JOURNAL OF FORENSIC SCIENCES

J Forensic Sci, 2017
doi: 10.1111/1556-4029.13472
Available online at: onlinelibrary.wiley.com

TECHNICAL NOTE

CRIMINALISTICS

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Feasibility of Canine Detection of Mass Storage Devices: A Study of Volatile Organic Compounds Emanating from Electronic Devices Using Solid Phase Microextraction

ABSTRACT: Detection of canines are well-known to be valuable in the location of contraband, such as explosives or narcotics. More recently, canines have been trained and utilized in the detection of concealed mass storage devices that might contain evidence of illegal activity such as child pornography. To lay the analytical foundation for this detection work, research was carried out to determine the volatile organic compounds associated with mass storage devices (MSD) that could be used by trained canines for detection. Headspace analysis of a variety of electronic devices was performed using solid phase microextraction (SPME) with gas chromatography/mass spectrometry (GC/MS). Analyses found several volatile compounds common to SIM and SD cards, as well as USB drives, including 2-propenenitrile, styrene, isophorone, hydroxycyclohexyl phenyl ketone, and 2-furanmethanol, tetrahydro. Results indicated that mass storage devices do have a characteristic odor profile making detection with minimal false alerts feasible for trained canines.

KEYWORDS: forensic science, canine detection, headspace analysis, solid phase microextraction–gas chromatography/mass spectrometry, odor, mass storage devices

Canine detectors are often recognized for their superior ability to detect and locate contraband such as narcotics and explosives; however, they have also been utilized for the detection of a much wider range of targets beyond contraband. Uses for such detectors include, but are not limited to, mold and funguses damaging trees and crops, pests such as bed bugs and termites, onset of illnesses and medical events such as carcinoma and seizures, and electronic devices (1,2).

Current technology has made it difficult for law enforcement to prosecute child pornography cases, and other cases involving Internet-based crimes, due to the difficulty in obtaining evidence. Most pornography cases are uncovered by either tracing online purchases, through undercover online chats or messaging with the offender, or retrieval of files from the offender's home. Evidence is often difficult to uncover due to the recent surge in the use of wireless Internet and small storage devices, such as external hard drives, USB (universal serial bus) drives, SIM (subscriber identity module) cards, and DVDs (digital versatile disks), as well as the use of increasingly secure passwords, encryption, and proxy servers (3).

Recently the Federal Bureau of Investigations (FBI) has trained canines to uncover concealed mass storage devices (MSDs) for the purpose of the collection of evidence of child pornography, intelligence for terrorism, financial crime records, and records of other illegal and fraudulent transactions. One such canine was used to search the home of Jared Fogle, former Subway® spokesperson. The canine found a hidden USB drive not previously discovered by crime scene investigators. Evidence from the drive was used to convict Fogle for possession of child pornography (4). There were also previous instances where canines have been used to find similar electronic devices. In 2008, The Motion Picture Association used trained canines to find pirated DVDs (5), and in several states, the Department of Corrections has used canines to find illegal cell phones in prisons (6).

Compared to instrumental detectors, canines have superior sensitivity and selectivity capabilities. Canines are able to discriminate between complex odors, such as between different humans or between target and background odors. Additionally, they are mobile detectors with integrated sampling systems that have the unique ability to use concentration gradient of the odor of interest to determine directionality, a feat no instrumental detector has been able to mimic (2,7,8).

Olfaction is a biological process for chemically sensing chemical vapors (9). Olfaction occurs when odor molecules, or odorants, bind to olfactory receptors, activating the olfactory neurons. An odorant is the single molecule binding to the receptor, while an odor is the result of a group of odorants on the olfactory receptors. For a dog to perceive an odor, odorant molecules must reach the nostril, either as a volatile molecule or attached to a particle. When no particles are present, such as in the case of a concealed item, vapor will diffuse from the source

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Received 16 Sept. 2016; and in revised form 29 Dec. 2016; accepted 24 Jan. 2017.

in all directions, effected by air currents, temperature, and humidity. This is known as the vapor plume, and it is this vapor plume that the canine uses to locate the item of interest (7).

The collection of odorants making up the odor of a target item is often known as the “odor profile” or “odor signature” of that target. It is understood that often the odor signature does not actually include the target molecule itself, but instead, other odorant molecules associated with it (10,11). For example, methyl benzoate is the main volatile component found in the headspace of cocaine. It has been shown that canines do not detect the cocaine molecule itself, but the methyl benzoate associated with it (10). Much work has been carried out determining the odorants associated with various detection targets. There is an extensive library of work determining the odor signature of canine targets, particularly explosives and narcotics (8,10–14). Identification of the odorants comprising an odor signature is important in understanding the basic science of olfaction, improving canine performance, reliability, and limits of detection, and creating or improving training aids or mimics (2,8,12).

In this research, the odor signatures of mass storage devices were characterized in order to assess the feasibility of canines to detect such targets. Sampling was carried out using solid phase microextraction (SPME) with analysis by gas chromatography/mass spectrometry (GC/MS). Depending on the SPME fiber phase selected, SPME has the capability of extracting polar and nonpolar, volatile and semi-volatile compounds from the headspace of forensic specimens. Lorenzo et al., as well as other researchers, have demonstrated that SPME-GC/MS is an effective method for identifying the volatile compounds canines use to detect a variety of targets (8,12). Using this technique, volatile compounds from the SIM cards and USB drives were discovered that were characteristic to these MDSs in comparison with a variety of other household electronic devices.

Materials and Methods

Electronic Devices

The volatile components composing the headspace of a variety of SIM cards, SD (secure digital) cards, and USB drives were compared. SIM cards tested included T-Mobile 3-in-1 SIM card, Net10 Wireless SIM card, AT&T go phone SIM card, H20 Wireless Smart SIM 3-in-1 SIM card, and Simple Mobile Dual SIM card. The SanDisk Ultra microSDHC UHS-I card and PNY High Performance SD card were also tested. Four USB drives including SanDisk Cruzer Glide USB Flash Drive, Gorilla Drive USB flash drive, Quicksilver capless USB flash drive, and Micron Lexar Jumpdrive S50 were also compared. All MSDs were purchased for this study.

A number of other electronic items were used as controls. These included AA batteries, circuit board connectors, multiwire cables, populated circuit boards, unpopulated circuit boards, an Ethernet cable, LR44 batteries, and multipin connectors. The headspace of the MSDs was also compared to several cell phones. These included an iPhone 4, Motorola flip phone, LG-VS660 smartphone, Samsung SCH-I200 smartphone, and HTC Aria smartphone.

Sampling and Analysis

For sampling, all MSDs and controls were placed in uncoated metal evidence cans (TriTech Forensics; Southport, NC). Sizes of 1 pint or 1 quart were used depending on the size of the electronic device. Holes for sampling were punched in the center of all can lids. Prior to sampling, all cans were cleaned with isopropyl alcohol and baked at 85°C for at least four hours. All electronic devices were cleaned in the same manner to remove any human-imparted odors that might be confused for target odor, as was carried out in Hudson et al. (15) and Kusano et al. (16). In both Hudson et al. and Kusano et al., gauze pads were baked at 105°C to remove any human-imparted odor (15,16). To protect the integrity of the rubbers/plastics of the MSDs, this temperature was lowered to 60°C, and the items were baked for no more than two hours.

Samples were placed into the evidence cans with the lids and were allowed to equilibrate at room temperature overnight for approximately 18 h. A piece of parafilm was placed over the hole in the can lid to prevent volatiles from escaping during this time. Blank cans not containing any electronic device were prepared in the same manner. After equilibration, a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) solid phase microextraction (SPME) fiber (Sigma-Aldrich; St. Louis, MO) was inserted for another 18 h, also at room temperature. DVB/CAR/PDMS fibers were chosen as they are able to extract the widest range of analyte polarities. All samples, including controls and blanks, were sampled in duplicate. Triplicate samples were analyzed only in cases where discrepancies were seen between the duplicate analyses.

Analytes were desorbed from the SPME fibers at 260°C into the inlet of a 6890 Agilent gas chromatograph (GC) with a 5975 mass spectrometer (MS) (Agilent Technologies, Santa Clara, CA) with a 30 m Rtx-5MS column (Restek; Bellefonte, PA). The flow rate through the column was 2 mL/min with a 10:1 split at the injector. During each separation, the GC oven was programmed to 50°C for 30 s after which the oven temperature was increased to 100°C at a rate of 40°C/min and then to 260°C at 20°C/min. The final temperature was held for 1 min. The MS transfer line was heated to 250°C and the MS scanned from *m/z* 29–300 during each run.

Results and Discussion

Volatile headspace components of a variety of MSDs were assessed. The MSDs were divided into two categories: SIM/SD cards and USB drives. Headspace components that were found in at least 75% of either the SIM/SD cards or USB drives are listed in the left column of Table 1. Table 1 also indicates whether these compounds were present in the headspace of any of the electronic devices used as controls or the cell phones. Example chromatographs of SIM cards (Fig. 1*a*) and USB drives (Fig. 1*b*) are overlaid and labeled with some key headspace components.

Of the compounds listed in Table 1, acetic acid, propanoic acid, octanal, nonanal, and decanal were all determined to be from the background and not characteristic of any electronic device. 2-ethyl-1-hexanol was found in all electronics and was not unique to the MSDs. 2-ethyl-1-hexanol is used in many products to include solvents, lubricants, and fuels (17), and it also has been listed as a characteristic compound associated with certain explosives (18,19), blood plasma from cancer patients (20), and currency ink (21). Other compounds, however, were highly characteristic. 2-propenenitrile was found only in the SIM cards and was a likely volatile product of an acrylonitrile-based polymer (22) plastic making up the SIM card, such as acrylonitrile butadiene styrene (ABS) or styrene acrylonitrile (SAN). Styrene was found solely in both SIM cards and USB drives and

TABLE 1—*Compounds found in the headspace of SIM and SD cards and USB drives, and their presence in other electronic devices or cellular phones.*

Volatiles in MSDs	Controls						Cell Phones					
SIM and SD cards	AA Batteries	Circuit Board Connectors	Multiwire Cables	Populated Circuit Board	Unpopulated Circuit Board	LR44 Batteries	Multipin Connectors	LG Smart Phone	Motorola Flip Phone	Samsung Smart Phone	HTC Smart Phone	iPhone
2-propenenitrile												
Acetic acid		×	×	×	×	×	×	×	×	×	×	×
Propanoic acid		×		×		×	×					
Styrene			×									
2-ethyl-1-hexanol	×		×	×		×	×	×	×	×	×	×
Nonanal	×		×	×	×	×	×	×	×	×	×	×
Hydroxycyclo hexylphenyl ketone								×		×		×
USB drives												
Acetic acid	×	×	×	×	×	×	×	×	×	×	×	×
Styrene			×	×								
2-furanmethanol, tetrahydro												
Octanal	×		×	×	×	×		×	×	×	×	×
2-ethyl-1-hexanol	×		×	×		×	×	×	×	×	×	×
Nonanal	×		×	×	×	×	×	×	×	×	×	×
3,5,5-trimethyl-2-cyclohexen-1-one								×				×
Decanal	×		×	×	×		×	×	×	×	×	×

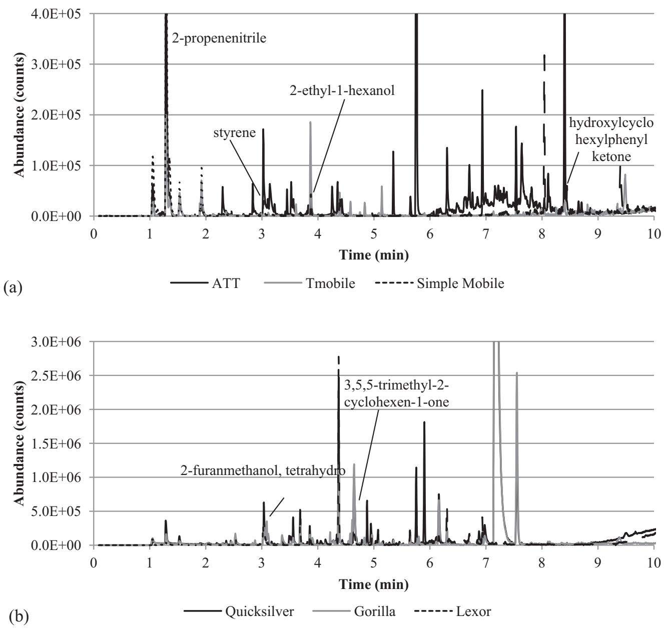

FIG. 1—*Overlaid total ion chromatograms with key compound labeled for (a) selected SIM cards and (b) selected USB drives.*

was likely derived from the same or similar type of polymer plastic. Hydroxycyclohexyl phenyl ketone was found in all SIM cards, SD cards, and smart phones. This compound is used as a photoinitiator in UV-cured circuit printing technologies (23). 3,5,5-trimethyl-2-cyclohexen-1-one (isophorone) was found in all USB drives and two of the smartphones. The exact origin of this compound is unknown, but isophorone is a solvent used in inks, adhesives, resins, and coatings (24). Tetrahydro-2-furanmethanol was found in all USB drives. It is also a solvent and is of unknown origin in MSDs.

These key volatile compounds associated with MSDs are summarized in Table 2. None of these compounds are completely unique on their own. For example, several likely originate from the plastic of which the items are fabricated. They are thus likely to be found in other items made from the same plastic not analyzed in this study. The combinations of these key compounds with other compounds found, such as 2-ethyl-1-hexanol, make up the overall characteristic odor profile of the mass storage devices. To further establish which compounds are important for canine detection, and in what ratio, further canine testing should be carried out. Future work could also expand upon the list of MSDs tested to include additional devices, such as hard drives and hard drive components.

TABLE 2—*Important volatile compounds associated with and unique to certain mass storage devices.*

Key Compounds	Occurrence in MSD
2-propenenitrile	SIM cards
Styrene	SIM cards and USB drives
2-ethyl-1-hexanol	Not key compound, but common to electronics and may make up odor profile
Hydroxycyclohexyl phenyl ketone	SIM and SD cards, smart phones
3,5,5-trimethyl-2-cyclohexen-1-one (isophorone)	USB drives and some smart phones
2-furanmethanol, tetrahydro	USB drives

Conclusion

In the evaluation of the headspace of MSDs and other electronic devices, several compounds were determined to be exclusively associated with the MSDs. These included 2-propenenitrile, styrene, hydroxycyclohexyl phenyl ketone in SIM/SD cards, and styrene, isophorone and 2-furanmethanol, tetrahydro in USB drives. These results indicate that MSDs do have a characteristic odor making detection with minimal false alerts feasible for trained canines.

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