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Detection of Ammonium Nitrate Variants by Canine: A Study of Generalization Between Like Substances

Lauryn E. DeGreeff

Navy Tech Center for Safety and Survivability
Chemistry Division

Kimberly Peranich

Explosive Ordnance Disposal Technology Division
Naval Surface Warfare Center Indian Head

Alison Simon

Post-doctoral fellow, National Research Council

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U.S. Naval Research Laboratory
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Leveraging the analytical capabilities of the Naval Research Laboratory in collaboration with the Naval Surface Warfare Center Indian Head Naval EOD Technology Division with funding through the Office of Naval Research, this research explored the capability of canines to generalize or discriminate between related target odors including single target odors and binary mixtures. The explosive targets used in this study were ammonium nitrates (AN) of various brands, manufacturing processes, or forms (i.e. ground or prill). Mixtures included AN with fuel sources that commonly make up homemade explosives (HMEs). The study went further to pose the question of how training increases or decreases the canines' tendency to generalize between like substances. Concurrent laboratory analyses were carried out examining the volatile components available in the headspace of the AN variants.

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EXECTUTIVE SUMMARY

Leveraging the analytical capabilities of the Naval Research Laboratory in collaboration with the Naval Surface Warfare Center Indian Head Naval EOD Technology Division with funding through the Office of Naval Research, this research explored the capability of canines to generalize or discriminate between related target odors including single target odors and binary mixtures. The explosive targets used in this study were ammonium nitrates (AN) of various brands, manufacturing processes, or forms (i.e. ground or prill). Mixtures included AN with fuel sources that commonly make up homemade explosives (HMEs). The study went further to pose the question of how training increases or decreases the canines' tendency to generalize between like substances. Concurrent laboratory analyses were carried out examining the volatile components available in the headspace of the AN variants.

The study determined that some of the canines did tend to generalize across multiple AN variants following initial training, and continued to generalize throughout the study. However, not all canines showed this tendency, and it was shown that further training on additional variants did not improve generalization. Data did show that type of AN used during training, as well as training practices as correlated to the tendency to generalize.

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BACKGROUND

Improvised explosive devices (IEDs) have been the leading cause of injury and death in recent Middle East conflicts. Approximately two-thirds of all American deaths in combat were by IED attacks, according to the Joint IED Defeat Organization (JIEDDO, now the Joint Improvised-Threat Defeat Organization) [1] [2]. IEDs are not only threats abroad, but also pose a great threat to homeland security. Their prevalence at home and abroad is due to both the ease of acquiring the explosive components, as well as constructing the devices. In recent years, IEDs have been most commonly composed of homemade explosives (HMEs), explosive materials that can be easily synthesized from improvised and commercially available materials [3].

Many HMEs are composed of simple binary mixtures of fuels and oxidizers. The most commonly-used oxidizer is ammonium nitrate (AN). Of the IEDs seen in Afghanistan by 2012, 86% contained HMEs, and 83% of these were AN-based [4]. AN is a popular choice due to its high commercial availability and high explosive power when mixed with fuel. It is commercially available as a fertilizer, where it is usually in the form of small, compressed pellets, or prills. AN, however, is most effective ground and is often found in this form. In an attempt to thwart the use of AN for terrorism, it is often sold in the form of calcium AN or CAN; however, the calcium carbonate can easily be removed by dissolution in water [3].

AN is a white crystalline salt. It is highly hygroscopic, becoming liquefied (deliquescing) in humid air above 62 % RH (25 °C). The hydration of AN is an endothermic process making it also useful for use in instant cold packs (when crushed, AN prills mix with water setting off the endothermic reaction and causing the water to freeze.). AN also dissociates under ambient conditions into its precursors, ammonia and nitric acid. The vapor pressure, owing to these vaporous products, is similar to that of trinitrotoluene (TNT) at 1.93×10^{-3} Pa at 25 °C. The vapor pressure can be affected by the presence of contaminants, the form in which the AN is found (i.e. prill, ground, or crystalline), and environmental conditions (i.e. temperature and humidity) [5].

AN alone is extremely insensitive and unlikely to explode, but when mixed with a fuel it becomes an effective secondary explosive. Common fuels are also commercially available. Examples

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include fuel oil (ANFO), aluminum powder (AN-Al; commercially available as tannerite), petroleum jelly, or sugar [3].

Though many devices exist for the detection of HMEs, canines continue to be the most effective tool both at home and abroad. In 2012, as many as 280 IED Detector Dogs were deployed to Afghanistan [6], and canines continue to be an essential tool to the military, including the Navy SEALs [7]. Such canine rely on olfaction for detection, and, although they have been vital in protecting marines from IED detonations during the course of their mission, there is still a dearth of information regarding canine olfaction capabilities, which could improve training and detection proficiency.

As an example, there is a lack of peer-reviewed data regarding the canine's ability to discriminate or generalize between like odors, and the implications that such data would have on training protocols for working dogs. It is known that increased training on a target odor increases sensitivity to that odor and improves canine performance by enhancing the ability to discriminate between the target odor and background odors [8]. Several studies with explosive-detection canines have illustrated the consequence of an imbalance of the generalization-discrimination continuum due to training deficiencies. In one study, explosive detection canines, previously trained to a single brand of flake TNT, were presented with TNT of different origins. The canines were expected to generalize from the type of TNT used for training to the other types presented. These canines, however, did not readily generalize, and showed a low proficiency at detecting the alternative forms of TNT [9].

A similar shortcoming was discovered when testing canines, previously trained on a single variant of ammonia nitrate (AN), to similar compounds including other ammonium- and nitrate-containing salts (sodium nitrate and ammonium sulfate), other AN forms (fertilizer-grade AN), and AN mixtures (AN in soil and AN with aluminum powder). The canines in this study did detect these variants at a rate greater than chance; however, the detection rates were low, ranging from 58% on the related salts to 73% on the AN in soil. The performance for the trained AN variant was above 80% [10].

Another study by Lazarowski examined generalization from potassium chlorate, another common HME oxidizer, to potassium chlorate mixtures. It was found that when trained to potassium

chlorate alone, most canines in the study (87%) did not detect at least one of the four mixtures. When the canines were further trained to the potassium chlorate mixtures, however, there was a significant increase in their detection [11].

PART 1. COMPARATIVE HEADSPACE ANALYSIS OF AMMONIUM NITRATE VARIANTS

Methods

Six AN variants were tested and are included in Table 1. For analysis, 20 mL headspace vials were filled about 1/3 full to equal approximately 6 mL of AN (total mass varied with AN type). The samples were allowed to equilibrate for 24 hours prior to sampling. The headspace of the AN was then sampled by solid phase microextraction (SPME) and analyzed by gas chromatography / mass spectrometry (GC/MS). All samples were taken in triplicate and were compared to blank vials.

Table 1. AN type / source used in study.

AN type	**Source / manufacturer**
Laboratory-grade (crystals)	Sigma-Aldrich
Industrial-grade, prill	GSF Chemical
Industrial-grade, ground	GSF Chemical
Fertilizer, prill	Garden Naturals
Fertilizer, ground	Garden Naturals
Instant cold pack (prill)	Dynarex
Calcium AN (CAN) (prill)	Yara (YaraBela CAN 27)

Two separate SPME methods were used in this analysis, one for the detection of ammonia (from the dissociation of AN), and one for the detection of all other volatiles coming from impurities in the AN variants. Detection of ammonia vapor is problematic for both extraction by SPME and analysis by GC/MS due to poor trapping/retention and separation on typical stationary phases. For this reason, an on-fiber derivatization technique, developed by Brown et. al., was used. Two mL of the derivatizing agent, butylchloroformate, was pipetted into a 20 mL headspace vial, and allowed to equilibrate. An 85 μm, polyacrylate SPME fiber was exposed to the butylchloroformate for 1 minute. The SPME fiber was then immediately removed and exposed to the AN samples for 1 hour. The derivatized ammonia was detected as butyl carbamate. For extraction of the other volatiles, a polydimethylsiloxane/divinylbenzene/carboxen (PDMS/DVB/CAR) SPME fiber was

exposed directly to the headspace of the AN samples for 4 hours. Following extraction, analytes from the SPME fibers were thermally desorbed in the GC inlet at 260 °C with a flow rate of 2 mL/min. Both analyses utilized a Rtx-5MS GC column (15 m x 0.25 mm ID x 0.25 μm thickness; Restek Co.). Other GC/MS parameters are listed in Table 2. All compounds in the headspace were assigned based on mass spectra matches to the NIST mass spectral library.

Table 2. GC/MS parameters for two SPME extraction methods.

	Ammonia extraction parameters	**Volatiles extraction parameters**
Oven temperature program	1. 40 °C, hold 0 min.	1. 40 °C, hold 1 min.
	2. 40 °C/min to 240 °C	2. 40 °C/min to 240 °C
	3. Hold 2 min	3. Hold 3 min
Inlet split ratio	Splitless	10:1
MS scan range	*m/z* 33-220	*m/z* 30-300

All headspace measurements were made at room temperature (22 °C ±1, 32% RH ±5%). In addition, the headspace of some of the AN variants were compared at varying temperatures and humidities using an environmental test chamber. The test chamber provides a temperature range of -34 to 85 °C and a relative humidity range of 10 – 95%. It houses an exhaust apparatus that purges the air at 300 CFM. Temperatures and humidities were chosen to mimic outdoor conditions in the mid-Atlantic region, and included 6 °C at 25% RH, 20 °C at 20% RH, 26 °C at 40% RH, and 32 °C at 60% RH. For these analyses, AN was first placed in the 20 mL headspace vials, approximately 1/3 full, under ambient temperatures. The samples were then carried to the environmental chamber and left open (no lid) in the chamber, allowing the AN to interact with the environment, for one hour. After this time, the vials were closed, and allowed to equilibrate for an additional 1 hour prior to the SPME extraction. Extraction and analysis protocols were the same as previously described. Three AN variants, representing three AN forms, were tested including laboratory-grade (crystalline), industrial-grade (ground), and industrial-grade (prill). Fresh samples were used for each SPME extraction method, and all samples were taken in triplicate. Vial blank samples were also taken at each temperature/humidity combination.

Results

Ammonia available in the headspace of the six AN variants is compared in Figure 1, and is given as the peak area of derivatized ammonia (i.e. butyl carbamate). The amount of ammonia present was correlated to AN purity with the more pure substances releasing less ammonia vapor. The laboratory-grade material yielded the least amount of available ammonia compared to the other samples, and only small amounts of ammonia were extracted from the industrial-grade as well. CAN, AN mixed with 19% calcium magnesium carbonate, produced the greatest amount of ammonia in the headspace. Grinding the fertilizer AN liberated significantly more ammonia than was measured in the prill sample, but this was not the case for the industrial-grade material. Other volatiles extracted from the headspace are summarized in Table 3. As AN is a simple salt composed solely of ammonia and nitric acid, all other volatiles are imparted through manufacturing or packaging/storage. Besides ammonia, no one volatile was detected in all samples, though methylphenyloxime was found in all samples but the CAN. AN from the instant ice pack had significant more vaporous contaminants than any other sample.

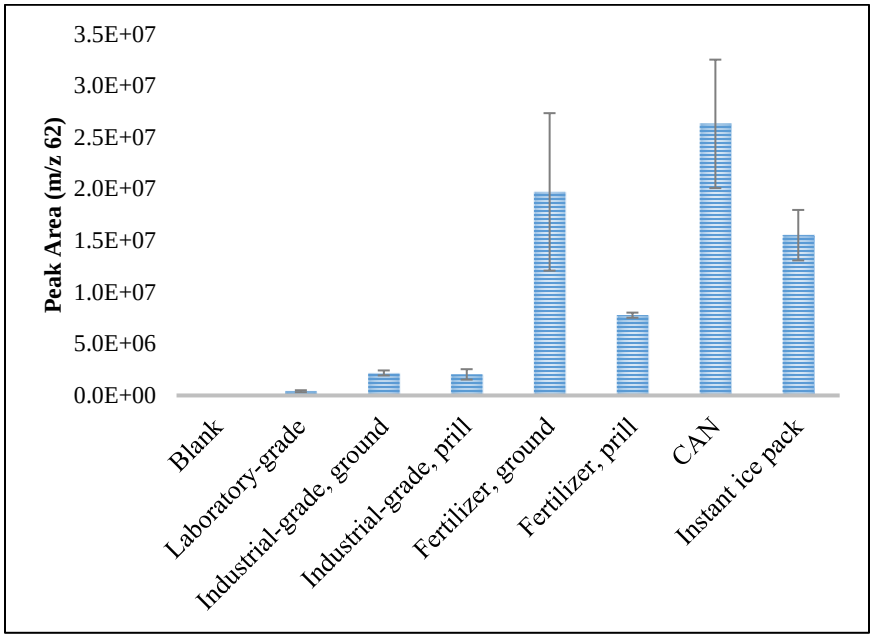


*Figure 1. Ammonia vapor measured from the headspace of AN variants. The magnitude of ammonia vapor present is given as the peak area of the main ion, m/z 62, of butyl carbamate, which is the product of ammonia derivatization. *Note. Error bars equal one standard deviation.*

*Table 3. Volatiles detected in the headspace of AN samples, excluding ammonia. All compounds were identified by comparison to the NIST mass spectral library. *Note. All volatiles also found in the blank vial have been removed from this data.*

AN variant / HS component	**Lab**	**Indust, ground**	**Indust, prill**	**Fert, ground**	**Fert, prill**	**CAN**	**Ice pack**
acetic acid	X	X	X			X	
propanoic acid	X						
methylphenyloxime	X	X	X	X	X		X
1-butanol				X	X		X
acetamide						X	
2-ethyl-1-hexanol						X	
acetone							X
pentanal							X
hexanal							X
pyridine							X
2-methyl pyridine							X
4-methyl pyridine							X
2,6-dimethyl pyridine							X
2,4-dimethyl pyridine							X
2,3-dimethyl pyridine							X

The relative quantity of ammonia in the headspace of AN samples at varying temperatures and humidities are compared in Figure 2. As to be expected, there was an overall increase in ammonia in the headspace corresponding to an increase in temperature and humidity, with a significant increase in ammonia vapor moving from the 20 °C / 20 RH data point to the 26 °C / 40 RH. Much of this substantial increase could likely be attributed to the increase in humidity at this point, in addition to the increase in temperature, as ambient humidity is known to increase the dissociation of AN [5]. Interestingly, in the industrial-grade samples, the maximum ammonia was collected at 26 °C / 40 RH, with 32 °C / 60 RH being appreciably lower, while this was not the case for the laboratory-grade material. It appears that the environmental conditions affect the different AN forms differently. Without further study, it is difficult to say if this divergence was owing to

differences in how the AN form interacts with change in humidity, temperature increase, or a combination of both.

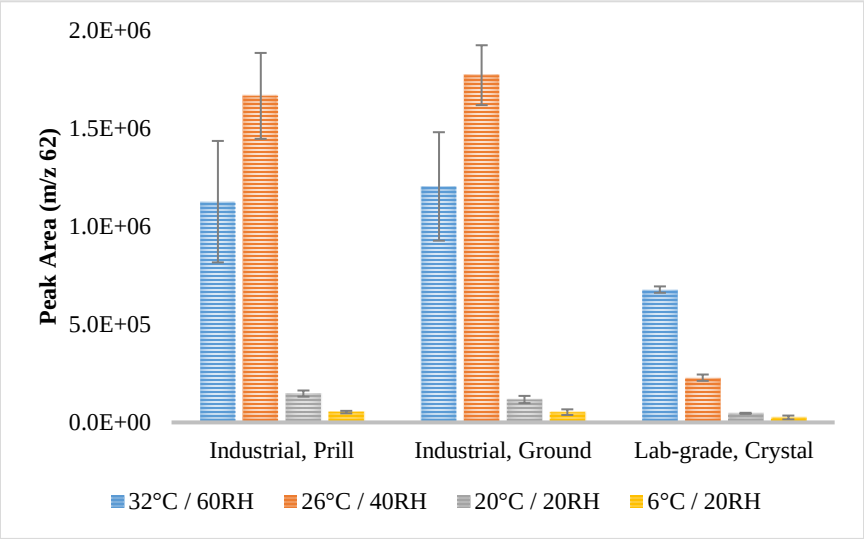
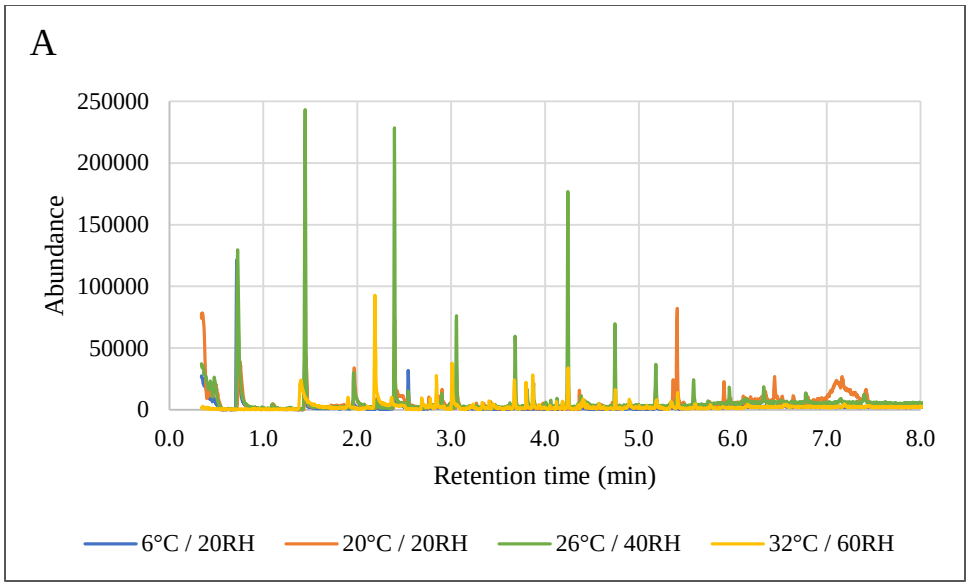


*Figure 2. Ammonia vapor measured from the headspace of AN samples at varying temperatures and humidities. The magnitude of ammonia vapor present is given as the peak area of the main ion, m/z 62, of butyl carbamate (derivatized ammonia). *Note. Error bars equal one standard deviation.*

Again, a second analysis was carried out comparing other volatiles in the headspace of the AN samples. Chromatograms for each variant at the differing environmental conditions are compared in Figure 3. Both industrial-grade samples, ground (Fig. 3B) and prill (Fig. 3C), yielded similar volatiles in similar quantities. In these samples there was a significant increase in hydrocarbons, particularly branched aromatics, branched cyclics, aldehydes, and alkanes, as these samples were heated above room temperature. The colder temperature suppressed nearly all of these components, leaving only several branched naphthalenes and several aldehydes (C9-C11) to be detected. When heated above room temperature, the laboratory-grade sample (Fig. 3D) yielded significant amounts of acetic acid in addition to 2,4,4-trimethyl-3-(3-methylbutyl) cyclohex-2-enone, and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, both likely artifacts of the manufacturing process. When chilled, acetic acid was the only volatile detectable in this sample besides ammonia The significant increase or decrease in volatiles from impurities or manufacturing alters the scent picture appreciably and could confound detection. For this reason, the ambient working conditions should be taken into account during testing.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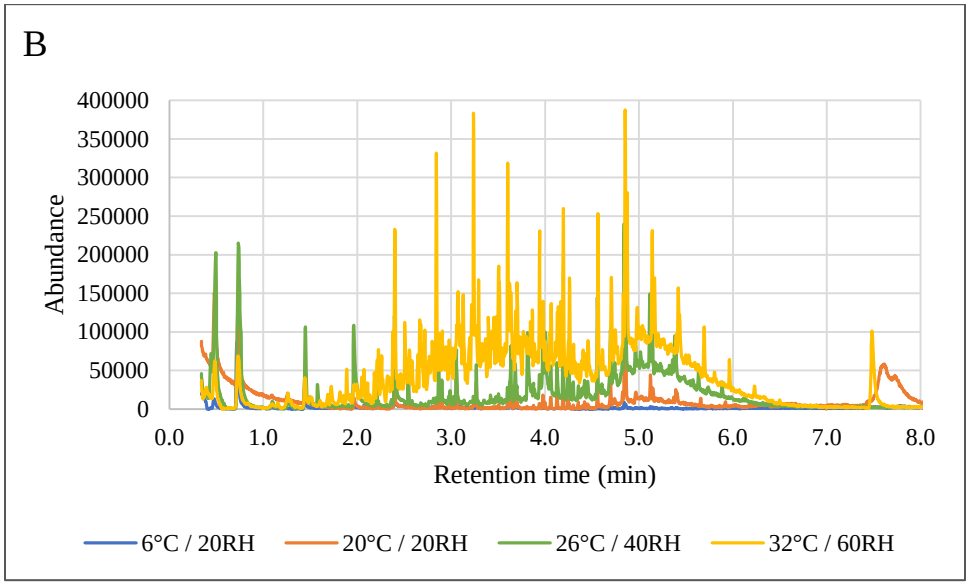
32°C / 60RH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Retention time (min)
6°C / 20RH
20°C / 20RH
26°C / 40RH
32°C / 60RH

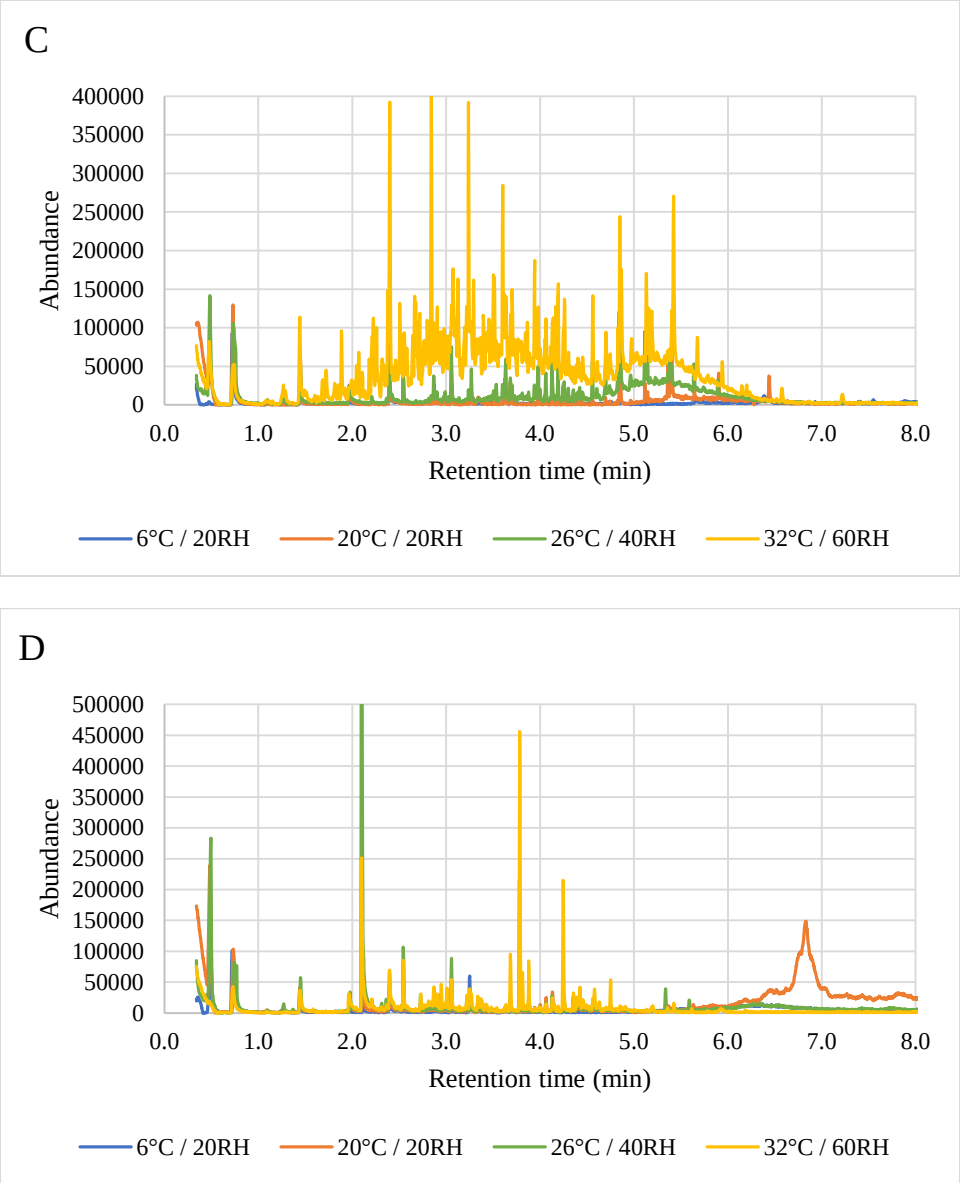

Figure 3. Total ion chromatograms of (A) blank vials, and (B) industrial-grade, ground, (C) industrial-grade, prill, and (D) laboratory-grade AN samples. Traces for each temperature / humidity combination are overlaid for each AN type.

PART 2. GENERALIZATION / DISCRIMINATION BETWEEN AMMONIUM NITRTATE VARIANTS

Methods

Study design – The canine detection study was carried out as a series of three separate trials used to test the canines' tendency to generalize from one type of AN to other types. Canines were initially trained to a single AN type. After the canines were proven to be proficient at detecting

this training material, their ability to detect other untrained AN variants was evaluated. This culminated the first trial. The canines were then trained to a second type of AN, and were then tested again on other variants. This was repeated for the third trial, with the canines being trained on three AN types. Increased generalization or discrimination to the untrained AN variants with subsequent training was evaluated.

For each trial, validation assessments were used to confirm that each canine could detect their trained odor(s). Each of the three trials incorporated four validation assessments that included a combination of searches and odor recognition tests (to be described below). The data from any canine that did not detect the target odor in at least three of the four validation tests was not included in the results. An odor recognition test (ORT) is defined as "a test of the dog's ability to alert to a target odor" [12]. It is a standardized method used to demonstrate the canine's ability to recognize a desired odor. In these trials, the ORTs consisted of a line of five 1 quart evidence cans held in place by a rigid PVC "ladder", as can be seen in Figure 4. Each set of 5 cans contained 1 target, 1 distractor, and 3 blanks. Negative runs were also used and consisted of 1 distractor and 4 blanks. Validation searches consisted of containers, such as luggage, boxes, etc., and furniture spread sporadically throughout an interior space. An example of a container search is shown in Figure 5. Validation searches only contained a target odor(s) (one or two, depending on the size of the search area).

Figure 4. Canine participant completing an odor recognition test (ORT). The ORT consisted of five cans held in place by a PVC ladder. Each can held a target odor, distractor odor, or a blank.

Figure 5. Canine performing indoor container/area search.

Odors and odor delivery – Training and testing odors were from the same lots as that used for the headspace experiments, and are given for each trial in Table 4. All canines were initially trained on laboratory-grade AN. After the first trial the canines were split into two groups at random, one group being trained to ground fertilizer AN, and the other to prill fertilizer AN. For the third trial, all canines were trained on both ground and prill fertilizer AN. All canines continued to train on the laboratory-grade throughout the study. ORTs contained one distractor odor, which included crayons, nitrile gloves, bar soap, band aids, deodorant, unused tea bag, or shampoo, selected at random.

Table 4. Training and testing odors for Trials 1-3.

	Trial 1	Trial 2	Trial 3
Training Odor(s)	Laboratory-grade	Laboratory-grade, fertilizer prill (Group A only) OR fertilizer ground (Group B only)	Laboratory-grade, fertilizer prill AND fertilizer ground
Testing Odor 1	Fertilizer ground	Fertilizer ground (Group A) OR prill (Group B)	Industrial ground
Testing Odor 2	Fertilizer prill	Industrial ground	Industrial prill
Testing Odor 3	Industrial ground	Industrial prill	CAN
Testing Odor 4	Industrial prill	CAN	Ice pack
Testing Odor 5	CAN	Ice pack	n/a
Testing Odor 6	Ice pack	n/a	n/a

For all testing and training, 500 mg of each AN variant, or an equivalent amount of the distractor, was placed in small “breather” tins. The tins were 2 oz., round, rust-resistant, screw top, steel tins (purchased from PaperMart). Five small holes were drilled in the tin lids to allow odor to escape during testing or training. For the ORTs, the breather tins were placed into the 1 quart cans and

allowed to equilibrate for a minimum of 30 minutes. When not in use, odor tins were topped with solid lids and stored in either glass jars or metalized Mylar barrier bags (ESP Packaging).

Canine participants – All canine training and trials were carried out through a Cooperative Research and Development Agreement (CRADA) with the National Association of Canine Scent Work®, LLC (NACSW™); a.k.a. K9 Nose Work® [13]. K9 Nose Work is a social group that trains non-working (pet) canines in search and scenting activities using scents from essential oils (birch, anise, and clove). The group offers classes and competitions in scent detection that mimic training and testing scenarios for actual working dogs. Upon receipt of the training odor(s), canine handlers were instructed to train "as usual", meaning in the same manner in which they train with K9 Nose Work odors. Through competitions, canines and handlers earn title levels from NW1 to NW3 and NW3 Elite. All canine participants in this study had earned their NW3 or NW3 Elite titles.

Test integrity – All trials were double-blind, meaning neither the handler nor the assessors knew the identity or location of the target odors. The location of each target within an ORT was chosen by a random number generator for each canine. Test areas were inspected and, if necessary, cleaned after each trial. Canines and handlers waiting to be tested were prevented from observing other canines during testing. To minimize "learning" of the novel odors, no canine saw any of the novel odors more than once per trial.

Data collection and analysis – All trials were observed by two impartial assessors, both experienced in reading canine behavior during olfaction exercises. Canine responses were categorized as a positive alert, false alert, interest, or strong interest. Handler error was further noted as necessary for responses labelled "strong interest" or "false alerts". All data was then tabulated, excluding any canine that did not successfully locate 75% of the validation odors or with excessive false alerts.

Several statistical methods were used to compare canine response rates to training and testing odors, and to compare response distributions between groups of the canines. Positive predictive value (PPV) gives the probability that an alert was correct compared to false alert rates given by Equation 1. The closer the PPV is to 100%, the higher the probability that a given alert from this group of canines was correct (i.e. not false).

Equation 1. Positive predictive value.

$$\frac{True\ positive}{True\ positive + False\ positive}$$

The McNemar chi-square test is used for paired nominal data to test for consistence in responses across two variables using 2 by 2 contingency tables (example given in Table 5). For this data, the test was used to determine if the probability of a canine detecting a testing odor was similar to a canine detecting a trained odor. The chi-square value was calculated by Equation 2 and was compared to the χ^2_{crit}. The null hypothesis states that probabilities for each outcome were the same. If χ^2 is significant (i.e. greater than χ^2_{crit}), the null hypothesis was rejected.

Table 5. Example 2 by 2 contingency table used in McNemar test.

		Testing Odor	
		Y	N
Training odor	Y	a	b
	N	c	d

Equation 2. McNemar chi-square test.

$$\chi^2 = \frac{(b-c)^2}{(b+c)}$$

Finally, the chi-square test for independence was used to compare the distribution of discrete responses for independent comparison groups. The null hypothesis states that there was no difference in outcomes between groups. The alternative hypothesis states that there was a difference in the distribution of responses to the variables among comparison groups. For this research, the chi-square test for independence was used to compare the responses of Group A and Group B canines to the testing odors in each trial. An example contingency table with Groups A and B as columns and canine response as rows is given in Table 6. The total sample size is given by N, the sum of row or column totals. The chi-square value was calculated for each group using Equation 3. The observed value (O) was determined from the sample data, and the expected value (E) was calculated from the expected frequencies. When the value of χ^2 was greater than χ^2_{crit}, the null hypothesis was rejected.

Table 6. Example contingency table used for chi-square independence test.

	Alerts	*Misses*	*Row total*
Group A			*x*
Group B			*y*
Column total	*a*	*b*	*N*

Equation 3. Chi-square calculation used in chi-square test for independence.

$$\chi^2 = \sum \frac{(O - E)^2}{E}$$

Participants were also asked to complete surveys regarding their effort during the trials. Surveys included the following questions: (1) How would you compare your effort level for training in preparation for the Navy study as compared to NACSW trials (i.e. less, about the same, or more)?; (2) Were you actively training on your NACSW odors during the Navy study?; (3) Estimate how much time you spent training for the Navy study per week. Responses were tabulated and evaluated for correlation to canine performance during the trials.

Results

It was the intention for canines to have no more than 4-8 weeks of training prior to each trial; however, due to scheduling conflicts this was not always possible. Trial dates and environmental conditions during testing (temperature and humidity) are listed in Table 7.

Table 7. Dates and environmental conditions of canine trials.

Trial	**Date**	**Avg. Temp/humidity**
Trial 1	March 26/27	21°C (± 0.5°C) / 55 % RH
Trial 2	April 23 / 24	22°C (± 2°C) / 51 % RH
Trial 2	July 30 / 31	23°C (± 2°C) / 49 % RH

Trial 1 – All data for each canine and each trial are given in Appendix 1. In trial 1, all canines were trained to the laboratory-grade AN only. A total of 18 canines participated in Trial 1, though 3 canines were not included in the final data due to unsuccessful detection of at least 3 of the 4 validation odors or due to high false alert rates (particularly on distractor odors). A summary of Trial 1 results are included in Figure 6. The canines included in the data had a 96% detection rate for their trained odor and a 7.9% false alert rate on all non-target odors (for comparison, working

dog requirements generally range from 90 – 95% proficiency [12] [14]). The alert rate for all testing odors ranged from 33% to 67%, significantly lower than the trained odor, with no obvious trends. A majority of the canines alerted to less than four of the six novel odors, with no single canine alerting to all six testing odors and only 3 canines detected 5 of the testing odors. The type and number of variants to which the canines generalized appears to be dependent on the individual canine olfaction process.

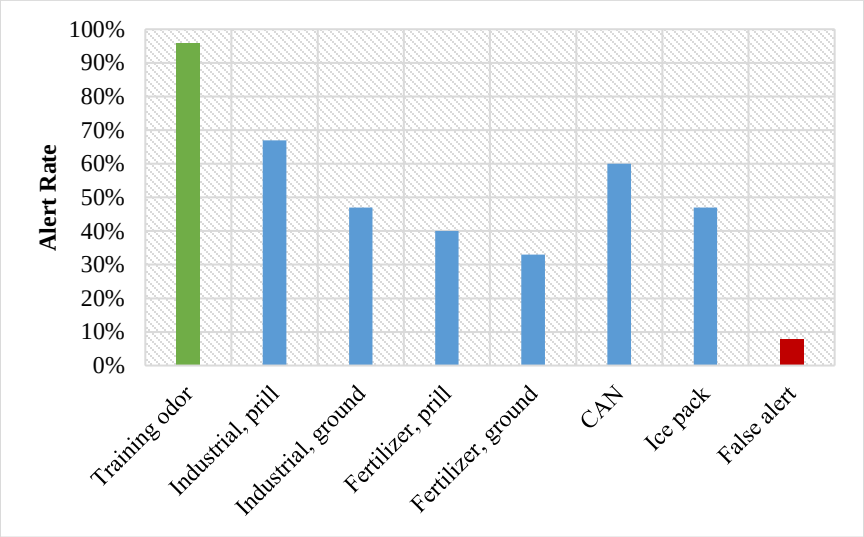

Figure 6. Results from Trial 1 - Alert rate for the known (training) odor compared to the novel AN variants.

Trial 2 – In Trial 2, a total of 18 canines participated, and 16 were included in the data. Comparing Trial 1 to Trial 2 for all canines, Figure 7 indicates that individual canines alerted to a greater number of testing odors, thus training did seem to increase generalization across the novel odors. However, the alert rate for the training odors for Trial 2 decreased slightly to 91%. Looking at the alert rates to the individual variants in Figure 8, there was no particular variant to which the canines were more likely to detect in the second trial compared to the first. Of the included canines, 9 were in Group A, trained to laboratory-grade and prill fertilizer AN, and 7 were in Group B, trained to laboratory-grade and ground fertilizer AN. Group A detected the training odors 92% of the time and Group B 89% of the time. Group A also detected more of the testing odors compared to Group B (Figure 9), which could indicate that training on the prill form increased generalization.

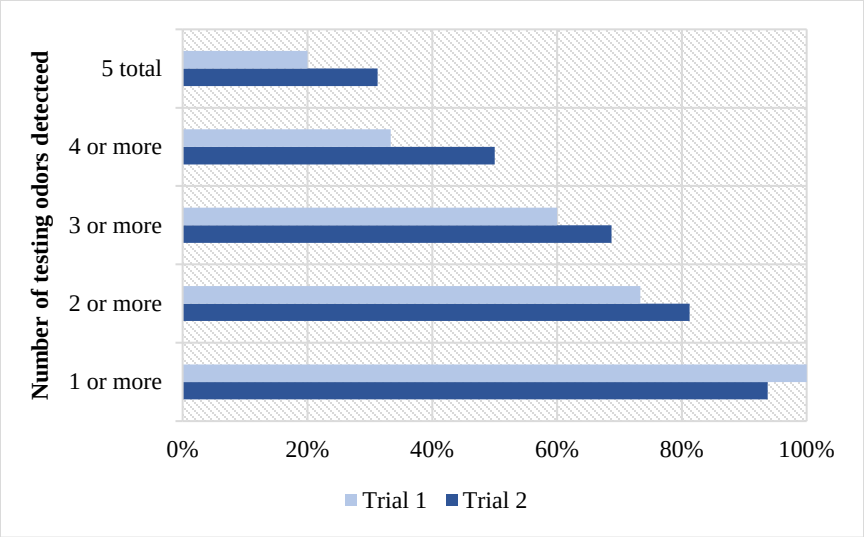

Figure 7. Summary of the total number of testing odors detected by canines in Trials 1 and 2.

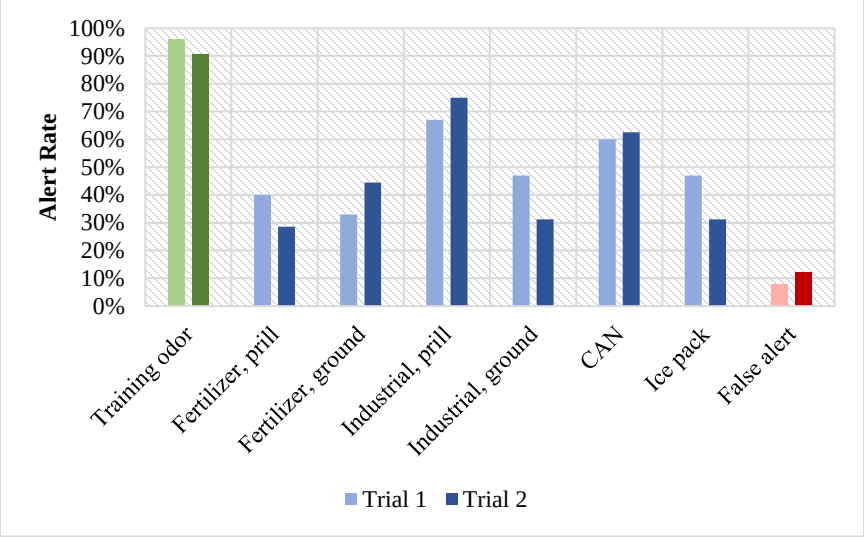

Figure 8. Results from Trial 1 vs. Trial 2 - Alert rate for the known (training) odor compared to the novel AN variants.

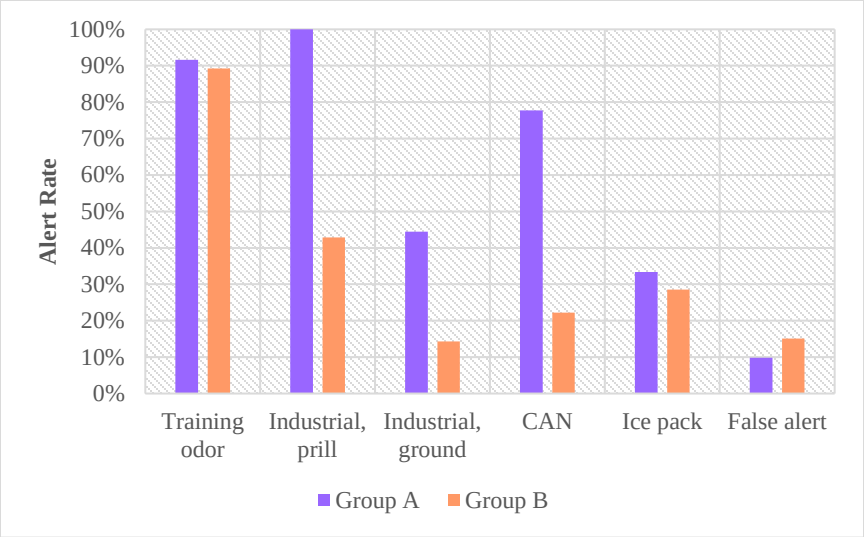

Figure 9. Alert rates for Group A, trained to prill fertilizer AN, and Group B, trained to ground fertilizer AN for Trial 2.

Trial 3 – 17 canines participated in Trial 3, and 11 canines were included in the results. The canines, overall did not detect as many of the novel AN odors in Trial 3, though the alert rate for the trained odors remained at 91%. The number of testing odors detected for each dog decreased (Figure 10) indicating more discriminating behavior in Trial 3. Overall, there was no significant increase in generalization or discrimination with training on additional AN variants from Trial 1 to Trial 3 (Figure 11).

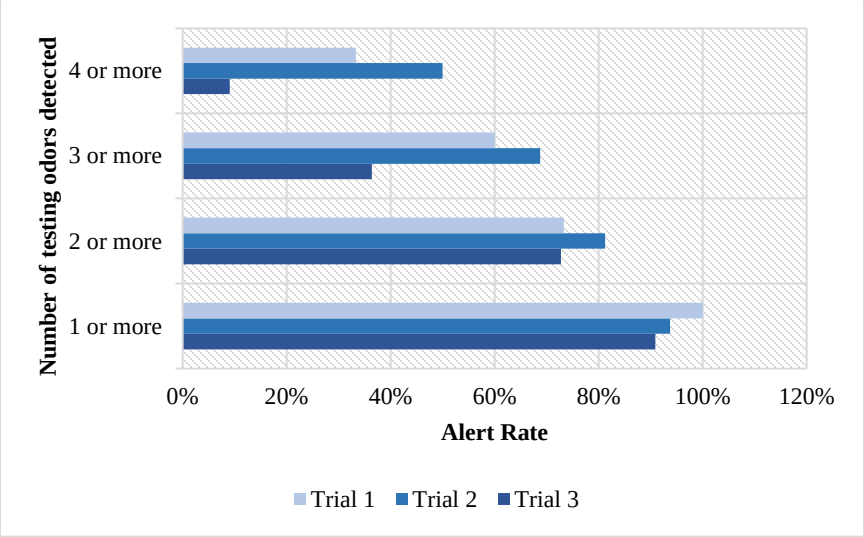

Figure 10. Summary of the number of testing odors detected by canines in Trials 1-3.

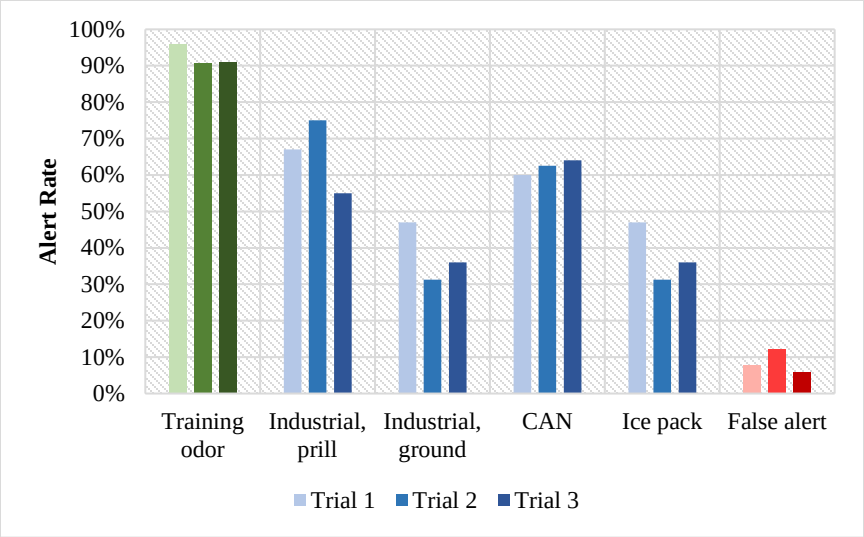

Figure 11. Results from all Trials - Alert rate for the known (training) odor compared to the novel AN variants.

PART 3. GENERALIZATION / DISCRIMINATION BETWEEN AMMONIUM NTRATE AND AMMONIUN NITRATE / FUEL MIXTURES

Methods

Study design – Canines were tested on their tendency to generalize to binary mixtures of AN with fuels, after being trained solely on AN. The fuels chosen included diesel fuel, petroleum jelly, and aluminum, all commonly mixed with AN to create HMEs. The canines were tested on the mixtures during the third trial, after they have had sufficient time to be thoroughly familiar with the AN odor through training on three varieties of AN alone. Testing was in the form of a simple interior room search where containers with the mixtures or distractors were placed around a room in clear view of the canine and handler. Each search consisted of one container with the AN mixture or AN alone, and four containers with distractor odors or a blank. Laboratory-grade AN was used for all mixtures. Distractor odors included Downy wrinkle releaser, nitrile gloves, and shampoo. The blank container and those holding the distractor odors all contained the same type of vials used to contain the AN and fuel mixture components. The placements of the targets and distractors in the room were determined by a random number generator and were changed for each canine. All other aspects of the testing protocol established for testing of the AN variants were retained for this portion of the study.

Odor delivery – It was necessary to deliver the odor of mixed AN and fuel without physically mixing the components and thus creating hazardous explosive mixtures. The Mixed Odor Delivery Device (MODD) [15] was used for this purpose. The MODD functions to safely separate up to four components in separated removable vials. Within the MODD, individual odorants disperse from the vials into a narrow neck where they meet and mix. Odorants then continue to disperse through the neck where they exit and are sampled by the canine as a mixture (Figure 12). PTFE vials containing the laboratory-grade AN, a fuel, or a distractor were placed inside of the MODDs according to Table 8.

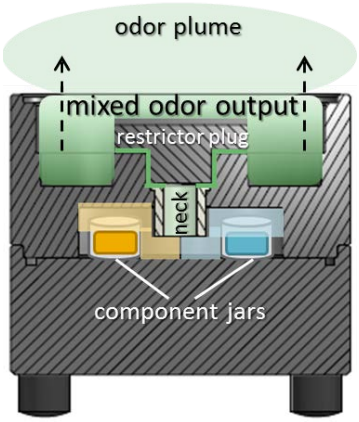

Figure 12. The Mixed Odor Delivery Device (MODD) used to deliver the mixed odor from separated AN and fuel components.

Table 8. Contents of MODDs used for testing canines on binary mixtures of AN and fuel.

MODD #	CONTENTS
1	AN
2	AN and Diesel fuel
3	AN and Petroleum jelly
4	AN and Aluminum powder
5-7	Distractors
8	Blank (contained empty vials)

Results

During the third trial, canines were also tested on AN mixtures and AN alone in the MODDs, as described above. Individual canine responses are given in Table 9. Only canines that had a large number of false alerts were not included in the data. Canines alerted to AN mixed with aluminum and petroleum jelly at the same rate (67%) as the AN alone; however, the alert rate for AN with diesel fuel was higher (80%). Canines that alerted to the AN alone also alerted to at least two of

the mixtures, while most of the canines that did not detect the AN alone, found none or only one of the mixtures. Overall, the presence of the fuel odor did not seem to deter detection.

Table 9. Canine response to AN alone and in mixtures with aluminum powder (Al), diesel fuel (FO), or petroleum jelly (PJ). Note: Alert indicated by 1, miss indicated by 0.

Dog #	*AN alone*	*AN-Al*	*AN-FO*	*AN-PJ*
302	1	1	1	1
303	0	0	0	0
304	0	1	0	0
305	1	0	1	1
307	1	1	1	1
308	1	1	1	1
309	0	1	1	1
312	1	1	1	1
313	1	1	1	0
315	0	0	0	0
317	0	0	1	0
318	1	1	1	1
319	1	1	1	1
320	1	0	1	1
321	1	1	1	1
Alert Rate	*67%*	*67%*	*80%*	*67%*

SUMMARY AND DISCUSSION

In the first trial, canines were trained to laboratory-grade AN and asked to detect other less pure AN variants. This is a common practice in operational canine training, where canines are often trained on the purest form of a substance, but are expected to detect less pure forms in the field. After initial training, all canines did show some generalization to the AN variants as all were detected at a rate significantly higher than chance (see Appendix 2). This was, however, significantly lower, for most variants, than the detection rates of the training odor (see Appendix 2). It was suggested that the detection rate on the trained material was artificially high because the searches used in three of the four validations were easier for the canines than the ORTs. However, taking only the ORT validation into consideration, the alert rate remained at 82%, still higher than any of the non-training odors. These results agree with the previous study carried out by Larazowski et. al. (2015) [10].

No particular variant was found to be more "similar" or more "distinct" to the training odor by this group of canines. "Similarity" seemed to be up to the interpretation of individual canines. The data from only the canines that did show a tendency to generalize (defined here as correctly locating 3 or more testing odors) were examined separately (Table 10). This group of canines did show a distinct preference for the prilled industrial AN variety, as well as a somewhat greater tendency to respond to the CAN. This trend was consistent across all three trials.

Table 10. Alert rates of canines on AN variants in each trial. Only canines that alerted on at least three testing odors (per trial) are included (n/a = trained odor).

	# of K9s included	**Ind. Prill**	**Ind. Grnd**	**Fert. Prill**	**Fert. Grnd**	**CAN**	**Ice pack**	**Training odors**
Trial 1	10	90%	70%	60%	40%	70%	50%	**97%**
Trial 2	6	100%	67%	n/a	n/a	83%	67%	**96%**
Trial 3	5	100%	60%	n/a	n/a	80%	80%	**90%**

It was hypothesized that the canine trial results would correlate in some way to the headspace analysis results. For example, the canines would be more or less likely to detect the AN variants that produced more ammonia vapor. The canine alerts, however, were not supported by the headspace measurements of ammonia. The initial trained odor, laboratory-grade AN, produced the lowest amount of ammonia in the headspace, thus the canines needed to have a very low threshold to detect the training odor. It is possible that this lower threshold made it easier for the canines to detect the other odors, and these results might thus be different had the canines been initially trained to the fertilizer-grade material.

It was also hypothesized that the presence of impurities from manufacturing that were not present in the trained AN samples would deter detection. The ice pack AN had the greatest amount of other volatiles present in the headspace, but canines had detected this AN at the same rates as the other non-trained variants. The presence of impurities alone did not seem to deter detection. However, acetic acid was a common headspace component across the laboratory-grade, industrial-grade, and CAN varieties. It is possible that the presence of this volatile influenced the detection of these particular variants by the canines included in Table 10.

For Trial 2, canines were split into two groups, Group A trained to AN prill and Group B trained to AN ground, and both continued training to laboratory-grade AN. There was no statistically

significant difference between the responses to the testing odors between Groups A and B (as determined by the chi-square test for independence in Appendix 2) in Trial 2; however Group A did alert to a greater number of testing odors than Group B in Trial 2, even though their alert rates to the training odors were nearly the same (Figure 9). This raises the question, did the canines randomly selected for Group A have greater tendency by chance, or is this difference actually due to training? Figure 13 compares the performance of the canines in Group A vs. Group B prior to Trial 2. Group B actually alerted to more often to the non-trained variants, not Group A, in Trial 1, thus the change in Trial 2 was likely to due to the differences in training odors between the two groups. Furthermore, by adding AN prill to Group B's training regimen for Trial 3, Group B's performance ended up being very similar to Group A's, as can be seen in Figure 14. These results do suggest that training on prill versus ground AN does affect the canines' overall tendency to generalize. Future work might include comparing the performance of canines initially trained with either laboratory-grade AN, AN prill, or AN ground.

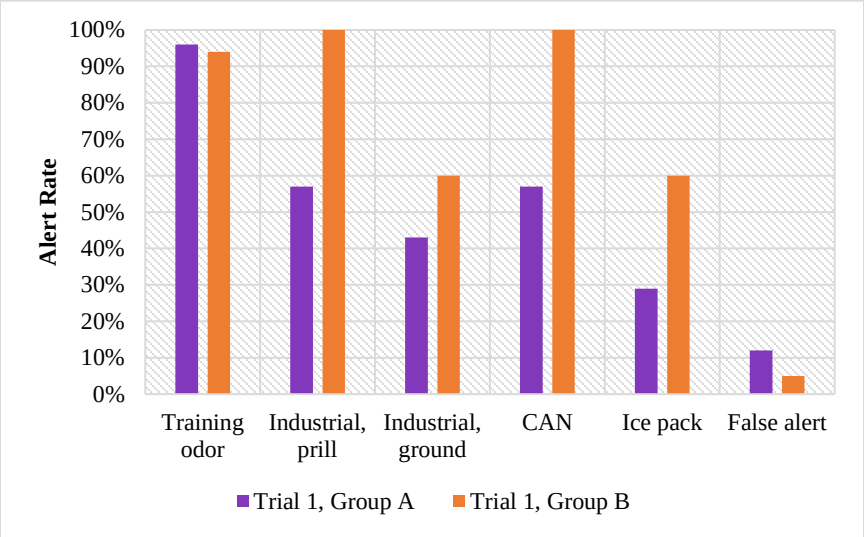

Figure 13. Alert rates for Group A and Group B for Trial 1.

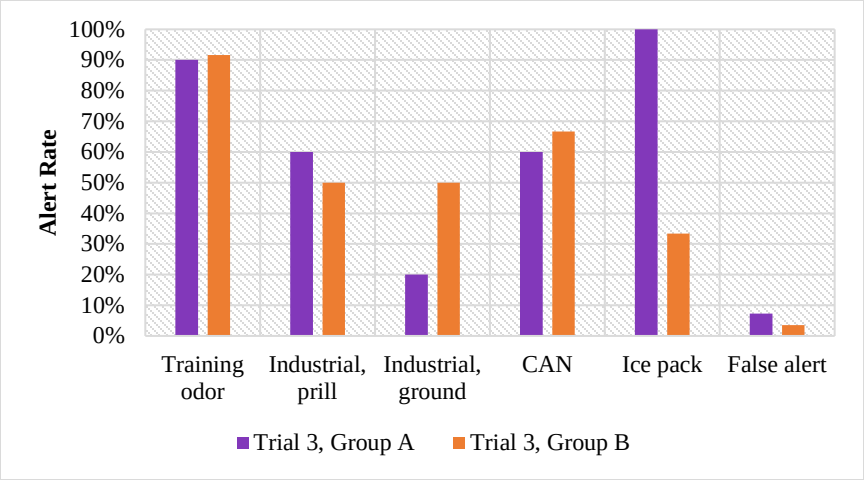

Figure 14. Alert rates for Group A and Group B for Trial 3.

The canines' tendency to generalize remained similar from Trial 1 to Trial 3. The detection rate for each testing variant remained statistically above chance (Appendix 2), but below that of the trained odors. Based on these results, best practice would be to continue to train on as many variants as available.

The canines were also tested on the odors of HME mixtures containing AN. They were tested on AN alone in comparison to AN mixtures. The data showed that the canines that found AN alone, also found most (2 of 3) or all of the mixtures, while most of the canines that could not find AN alone found none or one of the mixtures. Of the ten canines that alerted to AN alone, there was no significant difference in the alert rates to AN alone (100%), AN-Al (80%), ANFO (100%), and AN with petroleum jelly (90%). These results are in disagreement with Larazowski et. al. (2014), where 87% of the canine tested on PC mixtures were not proficient at detection [11]. This divergence could be due to differences in training methods (i.e. training for operational detection vs. sport detection). Also, potassium chlorate, the oxidizer used in the Lazarowski study is significantly less volatile than AN. It is thus possible that the odor of the potassium chlorate was more readily masked by the fuel components, making it more difficult to detect.

Finally, a survey was used to compare canines' tendency to generalize (detecting 3 or more AN variants per trial) to reported effort levels (Table 11). The most notable correlation was that all canines that showed the tendency to generalize in at least two of the trials, were also reported to have been trained concurrently on the NACSW odors. These results suggest that, while training specifically on multiple variants of the same target does not necessarily enhance generalization,

training to a number of odors, in general, improves the canine's overall understanding of their trained odors and increases generalization. Furthermore, that group also had a greater chance to have trained at the same or higher effort level compared to normal NACSW training than to have trained with less effort, although the correlation was not as strong. There was no apparent relationship between generalization and reported training time per week.

*Table 11. Results of handler survey compared to whether or not canine generalized (detected three or more variants in one trial) in each trial. Question 1 (Q1) = How would you compare your effort level for training in preparation for the Navy study as compared to NACSW trials (i.e. less, about the same, or more)?; Question 2 (Q2) = Were you actively training on your NACSW odors during the Navy study?; Question 3 (Q3) = Estimate how much time you spent training for the Navy study per week. * Average time spent training per week was reported in hours or sessions per week.*

Dog ID #	Generalize Trial 1?	Generalize Trial 2?	Generalize Trial 3?	Q1. Effort compared to NACSW	Q2. Concurrent training on NACSW odors?	Q3. Avg. time spent training per week*
308	N		N	less	N	not reported
318				less	N	not reported
310	Y	N		more	N	2-3 hours
313	Y	N	N	more	N	2.5-3 hours
307	Y	N	N	same	N	2-5 sessions
315	N		Y	same	N	1-2 sessions
302	Y	Y	Y	less	Y	3 sessions (Trial 1); 0.5 sessions (Trials 2 and 3)
303	N	N		less	Y	0.2 hours
309	Y	N	N	less	Y	1 hour
312		N		less	Y	7 hours
316		Y		less	Y	2-3 sessions
317	Y	Y		less	Y	0.2 hours
320	N	N	N	less	Y	7 hours
306	Y	Y		more	Y	7 sessions (20 min each)
304		N	N	same	Y	2-3 hours
305	Y		Y	same	Y	3-4 hours
311		N	Y	same	Y	1-1.5 hours
314	Y	Y	Y	same	Y	21 sessions (3 times per day, 5-10 each)
319	Y	Y		same	Y	2-3 hours (Trial 1); 0.5 (Trials 2 and 3)
321	N	Y		same	Y	0.5-1 hours

CONCLUSION

The underlying hypothesis of this study was disproved; increasing the number of AN variants in training did not improve generalization to other variants. However, several other interesting trends were extracted from the data. Data showed that the canines that tended to generalize initially in Trial 1, tended to generalize throughout the study and vice versa. This tendency to generalize was also shown to be correlated to concurrent training on other odors. Additionally, the type of AN used during training (i.e. prill vs. ground) affected the detection of AN variants with canines trained on AN prill detecting more variants than those trained on ground material. More research should be done to further explore these and related subjects, for the purpose of improving training efficiency and canine detection proficiency.

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APPENDIX 1

*Table 12. All data from Trial 1, excluding canines that did not qualify due to high number of false alerts or inability to detect training odor at a rate of 75% or better. (A = Alert, N = No response). *Note: Some dogs tested were only able to complete 3 of the 4 planned validation tests. The missed test is noted in table; the miss did not count against them.*

Dog ID	*Ind. Prill*	*Ind. Grnd*	*Fert. Prill*	*Fert. Grnd*	*CAN*	*Ice pack*	***Testing odors (out of 6)***	***Lab-grade (training odor; out of 4 or 3*)***	***False alerts (out of 33 possible)***
TD302	A	A	A	N	A	A	**5**	**4**	**4**
TD303	A	N	N	N	A	N	**2**	**3**	**1**
TD305	A	A	N	N	N	A	**3**	**3***	**5**
TD306	A	A	A	A	N	N	**4**	**4**	**5**
TD307	A	N	A	A	N	N	**3**	**4**	**0**
TD308	N	N	N	N	N	A	**1**	**3***	**1**
TD309	A	A	N	N	A	A	**4**	**4**	**2**
TD310	A	A	A	N	A	A	**5**	**4**	**0**
TD313	A	N	N	N	A	A	**3**	**3***	**1**
TD314	A	A	A	A	A	N	**5**	**3***	**3**
TD315	N	N	N	A	N	N	**1**	**3***	**1**
TD317	A	A	N	N	A	N	**3**	**3**	**5**
TD319	N	N	A	A	A	N	**3**	**4**	**3**
TD320	N	N	N	N	A	N	**1**	**3***	**4**
TD321	N	N	N	N	N	A	**1**	**4**	**4**
Total	***10***	***7***	***6***	***5***	***9***	***7***	***44***	***96%***	***7.9%***

Table 13. All data from Trial 2, excluding canines that did not qualify due to high number of false alerts or inability to detect training odor at a rate of 75% or better. (A = Alert, N = No response. n/a = trained odor).

Dog ID	*Ind. Prill*	*Ind. Grnd*	*Fert. Prill*	*Fert. Grnd*	*CAN*	*Ice pack*	***Testing odors (out of 5)***	***Training odors (out of 4)***	***False alerts (out of 35 possible)***
TD302	A	A	n/a	A	A	A	**5**	**4**	**3**
TD303	N	N	N	n/a	A	A	**2**	**3**	**5**
TD304	A	N	n/a	N	N	N	**1**	**4**	**2**
TD306	A	A	n/a	A	A	A	**5**	**4**	**5**
TD307	A	N	n/a	N	A	N	**2**	**3**	**5**
TD309	N	N	A	n/a	N	N	**1**	**4**	**10**
TD310	N	N	N	n/a	N	N	**0**	**3**	**6**
TD311	A	N	N	n/a	N	N	**1**	**4**	**6**
TD312	A	N	n/a	N	A	N	**2**	**4**	**2**
TD313	N	N	N	n/a	A	N	**1**	**3**	**1**
TD314	A	N	A	n/a	A	N	**3**	**4**	**6**
TD316	A	A	N	n/a	N	A	**3**	**4**	**3**
TD317	A	A	n/a	A	A	N	**4**	**3**	**5**
TD319	A	N	n/a	A	A	A	**4**	**4**	**2**
TD320	A	N	n/a	N	N	N	**1**	**4**	**2**
TD321	A	A	n/a	N	A	N	**3**	**3**	**5**
Total	**12**	**5**	**2**	**4**	**10**	**5**	**38**	**91%**	**12%**

Table 14. All data from Trial 3, excluding canines that did not qualify due to high number of false alerts or inability to detect training odor at a rate of 75% or better. (A = Alert, N = No response).

Dog ID	*Ind. Prill*	*Ind. Grnd*	*CAN*	*Ice pack*	***Testing odors (out of 4)***	***Training odors (out of 4)***	***False alerts (out of 29 possible)***
TD302	A	A	A	A	**4**	**4**	**1**
TD304	A	N	N	A	**2**	**4**	**3**
TD305	A	N	A	A	**3**	**3**	**6**
TD307	N	N	A	A	**2**	**3**	**2**
TD308	N	N	N	N	**0**	**4**	**1**
TD309	N	A	A	N	**2**	**4**	**0**
TD311	A	N	A	A	**3**	**4**	**2**
TD313	N	N	A	N	**1**	**4**	**0**
TD314	A	A	A	N	**3**	**4**	**0**
TD315	A	A	N	A	**3**	**3**	**0**
TD320	N	N	N	A	**1**	**3**	**4**
Total	**6**	**4**	**7**	**7**	**24**	**91%**	**6.0%**

APPENDIX 2.

A.) *Positive predictive value (PPV)* was calculated for each target (training odor and AN variants) and each trial using Equation 1. In this case, all canines were considered as one group.

Table 15. Positive predictive value results for Trial 1, comparing true positive (alert) rates for both the training and testing odors to the false positive rates for all canines.

Target	*True positive rate*	*False positive rate*	***PPV***
Training odor	96.00%	7.88%	***92%***
Industrial, prill	67.00%	7.88%	***89%***
Industrial, ground	47.00%	7.88%	***86%***
Fertilizer, prill	40.00%	7.88%	***84%***
Fertilizer, ground	33.00%	7.88%	***81%***
CAN	60.00%	7.88%	***88%***
Ice pack	47.00%	7.88%	***86%***

Table 16. Positive predictive value results for Trial 2, comparing true positive (alert) rates for both the training and testing odors to the false positive rates for all canines.

Target	*True positive rate*	*False positive rate*	***PPV***
Training odor	91%	12.14%	***88%***
Industrial, prill	75%	12.14%	***86%***
Industrial, ground	31%	12.14%	***72%***
CAN	63%	12.14%	***84%***
Ice pack	31%	12.14%	***72%***

Table 17. Positive predictive value results for Trial 3, comparing true positive (alert) rates for both the training and testing odors to the false positive rates for all canines.

Target	*True positive rate*	*False positive rate*	***PPV***
Training odor	91%	6.0%	***94%***
Industrial, prill	55%	6.0%	***90%***
Industrial, ground	36%	6.0%	***86%***
CAN	64%	6.0%	***91%***
Ice pack	36%	6.0%	***86%***

B.) *The McNemar chi-square test* was used to determine if the probability of a canine detecting the testing odor is similar to the probability of detecting the training odor. The number of alerts for each variant was compared to the alert rate for the testing odor for all canines as one group. To make the data paired, the number of correct alerts to the testing odors was divided by four (to account for the four validation tests on testing odors vs. the single test on the training odors). All data was put into 2 x 2 contingency tables (example given in Table 5) and the χ^2 value was

determined by Equation 2. This value was compared to the χ^2_{crit} for one degree of freedom at a 95% confidence level ($\chi^2_{crit} = 3.84$).

Table 18. McNemar chi-square results for Trial 1. A significant difference (Sig diff) indicates that there was a difference in the alert rate to the testing odors compared to that of the training odors.

Target	*Total tests*	*Yes*	*No*	χ^2	*Sig diff?*
Training odor	**15**	**13**	**2**		
Industrial, prill	15	10	5	1.286	*N*
Industrial, ground	15	7	8	3.600	*N*
Fertilizer, prill	15	6	9	4.455	*Y*
Fertilizer, ground	15	5	10	5.333	*Y*
CAN	15	9	6	2.000	*N*
Ice pack	15	7	8	3.600	*N*

Table 19. McNemar chi-square results for Trial 2. A significant difference (Sig diff) indicates that there was a difference in the alert rate to the testing odors compared to that of the training odors.

Target	*Total tests*	*Yes*	*No*	χ^2	*Sig diff?*
Training odor	**16**	**14.5**	**1.5**		***3.84***
Industrial, prill	16	12	4	0.667	*N*
Industrial, ground	16	5	11	6.231	*Y*
CAN	16	10	6	2.000	*N*
Ice pack	16	5	11	6.231	*Y*

Table 20. McNemar chi-square results for Trial 3. A significant difference (Sig diff) indicates that there was a difference in the alert rate to the testing odors compared to that of the training odors.

Target	*Total tests*	*Yes*	*No*	χ^2	*Sig diff?*
Training odor	**11**	**10**	**1**		***3.84***
Industrial, prill	11	6	5	1.286	*N*
Industrial, ground	11	4	7	2.778	*N*
CAN	11	7	4	0.667	*N*
Ice pack	11	7	4	0.667	*N*

Table 21. McNemar chi-square results for AN mixtures. A significant difference (Sig diff) indicates that there was a difference in the alert rate to the mixtures compared to the AN alone

Target	*Total tests*	*Yes*	*No*	χ^2	*Sig diff?*
AN alone	**15**	**10**	**5**		
AN-Al	15	10	5	1.286	*N*
AN-FO	15	12	3	0.200	*N*
AN-PJ	15	10	5	1.286	*N*

C.) *The chi-square test for independence* was used to compare the distribution of responses to testing odors for Group A to Group B for each trial. All data was put into 2 x 2 contingency tables (example given in Table 6) and the χ^2 value was determined by Equation 3. This value was compared to the χ^2_{crit} for one degree of freedom at a 95% confidence level ($\chi^2_{crit} = 3.84$).

Table 22. Results from the chi-square test for independence comparing the response distribution of Group A vs. Group B canines for all trial. A significant difference (Sig diff) indicates that there was a difference in canine responses to the testing odors for Groups A and B.

	X^2_{crit}	X^2	*Sig diff?*
Trial 1	3.84	1.74	N
Trial 2	3.84	1.66	N
Trial 3	3.84	0.44	N