and the benzyl carbocation fragments did not display any significant changes with time. Overall, chemical analysis successfully showed that trace quantities of illicit drug residue adhered to various household-type surfaces (ABS plastic, laminate, artificial leather) and could be viably recovered for at least four weeks under the conditions examined (22 °C ± 1 °C, 1.01×10^5 Pa, and 16 % RH ± 2 %). Masses as low as 1.5 ng were detected in extracted samples out through 672 h of exposure to ambient laboratory conditions. This would be useful to investigators who may need to prove evidence of drug abuse for days or weeks after a smoking event and without needing to have the powdered drug present. The identifications of these drug residues were confirmed by IR spectroscopy using ATR, and crystalline features unique to the aerosols were observed using light and electron microscopy.

The work from this study has important implications in other areas besides forensic science. For example, swipe sampling for trace explosives and narcotics often uses an oven temperature between 200 °C and 250 °C. By volatilizing drug samples at 200 °C, this work is a first step to understanding how temperature affects volatilization in ambient ionization techniques. With the particle impactor, we collected approximately 10% to 20% of the drug as particles, but an unknown amount was either in the form of vapour phase molecules or was lost. Investigation into how temperature affects the particle/vapour ratio would be important to the detection and analysis of these chemicals of interest. This ratio may also be affected by the presence of other drugs, adulterants, or cutting and bulking agents. This work is also relevant to public and environmental health concerns regarding exposure to third-hand smoke, which is directly related to persistence. As was discovered here, the deposited particles and vapours that compose the smoke residue from a single small scale volatilization persisted for four weeks under relatively calm ambient conditions. Different environmental conditions, in conjunction with multiple smoking events, could produce a sustained persistence of these drugs or even convert them to more toxic products. Individuals indirectly exposed to those residues would then be at risk.

This persistence and aging study has provided an important introduction into the area of realistic smoke residues from illicit substances, a topic which has been largely absent from the literature. Physical characterization shed light on particle shape at different time frames, and chemical analysis helped provide understanding into the persistence and decomposition of smoke residues. These combined results imply that aerosol residues from drug smoking activity possess promising chemical and physical characteristics that could be utilized in future forensic investigations. However, deeper investigation is necessary to determine the robustness of these smoke residues as a form of trace evidence, including being able to quantify decomposition products. An in depth study exploring various extraction protocols for different substrate materials, and an examination of realistic environmental exposure conditions found in homes would acquire much needed information on persistence and viability of these smoke products. Additional work on mimicking realistic smoking events with multiple exposures over prescribed intervals of time would be useful in obtaining chemical information on build up and break down products. Future studies wish to address these key issues.

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Disclaimer

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Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's web site.

Table S1 – Extraction efficiencies for cocaine and methamphetamine from the various substrates used in this experiment. (*: vial results used to calculate the total efficiency for each substrate)

Table S2 – Average mass of recovered cocaine corrected for extraction efficiency for 15 replicates of all four substrates studied at each time point. Uncertainty is expressed as the standard error of the 15 measurements.

Table S3 – Average mass of recovered methamphetamine corrected for extraction efficiency for 15 replicates of all four substrates studied at each time point. Uncertainty is expressed as the standard error of the 15 measurements.

Figure S1 A schematic of the experimental set up used to perform the volatilization of cocaine and methamphetamine. The locations important to drug sample placement and collection are labeled.

Figure S2 The average data points ± standard deviation for each substrate token at each time point for cocaine (A) and methamphetamine (B) on silicon wafers. Each exposure time shows three data points for 0 h (black), 1 h (white), 3 h (red), 6 h (green), 12 h (yellow), 24 h (black), 48 h (white), 72 h (red), 120 h (green), 168 h (yellow), 336 h (black), 504 h (white), and 672 h (red). Each data point is the average of 5 injections.

Figure S3 Images captured using 10× objective in brightfield view of cocaine residue on microscope slides. (A) and (B) illustrate the opaque and translucent areas of the residue respectively at time zero, whereas (C) and (D) show the same areas after 120 h of exposure. All images have a horizontal field width of 700 μm.

Figure S4 A comparison of the methamphetamine crystals that formed after 120 h of exposure to ambient laboratory conditions as viewed by SEM (A) and light microscopy (B). Both images have a horizontal field width of 700 μm.

Figure S5 Cocaine crystals that formed on the silicon wafer as a result of exposure to ambient laboratory conditions. Horizontal field width of the image equals 56.6 μm.