

# Vapor Signatures of Double-Base Smokeless Powders and Gunshot Residues for Supporting Canine Odor Imprinting

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Cite This: *ACS Omega* 2022, 7, 22567–22576



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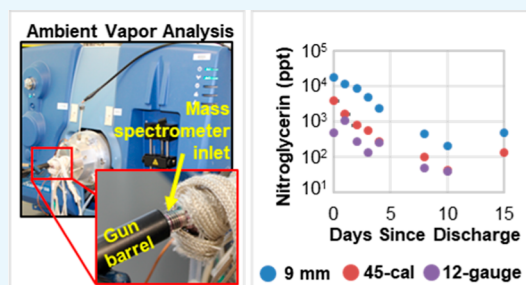


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**ABSTRACT:** Non-intrusive means to detect concealed firearms based on magnetometry are widely accepted and employed worldwide. Explosive detection canines can also detect concealed firearms provided that they are imprinted on materials that may be related to firearms such as nitroglycerin in double-base smokeless powders. However, there are hundreds of possible smokeless powder formulations across various manufacturers, presenting a challenge for trained canines to generalize across all possible powder compositions. In response, this paper reports a set of potential imprinting vapor(s) that may help detection canines generalize across a variety of double-base smokeless powders and gunshot residues. Statistical analysis was conducted on the smokeless powder database maintained by the National Center for Forensic Science, and headspace measurements targeting nitroglycerin and diphenylamine were collected from several powders. In addition, measurements were taken to track nitroglycerin and diphenylamine vapor concentration changes over time on the spent casings and gun barrels of four types of ammunition. The observed vapor concentration mixing ratios for nitroglycerin and diphenylamine from residues were in the part-per-billion to part-per-trillion range, which would be challenging to detect for many field-deployed explosive vapor detectors and indicate continued importance of canines for forensic investigation and crime prevention. Analyses suggest four potential vapor compositions for imprinting. For unburnt powders, 90% nitroglycerin and 10% diphenylamine appear adequate for most powders, and 90% dinitrotoluene and 10% diphenylamine is a possible candidate to increase generalization to powders that contain dinitrotoluene instead of nitroglycerin. 100% nitroglycerin appears adequate for many gunshot residues (GSRs). Diphenylamine may be present in some GSRs, and equal compositions of nitroglycerin and diphenylamine may be adequate for imprinting against these residues as they age (this study tracked signatures up to 7 weeks after discharge).



## INTRODUCTION

Explosive detection canines are often tasked with finding both concealed firearms and explosives, and many explosive detection canine teams already incorporate some form of scent imprinting against nitroglycerin, which is a common component of double-base smokeless powder. However, like many explosives and energetic materials, common smokeless powders used in firearms are mixtures that contain plasticizers, desensitizers, and stabilizers along with the energetic compound,<sup>1,2</sup> and manufacturers produce custom formulations and mixtures that are aimed to control powder properties such as burn characteristics. There are, therefore, hundreds of possible formulations for detection canines to generalize during operation, and determining the optimal imprinting formulations toward all of these threats is important.

Because there are hundreds of smokeless powder compositions, it is intuitive to anticipate gunshot residues (GSRs) to be similarly variable. The headspace of GSRs is expected to contain many of the same compounds as unburnt powder,<sup>1,3–5</sup> but the overall vapor signatures will be altered by degradation (e.g., from environmental exposure and the firing process) and how the firearm has been handled (e.g., how frequently the

firearm is cleaned and used). There are anecdotal accounts from canine trainers that the performance of a canine can decrease for old GSRs, which may be attributed to decreasing vapor concentrations and altering vapor compositions over time. It is important to note that past studies have tracked GSR vapor signatures for several weeks and shown that signatures can remain detectable, so some vapors may still be available for odor detection.<sup>6</sup>

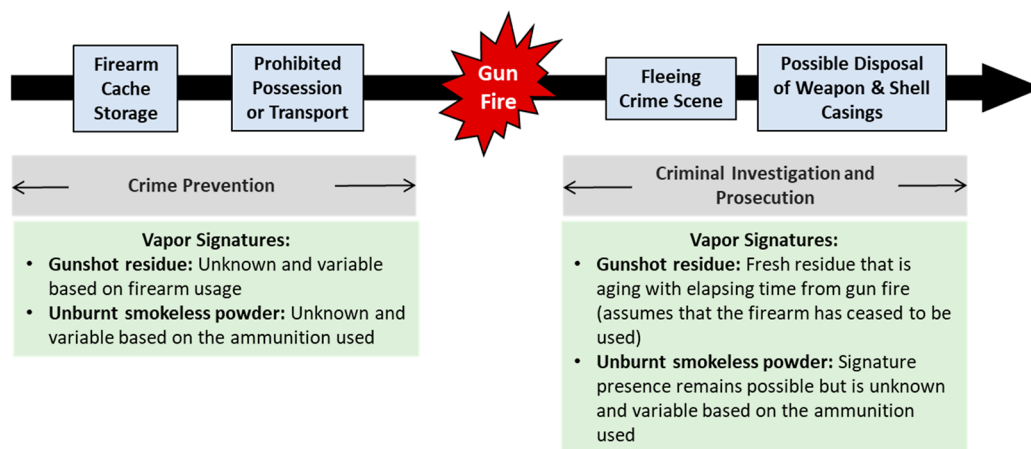
These considerations on powder and GSR signatures can be mapped onto a chain of events associated with a pre-planned firearm crime (Figure 1). Vapor signatures before a firearm crime event can be unknown and variable unless there is additional intelligence regarding the firearm's usage and ammunition. Signatures immediately after a gun crime should

Received: March 28, 2022

Accepted: June 7, 2022

Published: June 17, 2022





**Figure 1.** Firearm crime chain of events. Variations in firearm-associated vapors exist throughout the event chain. Odor imprinting that accounts for these variabilities can help canine teams serve in both forensic investigation and searching for prohibited concealed firearms.

contain fresh GSRs because the firearm has been recently discharged.<sup>7</sup> The GSR will then age with elapsing time after the event,<sup>5,8–12</sup> assuming that the firearm has ceased to be used. What can be seen in Figure 1 is the amount of uncertainties regarding signature composition and availability across the entire event chain. An improved understanding of vapor signatures for both smokeless powders and GSRs will improve canine operational proficiency not only for forensic investigation but also for searching for concealed firearms in areas where their possession is prohibited.

Though there can be large variabilities in vapor compositions, smokeless powders, and GSRs have in fact been analyzed extensively, and there is also an ASTM method for characterizing GSRs using scanning electron microscopy (SEM) and dispersive X-ray spectrometry.<sup>13</sup> For headspace analysis, solid-phase microextraction-gas chromatography/mass spectrometry (SPME-GC/MS) and its variations are among the most popular in the field of explosive detection,<sup>4–6,14–18</sup> including a recent demonstration by Nettles et al.<sup>18</sup>

Building on the wealth of MS applications for forensic science and other applications,<sup>19,20</sup> The goal of this study is to complement past measurements by using ambient ionization-MS (AI-MS) to narrow down promising imprinting vapor(s) for providing canine search performance across powder formulations and residue ages. This study used a triple-quadrupole mass spectrometer with a custom ionization source to directly measure vapor emanation from the sample.<sup>21</sup> The system in this study differs from many past MS measurements by (1) not requiring vapor sampling like SPME-GC/MS,<sup>3,4,6,15,22</sup> (2) not requiring liquid extraction of the solid sample,<sup>23,24</sup> (3) not heating the sample,<sup>25</sup> and (4) not requiring a sample desorption step like thermal desorption or desorption electrospray ionization (DESI). All measurements herein focused on naturally emanating vapor and were conducted in real-time under ambient conditions ( $\sim 20$  °C). We believe these experimental conditions better mimic how canines would encounter smokeless powders and GSRs in reality, so the results could subsequently be speculated as more impactful for informing odor imprinting.

A prior version of the instrument used in this study utilized secondary electrospray ionization (SESI) and had been published with technical drawings of the ionization source.<sup>21</sup> In this study, the electrospray emitters are replaced with a DC corona needle in the sample vapor flow path. Striking a DC

corona in air sets off a chain of reactions involving atmospheric components,<sup>26</sup> and analyte ionization can follow reaction pathways that are typical of APCI.<sup>26–28</sup> There are several prior demonstrations of vapor analysis with DC corona discharge ionization,<sup>29–32</sup> and other ionization methods that enable similar real-time MS measurements include SESI,<sup>33–37</sup> proton-transfer reaction (PTR),<sup>34,38</sup> atmospheric flow tube ionization (AFT),<sup>39–43</sup> selected ion flow tube (SIFT),<sup>44–46</sup> and dielectric barrier discharge ionization (DBDI).<sup>47–50</sup>

In terms of experimental design, this study is composed of two parts that separately focused on unburnt smokeless powders and GSRs. For smokeless powder analysis, hierarchical clustering analysis was conducted on entries in the National Center for Forensic Science (NCFS) Smokeless Powder Database,<sup>51</sup> which contains chemical analysis data (e.g., GC/MS data) for hundreds of powders. Based on clustering results, several powders were then selected for headspace validation measurements. For GSRs, headspace measurements were taken to track how headspace nitroglycerin and diphenylamine concentrations changed over the course of 7 weeks. Measurements were collected from the discharged spent casings and gun barrels of four types of ammunition (9 mm, 0.45 caliber, 5.56 NATO, and 12-gauge shotgun). The target analytes were nitroglycerin and diphenylamine because those two compounds were anticipated to be abundant and common among smokeless powders.

Lastly, it is important to mention that a common concern with smokeless powder and GSR detection is the ubiquity of their components in the environment. Firearms are legal in the United States, and common powder components like nitrocellulose, nitroglycerin, diphenylamine, and dibutyl phthalate all have other uses in pharmaceutical or industrial applications. These concerns eventually lead to considerations of acceptable false alarm rates, which is situation dependent and should be determined based on the sensor's mission areas and in consultation with the operational stakeholders.<sup>52</sup> In this case, in which a sensor (canine) alert may have underlying reasons that are benign, multiple orthogonal information sources may have to be utilized in order to achieve acceptable detection and false alarm rates.

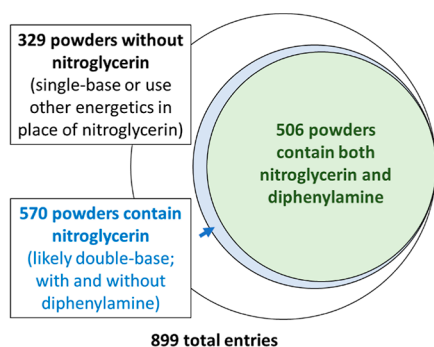
## RESULTS AND DISCUSSION

### Double-Base Smokeless Powder Vapor Signatures.

To examine unburnt smokeless powder signatures, entries in

the NCFS smokeless powder database were statistically analyzed to determine categories of smokeless powders based on the chemical composition. Selected powders were then subjected to laboratory headspace measurements.

**NCFS Database and Categorizing Double-Base Smokeless Powder.** The NCFS smokeless powder database is maintained by the University of Central Florida and contains both chemical analysis data (e.g., GC/MS) and physical descriptions (e.g., prill shape).<sup>51</sup> There are 899 entries in the database as of July 2021. Analysis started by using the database's interface to parse entries into those that are listed with (1) nitroglycerin, (2) diphenylamine, and (3) dinitrotoluene. Nitroglycerin is a common component of double-base smokeless powder, and diphenylamine is a popular powder stabilizer that slows degradation.<sup>14,24,53</sup> Based on their ubiquity and relatively high vapor pressures, nitroglycerin and diphenylamine were anticipated to be common and abundant headspace components, and their occurrence is summarized in Figure 2. Of the 899 entries, 570 entries list nitroglycerin



**Figure 2.** Description of the NCFS smokeless powder database with regard to nitroglycerin and diphenylamine compositions.

(63%), and 821 entries list diphenylamine (91%). 506 entries list both nitroglycerin and diphenylamine (56%). 400 entries list 2,4-dinitrotoluene (44%). This simple exercise shows that some combinations of nitroglycerin, diphenylamine, and dinitrotoluene are anticipated to be a part of the headspace for a large variety of powders.

The next step of analysis conducted powder classification using chemical data downloaded from the NCFS database—with the goal of identifying categories of potential vapor compositions for imprinting canines. GC/MS data from the database were used to make simple estimates of the headspace. First, all available data were curated to isolate entries that contain nitroglycerin. This decision underlies an assumption that imprinting vapors should ideally contain the energetic compound if possible. To estimate the headspace, the GC/MS peak area for each compound was assumed to be proportional to the powder's molar composition. The molar ratios were then converted to mass ratios based on each compound's molar mass, and then to volume ratios based on density. The volume ratios were lastly used to estimate headspace composition based on published vapor pressures.<sup>54,55</sup> Volume ratios were used for estimating headspace composition because sublimation rates correlate with the surface area,<sup>56</sup> and though still flawed, volume was anticipated to better reflect the surface area than the mass.

With the estimated headspace, hierarchical clustering analysis was conducted, and three powder categories were created (Table 1; dendrogram provided in Figure S1). The

**Table 1. Smokeless Powder Categories Based on the Estimated Headspace Composition and Hierarchical Clustering Analysis**

compound	headspace composition (%) <sup>a</sup>
All Powders (495 Entries)	
nitroglycerin	52.3
diphenylamine	40.4
dibutyl phthalate	4.4
Category 1 (413 Entries)	
nitroglycerin	45.2%
diphenylamine	48.4%
dibutyl phthalate	4.2%
Category 2 (80 Entries)	
nitroglycerin	93.9%
diphenylamine	3.4%
Category 3 (2 Entries)	
DNT	66.7%
diphenylamine	32.5%

<sup>a</sup>Components are listed in order of decreasing relative concentration until at least 95% of the headspace is accounted.

difference between each category is primarily driven by nitroglycerin, diphenylamine, and dinitrotoluene (DNT). This pattern is expected because these compounds have relatively high vapor pressures compared to the other components. Category 1 is the largest with 413 out of 495 entries and contains a near equal ratio of nitroglycerin and diphenylamine (83% of the analyzed entries). This category, being the largest, is also the most similar to the average of all powders. Category 2 is the second largest and contains mostly nitroglycerin (80 entries; 16% of the analyzed entries), and category 3 has DNT and nearly no nitroglycerin (less than 1% nitroglycerin; 2 entries; 0.4% of the analyzed entries).

**Smokeless Powder Headspace Analysis.** Based on clustering analysis, several powders were selected for laboratory validation headspace measurements (Table 2). Selections were made across clustering categories and across multiple powder prill shapes as listed in the NCFS database. The inclusion of prill shape was to enlarge consideration beyond headspace estimates to include some aspects of manufacturing approach.

Measurements were taken using a triple-quadrupole mass spectrometer in MRM mode equipped with a custom ambient ionization source.<sup>21</sup> Example data images are provided in the Supporting Information document, as shown in Figures S2 and S3. Measurements revealed a discrepancy from statistical estimates (Figure 3). When considering just nitroglycerin and diphenylamine, the headspace of powders from both Categories 1 and 2 were observed to contain ~90% nitroglycerin, even though Category 1 powders were estimated to contain a near 1:1 ratio of nitroglycerin and diphenylamine. One powder from Category 3 was analyzed, and 92% DNT was observed and no nitroglycerin. It is notable that powders appear even more similar based on measurements than from statistical estimates, which already suggests 83% of the powders falling into one category. The large similarities between powders can represent a challenge for unique identification of unknown samples, which has been investigated in depth elsewhere also using entries from the NCFS database.<sup>1,57</sup>

Discrepancies between the measured and estimated compositions in this study indicate that solid phase compositions do not easily relate to the headspace, even

Table 2. Smokeless Powders Selected for Headspace Validation Measurements

index	prill shape (reported in the NCFS database)	powder category (Table 1)	measured nitroglycerin concentration (ppt) <sup>a</sup>	measured diphenylamine concentration (ppt) <sup>a</sup>	relative nitroglycerin percent (%)	relative diphenylamine percent (%)
1	ball	category 1	$1.42 \times 10^4$	$1.24 \times 10^3$	92	8
2	ball	category 1	$1.35 \times 10^4$	$8.26 \times 10^2$	94	6
3	ball	category 2	$1.64 \times 10^4$	$1.56 \times 10^3$	91	9
4	cylinder	category 1	$4.80 \times 10^3$	$9.17 \times 10^2$	83	16
5	cylinder	category 2	$2.75 \times 10^4$	$5.22 \times 10^1$	100	0
6	cylinder	category 1	$3.74 \times 10^4$	not detected	100	0
7 <sup>b</sup>	cylinder	category 3	not detected	$2.58 \times 10^3$	0	8
8	cylinder	category 1	$4.98 \times 10^3$	not detected	100	0
9	disk	category 1	$3.98 \times 10^4$	$1.71 \times 10^2$	100	0
10	flattened ball	category 1	$1.34 \times 10^4$	$9.29 \times 10^2$	93	6
11 <sup>c</sup>	flattened ball and irregular	category 1	$2.27 \times 10^4$	$5.62 \times 10^3$	80	20
12	flattened ball and ball	category 1	$1.00 \times 10^4$	$1.85 \times 10^3$	84	16
13	flattened ball	category 2	$6.64 \times 10^3$	$1.66 \times 10^3$	80	20

<sup>a</sup>Part per trillion; defined as moles of target/moles of air. <sup>b</sup>This powder contains dinitrotoluene (measured  $2.91 \times 10^4$  ppt; 92% of headspace).

<sup>c</sup>Based on headspace estimates, this powder has a composition most similar to the average composition of all powders.

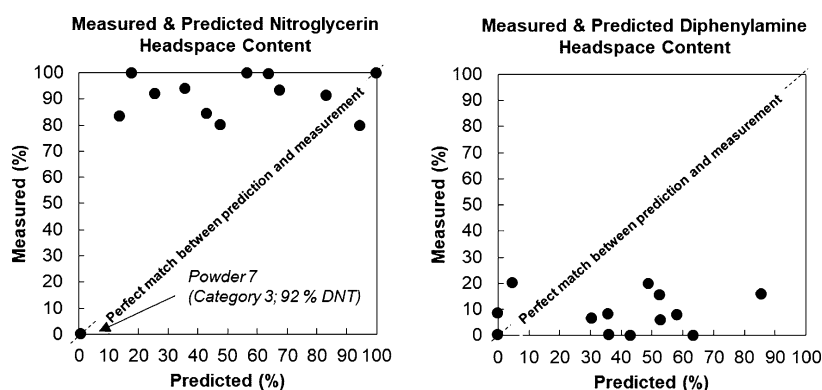


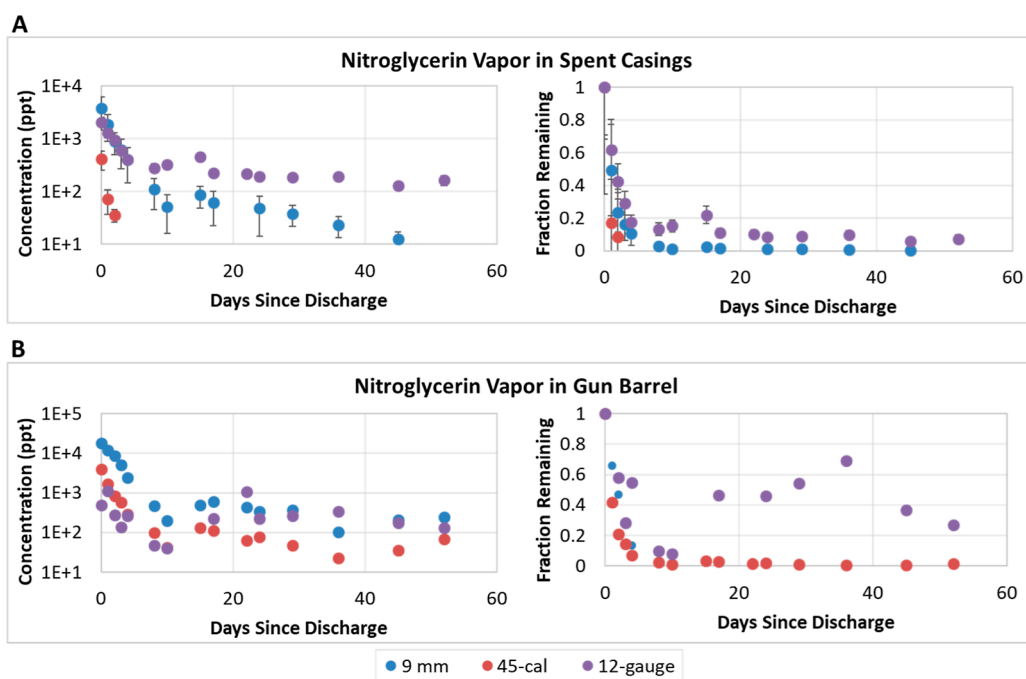
Figure 3. Measured and estimated relative nitroglycerin and diphenylamine headspace concentrations. The diagonal line indicates a perfect match between estimates and laboratory measurements.

after accounting for component vapor pressures. Anticipated sources of error include (1) volume ratios being flawed standards for the surface area and (2) manufacturing methods, which were unaccounted beyond selecting multiple prill shapes. Improved modeling may require additional factors such as potential prill coatings and how the components are mixed and layered within each prill.

In addition to challenges associated with predicting the headspace, another source of discrepancy may be biases of the analysis approach. This study conducted direct sample measurements in open air without chromatography. The analysis is, therefore, more susceptible to matrix interferences than traditional GC/MS or HPLC-MS studies. We can consider potential interferences to come from the laboratory air and the sample itself. To address interferences from the air, the instrument was calibrated for nitroglycerin and diphenylamine every day using separate vapor saturator tubes based on a prior protocol.<sup>21,37</sup> Calibration vapors were presented to the instrument in the same manner as the sample, with both the tubes and the produced vapors exposed to the laboratory. Matrix effects from the laboratory air were, therefore, accounted by this external calibration process. Further, because dedicated calibration curves were produced for each target analyte, inherent system biases toward one compound or another were also addressed.

Interferences from the sample are more challenging to address. Experimental options may include redesigning the ionization source to introduce vapor from an isotopically labeled internal standard or validating all results with a separate analytical approach. Considering only the data in this study, we first note that effects from the matrix typically manifest as ionization suppression. Our primary analyte targets were nitroglycerin and diphenylamine. For nitroglycerin, it had stronger signals that do not suggest ionization suppression. We also focused on detecting nitroglycerin precursor ions with a nitrate (62 Da) or a bicarbonate adduct (mass 61 Da). Nitroesters (like nitroglycerin) and nitramines (like RDX) have high affinities for these adducts, making them more robust against deleterious ion suppression. In fact, by optimizing reaction times for chemical ionization, nitrate adducts can even be used for detecting ambient vapor from RDX,<sup>43</sup> which at saturation is still in the low ppt range.<sup>39</sup> Lastly, we note that nitroaromatics like DNT and TNT do not form nitrate adducts as readily,<sup>58</sup> so interferences from those compounds are not expected (i.e., interference from DNT in the powder is not expected). For diphenylamine, the signal was lower. However, diphenylamine is an amine, and amines have high proton affinities that make them unlikely to be outcompeted by other matrix components. In fact, a review by Beauchamp and Zardin shows that amines have generally higher proton affinities than most other common chemical





**Figure 4.** Vapor concentration of nitroglycerin from gunshot residues. (A) Nitroglycerin vapor from spent casings in units of part-per-trillion (ppt; left) and fraction of vapor remaining after normalization to initial concentrations after firearm discharge (right). Each data point represents averaged results from five discharged casings and all quantified mass transitions (Table S1). The error bars represent one standard deviation. (B) Nitroglycerin vapor from gun barrels in units of ppt (left) and fraction of vapor remaining after normalization to initial concentrations after firearm discharge (right).

functionalities.<sup>59</sup> The inherent chemical properties of the target analytes and the observed signal strengths suggest that effects from the matrix are small in the presented data.

**Potential Vapor Compositions for Odor Imprinting Against Unburnt Double-Base Smokeless Powder.** Two potential vapor compositions for odor imprinting against unburnt double-base smokeless powder were found based on statistical analyses and laboratory measurements. For most double-base smokeless powders that contain nitroglycerin, 90% nitroglycerin and 10% diphenylamine is a potential composition regardless of the powder prill shape and relative composition of the solid material. To increase generalization to powders that contain DNT instead of nitroglycerin, an imprinting composition of 90% DNT and 10% diphenylamine appears to be promising. It is important to note that these observations have been made using only laboratory measurements, so validation with canine tests will be required prior to operational deployment.

**Gunshot Residue Vapor Signature Changes over Time.** To examine gunshot residue signatures, spent casings and used barrels from 9 mm, 0.45 caliber (45-cal), 5.56 NATO, and 12-gauge firearms were subjected to headspace measurements for up to 7 weeks after discharge. Measurements targeted nitroglycerin and diphenylamine as a continuation of this study's consideration on unburnt smokeless powder.

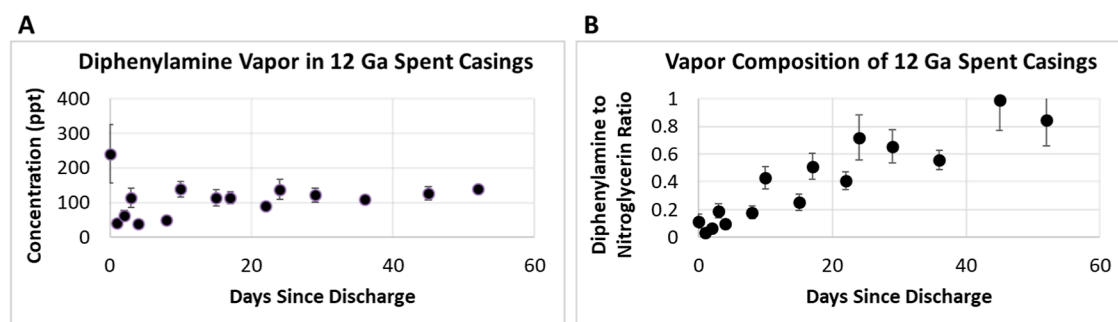
**Nitroglycerin Signatures from Spent Casings.** Nitroglycerin was observed from 9 mm and 12-gauge casings for the entire measurement period and not from the 5.56 NATO casings (Figure 4). Weak signatures were observed from the 45-cal casings that dropped below the quantitation limit after only three time points (2 days after firearm discharge). Prior studies have observed that smokeless powder could remain in

spent casings after a discharge,<sup>5</sup> and so it is unsurprising to detect nitroglycerin as a part of these residues.

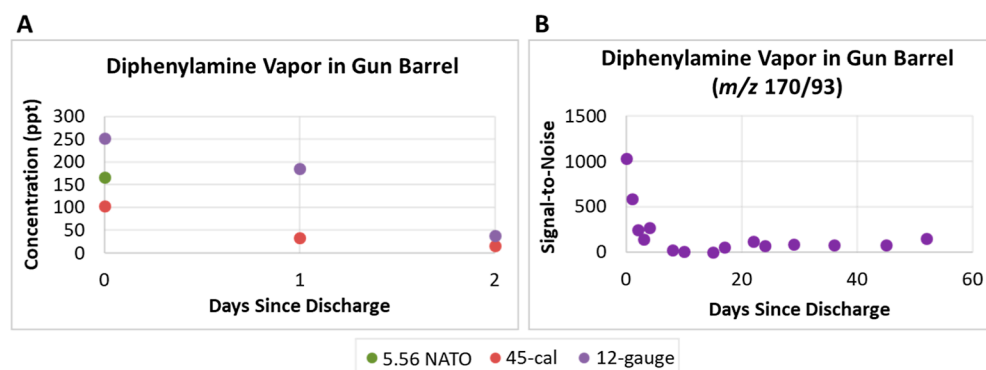
The clearance of residual nitroglycerin vapor was fitted to an exponential decay (Figure S4).<sup>56</sup> Analysis was conducted on data collected from whole casings (both the mouth and primer end of the casing; Figure S4A) and data from only the primer end (Figure S4B). The primer end presented both lower signatures and faster decay compared to whole casings. The decay constants for whole casings are  $-0.70/\text{day}$  and  $-2.23/\text{day}$  for only the primer end. Faster clearance from the primer end makes intuitive sense because (1) the smokeless powder is packed inside the casing before discharge, so more residues are anticipated to be inside the casing than on the primer end and (2) the primer end is more exposed to the environment than inside the casing, thus allowing faster vapor clearance.

**Nitroglycerin Signatures from Gun Barrels.** Similar to the spent casings, nitroglycerin was undetected from the 5.56 NATO barrel and detected from the 9 mm, 45-cal, and 12-gauge barrels, with also generally low signal from the 45-cal samples. More inter-day scatter was observed from the 12-gauge barrel, and signatures plateaued at an elevated level over time. The underlying causes remain to be investigated, but it may be contributed by a redistribution of residues during handling each day. The large size of the barrel could also cause more variations in the analysis location, as the barrel was held by hand in front of the instrument inlet during measurements.

Nitroglycerin cleared more slowly from the barrels than from the casings. A decay constant of  $-0.43/\text{day}$  was calculated for all barrels that presented detectable signatures (9 mm, 45-cal, and 12-gauge; Figure S4C). Because of data scatter and an unexpected elevated plateau, analysis was repeated after removing the 12-gauge data (decay constant of  $-0.54/\text{day}$ ; Figure S4D). Between spent casings and barrels,



**Figure 5.** Vapor concentration of diphenylamine from 12-gauge spent casings. (A) Diphenylamine concentrations. Each data point represents averaged results from five discharged casings and all quantified mass transitions. The error bars represent one standard deviation. (B) Diphenylamine and nitrolycerin ratios. Each data point represents averaged results from five discharged casings, and error bars represent the standard deviation.



**Figure 6.** Residual diphenylamine vapor signatures from gun barrels. (A) Signatures from 5.56 NATO, 45-cal, and 12-gauge barrels. (B) Qualitative signals from 12-gauge barrels (SNR for  $m/z$  170/93).

the rate of clearance slowed from casing primers (decay constant of  $-2.23/\text{day}$ ) to whole casings ( $-0.7/\text{day}$ ) to barrels ( $-0.43/\text{day}$  and  $-0.54/\text{day}$ ). This trend is consistent with the sample form factor and the extent of environmental exposure. The casing primer is the most exposed to the environment, so vapor clearance should occur the most rapidly. Gun barrels start off with more accumulated residue from multiple discharges, and barrel lengths are longer than casings which reduce environmental exposure, so the signature should decay slowly.

**Diphenylamine Signatures from Spent Casings.** Low diphenylamine concentrations were detected from the 9 mm, 45-cal, and 5.56 NATO casings. Of these three sample sets, the strongest signal was observed from the 45-cal casings, which had 9 ppt of vapor on the day of discharge (analyzed within several hours). The signal was low even when using the uncalibrated but sensitive  $m/z$  170/93 mass transition. The signal fell below the limit of quantitation after 1 day (i.e., signal-to-noise ratio less than 10).

Around 200 ppt of diphenylamine was observed from 12-gauge casings on the day of discharge (Figure 5A), and concentrations changed little during the measurement period. When considered in combination with the nitrolycerin measurements, near equal concentrations of nitrolycerin and diphenylamine were observed by the end of the measurement period (Figure 5B), a trend that was driven primarily by decreasing nitrolycerin concentrations.

**Diphenylamine Signatures from Gun Barrels.** Like the spent casings, low diphenylamine concentrations were detected from gun barrels. Figure 6A shows concentrations for three ammunitions for up to 2 days after discharge. Concentrations

fell below quantitation limits after this period and were no longer quantitatively tracked. For the 12-gauge barrel, however, it was still possible to qualitatively track concentrations using the uncalibrated  $m/z$  170/93 transition based on signal-to-noise ratios (SNRs; Figure 6B). SNR remained above 10 for the entire measurement duration except days 10 and 15, indicating there were still detectable diphenylamine signatures.

**Potential Vapor Compositions for Odor Imprinting on GSRs.** Two potential vapor compositions for odor imprinting against GSRs were found. The first composition contains only nitrolycerin—as most measurements detected nitrolycerin and no diphenylamine. However, both nitrolycerin and diphenylamine were detected throughout the study duration from the 12-gauge spent casings, and the ratio of the two compounds approached unity as the GSR aged. Imprinting on a second composition of equal nitrolycerin and diphenylamine may therefore also be useful. Prior studies have detected diphenylamine on a shooter's hands as well,<sup>9</sup> further supporting the inclusion of diphenylamine as a part of the imprinting odor.

Of note is the generally low observed vapor concentrations. Except for the first few time points, most measurements detected concentrations in the part-per-trillion range. Recent developments in AI-MS, including the technique used in this study, allow these concentrations to be observed without extensive pre-concentration.<sup>42,60</sup> However, these concentrations are still anticipated to be below the sensitivity of most portable vapor measurement techniques, such as colorimetry<sup>61</sup> and handheld ion mobility spectrometry (IMS) systems.<sup>62</sup> These results suggest that canines will remain operationally

**Table 3. Putative Imprinting Vapor Compositions for Detection Canines against Double-Base Smokeless Powder and Gunshot Residues**

target	potential imprinting compositions	comment
unburnt smokeless powder	90% nitroglycerin; 10% diphenylamine	appears adequate for most double-base smokeless powders
	90% dinitrotoluene; 10% diphenylamine	may extend generalization toward powders that contain dinitrotoluene instead of nitroglycerin
gunshot residue	100% nitroglycerin	appears adequate for most gunshot residues
	50% nitroglycerin; 50% diphenylamine	may extend generalization to residues that contain diphenylamine and have aged

relevant for explosive detection and are also promising options for firearm forensic investigation.

## CONCLUSIONS AND FUTURE WORK

Explosive detection canines are often tasked with finding concealed firearms, but the variety of smokeless powder composition varieties can present a challenge for odor generalization. Through statistical analyses and laboratory vapor measurements, four vapor compositions are suggested as potentially useful for imprinting canines against firearms (Table 3). A combination of 90% nitroglycerin and 10% diphenylamine appears to be promising against most unburnt smokeless powders, and 90% dinitrotoluene and 10% diphenylamine seem to have potential for expanding generalization to powders that contain dinitrotoluene instead of nitroglycerin. For imprinting against gunshot residues, 100% nitroglycerin appears to be representative of most fresh residues. If diphenylamine is also present, then a composition of equal nitroglycerin and diphenylamine may be useful for some older residues (this study measured residues up to 7 weeks after discharge).

It is important to note that additional developments must take place prior to deploying these results in operation. A set of additional laboratory measurements can include enlarging the number of smokeless powders that are considered, and altering the storage conditions for the discharged firearms to better mimic environmental exposure (e.g., altering temperatures, air flows, and sunlight exposures to mimic diurnal changes and material concealment). Of critical importance beyond laboratory analyses is to conduct canine validation tests to study how the vapors discussed in this study impact a canine's odor generalization gradient toward smokeless powders and GSRs.<sup>63</sup> Additional concerns, such as alerts caused by factors that are benign (e.g., legal possession of firearms), have not been a focus of this study but must be addressed. Lastly, this analysis focused on nitroglycerin and diphenylamine because they are putative dominant components of the double-base smokeless powder headspace. However, the total headspace is likely a complex mixture with many more chemicals, and there are many studies that list a bouquet of other volatiles in addition to nitroglycerin and diphenylamine.<sup>5,8,10–12,18,64</sup> It is also surprising that little diphenylamine signatures were detected, and degradation compounds of diphenylamine like nitrodiphenylamine and dinitrodiphenylamine are additional candidates for measurements and potential inclusion for odor imprinting. The extent that these other compounds may play a role in canine odor recognition remains to be studied.

## METHODS

**Mass Spectrometer Operation.** All MS measurements were performed on a Sciex 5500 QTRAP mass spectrometer (Sciex; Concord, Ontario, Canada) equipped with a custom ambient ionization source for vapor analysis. Ionization was

conducted using a DC corona held at  $\pm 4.5$  kV. The source was connected to both additional nitrogen gas supplies and a diaphragm pump in order to achieve a sampling flow rate of 1 L per minute. The source was held at 170 °C during operation.

MS measurements were conducted in multiple reaction monitoring modes (MRM). Nitroglycerin was detected in negative ion polarity (DC corona of  $-4.5$  kV), and diphenylamine was detected in positive ion polarity (DC corona of  $+4.5$  kV). The calibrated transitions were  $m/z$  288/46, 288/61, and 289/62 for nitroglycerin and  $m/z$  170/152, 170/153, and 170/77 for diphenylamine. Additional qualitative measurements for diphenylamine also used  $m/z$  170/92 and 170/93. Dinitrotoluene was measured in some cases using the  $m/z$  181/135 and 181/116 transitions. More details for the MRM methods are provided in the Supporting Information (Table S1). Example product ion scan mass spectra for nitroglycerin and diphenylamine, which were the primary analyte of focus, are provided in Figure S5. Example MRM chromatograms for analyzing a smokeless powder sample are provided in Figures S2 and S3.

Based on a previous protocol, instrument intensities were converted to vapor concentrations with external calibration curves generated using vapor saturator tubes for nitroglycerin, diphenylamine, and 2,4-dinitrotoluene.<sup>21,37</sup> Vapor saturator tubes for nitroglycerin or diphenylamine were held in front of the instrument inlet, and varying  $N_2$  flows were sequentially pushed through the tube to create different volumes of saturated vapor for generating a calibration curve.

Note,  $m/z$  170/92 and 170/93 were the most sensitive mass transitions for diphenylamine but were not used for quantitation in this study.<sup>53,65</sup> This decision was made due to a combination of diphenylamine's high proton affinity and volatility (several hundred parts-per-billion; ppb; defined as moles of the target/moles of air),<sup>54</sup> which challenged our calibration process because even diluted flow from vapor saturator tubes saturated the instrument's response (see "Data Processing and Signal Calibration"). Diphenylamine vapor was therefore quantified using less sensitive MRM transitions at  $m/z$  170/152, 170/153, and 170/77. The more sensitive  $m/z$  170/92 and 170/93 transitions were still monitored for qualitative analysis.

**Smokeless Powder Database.** Entries in the NCFs smokeless powder database were downloaded. The available GC/MS data were exported to .CDF file types. The exported files were processed using the XCMS library in R to isolate peak areas related to nitroglycerin, dinitrotoluene, diethyl phthalate, diphenylamine, methyl centralite, ethyl centralite, dibutyl phthalate, dipentyl phthalate, and dioctyl phthalate. Hierarchical clustering was done in R using the hclust function and average linkage clustering.

**Smokeless Powder Measurement.** Several powders were purchased for headspace measurements. The powders were placed in 20 mL glass scintillation vials and held by hand



in front of the ionization source inlet during measurements (~1 cm from the source inlet; ~1 min of measurement; Figures S2 and S3). The smokeless powder samples were allowed to equilibrate inside the vial for at least 1 day prior to measurements. Each scintillation vial was about half-filled with a powder.

**Gunshot Residue Measurement.** Five rounds of four ammunition types were discharged, including 9 mm, 0.45 caliber, 5.56 NATO, and 12-gauge. All ammunitions were loaded with factory charge. The barrel and the spent casings for each firearm were analyzed within hours after discharge. Measurements were repeated at multiple days up to 7 weeks.

Gun barrels were held by hand in front of the ionization source during measurements. The area of interest on the sample was held ~1 cm or closer to the mass spectrometer inlet during analysis. The muzzle end of the barrel was first analyzed for 30 s, then the barrel was flipped around, and the breech end was analyzed for 30 s.

Individual spent casings were placed in short pieces of open-ended stainless-steel tubes, and the tubes were clamped in front of the ionization source inlet during analysis (~1 cm or closer to the ionization source inlet). The mouth of the casing was first analyzed for 30 s. The casing was then flipped around and the primer end of the casing was analyzed for 30 s. The open-ended stainless-steel tubes were replaced for each spent casing, and all tubes were cleaned via sonication in methanol after analysis.

Firearm materials were stored exposed in ambient laboratory conditions. Laboratory temperature were maintained near 20 °C during the experiment time frame.

**Data Processing and Signal Calibration.** MS calibration curves for nitroglycerin and diphenylamine were collected every day that had sample measurement following methods described previously.<sup>21</sup> Briefly, a length of 1/4-inch (outer diameter) sulfinit stainless-steel tube (5 inches in length) was packed with 200 mg of deactivated glass wool (Restek; Bellefonte, PA). Several milligrams of nitroglycerin (1 mg/mL in acetonitrile; Sigma-Aldrich; Burlington, MA) or diphenylamine (≥99%; Sigma-Aldrich; Burlington, MA) were deposited into the packed tubes using standard solutions, and the solvents were dried at least overnight by passing N<sub>2</sub> through the tube (50 mL/min). Once dried, sequential flow rates of N<sub>2</sub> were passed through the saturator tube into the ionization source to create calibration curves.

For data processing, background and sample intensities were separately averaged per sample measurement. The background intensity was then subtracted from the sample intensity, and the difference was calibrated to vapor concentration. Concentrations from all monitored transitions were averaged together. For measurements of GSRs over time, the concentration for a time point was reported only if all transitions responded above the limit of quantitation (LOQ; signal to noise over 10).

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c01882>.

MS multiple reaction monitoring conditions, hierarchical clustering dendrogram, exponential fit of concentration change for gunshot residues, and example mass spectra and MRM chromatograms (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

DISTRIBUTION STATEMENT A. Approved for public release. Distribution is unlimited. This material is based upon work supported by the Department of Homeland Security, Science, and Technology Directorate through Inter-agency Agreements HSHQPM-17-X-00138 under Air Force Contract no. FA8702-15-D-0001. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Department of Homeland Security.

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