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Technical Note: The physical chemistry of odors – consequences for the work with detection dogs

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Abstract

Search dogs are used throughout the world in the search for illicit compounds or human individuals and similar tasks. Such search work is complex and not well understood in all its details which makes training of the dogs difficult. One important component for a successful education and deployment of search dogs is a good understanding of the behavior of scents under typical environmental conditions. This work summarizes up-to-date knowledge on the physico-chemistry of scents and discusses the consequences for the every-day work of dog handlers and trainers.

Key words: forensic science, search dogs, odor, scent tracing, physico-chemistry, storage of odor samples, cross-contamination

Introduction

Scent detection by trained dogs is a common technique to find explosives, illicit drugs, human remains or for matching human scents in order to identify suspects. Training as well as the operational work involves the handling of scents and their sources in multiple ways. Loss of scent as well as any kind of cross contamination or changes to the scent must be avoided. Also, a good quantitative control and reproducibility of the presented scent during training is needed. All this requires some fundamental understanding of the physico-chemical principles that govern the ´behavior´ of scent. The goal of this technical note is to gather the most important information on this topic in a short and concise form that can readily be implemented by dog handlers.

Most scents of interest are organic chemicals with a sufficiently high volatility to reside in the air to some degree so that they can be inhaled by dogs. Typically these are chemicals with a molecular weight between 50 and 500 g/mol. However, strict border lines cannot be defined because a) the sensitivity of a dog´s nose for different scents can differ by orders of magnitude so that some poorly volatile chemicals may be better detectable as some other very volatile chemicals and b) the ´volatility´ of a chemical very much depends on the context. In a scientific context, the term ´volatility´ is usually used synonymously to the saturated vapor pressure of a chemical. This number quantifies the air concentration of the chemical above its pure liquid or solid form in a closed container where a partition equilibrium has been established (i.e. there had been enough time for the air to become saturated). However in many practical scenarios the source of a scent is not its pure form but any kind of material (clothes, suitcases, plastic containers, bags, upholstery …) that contains traces of the scent in sorbed form and releases this scent to the air over time. The partition equilibrium of various scents between various kinds of materials and air often shows only little correlation to their saturated vapor pressures (e.g. see Fig. 18 in [1]). Fortunately, in recent decades quite reliable methods have been developed that allow to estimate the quantitative partitioning (or sorption/desorption) of organic molecules between many different materials and air just based on the molecular structure of the chemicals [2, 3] However, this knowledge can only be of use if the relevant scent is identified. This is often not the case. For example it is unknown which odors are used by dogs use in their search for human remains or when they identify human individuals. Even in the case of explosives this question is not simple to answer. TNT (trinitrotoluene), for example, usually contains traces of dinitrotoluene which is more volatile then TNT. Hence, the air surrounding an explosive device filled with TNT would typically contain higher concentrations of DNT than TNT even though only traces of DNT are present in the explosive powder[4]. This can make the search for DNT much more promising for a dog than the search for TNT itself. Due to our lack of knowledge concerning the exact molecular identity of the chemicals that dogs are searching for much of the existing specific knowledge on sorption of odors cannot be made use of in the training of search dogs. This work will therefore focus on that information that is generalizable and that applies to all scents.

Partitioning / Sorption Equilibrium of Odors

Understanding some principles of the partitioning or sorption (both terms are used synonymously here) of odors is a prerequisite whenever odors are collected, stored or presented to dogs. All odors do sorb to some degree from air to all materials. Hence, all materials in the vicinity of a source will sorb some of this scent via the air and when the odour source (human remains or an explosive device) is removed, these other materials will emit the odour to some degree which may then still be detectable by a dog. `Equilibrium´ means that each scent tries to attain a certain concentration ratio between its air concentration and its concentration in and on any kind of material. This ratio depends on temperature, on the molecular structure of the chemical and the sorbing materials. In any closed room or container this sorption equilibrium will be attained sooner or later i.e. the scent molecules insides this container will move (diffuse) between the air and all available solid and liquid materials until sorption equilibrium is reached. After equilibrium is reached no net transport of the odor will occur in this container unless the existing sorption equilibrium is disturbed e.g. by replacing the air in the container by fresh air without odor. The time frame needed to attain sorption equilibrium can vary between minutes and months and depends mostly on the type of sorption processes that were involved -adsorption or absorption- and the volatility of the odour. **Ab**sorption of odors, i.e. storage of odors within the bulk volume of a material happens in all liquids (water, oil , gasoline…) and in all polymers (plastic). **Ad**sorption is the storage of odors on the surface of materials. This happens on all surfaces but it is only relevant for those materials that cannot absorb chemicals (metals, glass, minerals, salts). Adsorption on surfaces is a very quick process but the storage capacity of surfaces is usually very small compared to the bulk storage capacity of absorbing materials (an exception to this rule are technically produced adsorbent materials like activated charcoal or zeolites that have a specific surface area of several hundred square meters per gram material). The process of absorption can be quite slow because the molecular diffusivity in polymers is small [5]. The following example may demonstrate what this can mean in practice: in a room in which explosives or illicit drugs were handled some of the odors are constantly diffusing from their source to the air and from there to all other materials in the room where they will sorb until sorption equilibrium is reached or until the odor source is removed. Some materials (such as glass, metals but also cellulose such as cotton or wood) will sorb only little of these odors but other materials (mostly plastic) will sorb rather high concentrations of these odors if time allows. Among these plastic polymers the soft (rubbery) ones like silicon, polyethylene, polypropylene, polyurethane (upholstery) will sorb these odors much quicker than hard (glassy) materials like polyacrylate or polystyrene [5]. If the odor source is removed from this room and the air is replaced by fresh air or if some of the items from this room are brought into fresh air outside (e.g. plastic bags, suitcases …) they will start to release the sorbed odor to the fresh air in order to obtain equilibrium with the air again. The release rate of the odor and the half-live of the odor in these materials in contact with fresh air can differ between minutes and years and depends on many different factors (thickness of the material, surface to volume ratio, chemical structure of the odor and the sorbing material, temperature..). Surfaces like glass and metals will quickly release the rather small amount of adsorbed odors to fresh air. Plastic that had enough time to equilibrate with the original odor source, will release odors at a rather high rate and over a rather long time period because a given volume of plastic may contain a million or a billion times more scent molecules than the equal volume of air can take up in equilibrium.

Storage of odors

In principle it is possible to store air that contains odor molecules. However, the small volume of air that one could store (may be one liter per sample) would only contain minute amounts of any odor and this will be almost instantaneously gone (i.e. diluted with fresh air) once the container is opened. Hence, it makes sense to store either the odor source or an item that has the odor sorbed so that larger amounts of odor are available and can be presented to the dog. In any case storage of scent items has to occur in containers that cannot be penetrated by organic molecules. This means that any containers made from plastic are inacceptable. In fact, the often used zip-lock bags and other bags made of polyethylene let odors penetrate within hours or less. One can easily try this out by relying on ones own nose: put a few crystals of pure vanillin (from a drug store) in such a bag, seal it and after about 2-3 hours you will be able to clearly smell the vanillin outside the bag. Other odors may pass even quicker through the bag. Scent samples stored in such containers are not only losing their scent over time but what is worse they are subject to cross-contamination with scents that penetrate into the bags from the outside (e.g. from another sample bag stored nearby). Boxes made from high-density polyethylene (HDPE) are less susceptible to cross contamination from one box to another because the material is much thicker and the diffusivity in HDPE is one order of magnitude smaller than in low-density polyethylene (LDPE)[5]. However, there will still be cross-contamination between samples if different samples are stored in the same container one after another. Note, that there is no method that would allow to clean any kind of plastic box from the odors that it has taken up over time from the stored items. Save storage is only possible in glass jars or metal containers. In most cases glass jars with a metal lid will be first choice because they are also easy to clean (for most odors a regular dish washer will do the job). These containers will not only prevent any odor from passing between the inside and the outside they will also adsorb only very little of the odor to their inner surface so that the stored scent item is not significantly depleted from its scent Note: the metal lids of glass jars possess a polymer coating on the inside for air tight sealing. This polymer coating will sorb larger amounts of the scent than the glass surface. If this is deemed to be critical, covering the opening of the glass jar with aluminum foil before screwing on the lid can minimize the problem. Sorption to this polymer lining of the lid could also lead to cross contamination when the lid is used on a new glass jar with a different sample. Hence, new lids should always be used for each new storage item because effective cleaning of the lids is hardly possible. Scent items that are too big to be stored in a glass jar can be wrapped in aluminum foil. While this is not air tight it does quite efficiently restrict fresh air from passing along the surface of the scent item and –because aluminum foil is not penetrable- it prevents odor molecules from diffusing to or from the scent item. The wrapped item may then be stored in a plastic bag to keep the foil in place, to minimize air venting and for the ease of handling.

For the same reasoning as above, plastic material must not be involved in any devices that are used to present a set of odor samples to a dog. A metal carousel with metal sample holders is ok because it can sorb only very little odor and is easily cleaned. Plastic boxes or plastic pylons for holding the odor samples are inappropriate because of inevitable carry-over effects because these materials cannot be cleaned efficiently. This also holds for Teflon (PTFE) which is supposed to be ´inert´. While the diffusivity in and sorption capacity of Teflon is smaller than for many other polymers it is still significant.

Storing items for days or weeks requires that these items are dry (or stored in a freezer) otherwise the growth of mold and bacteria can quickly alter and eventually destroy the original odor pattern of the sample. Also storage in the dark is advisable because some odors can be degraded by sun light.

Side remark: for the handling of training items dog handlers usually use disposable gloves so that the training items do not become contaminated with their own individual scent. Disposable gloves can be purchased from quite different materials all of them belonging to the large class of polymers. A simple test with vanillin again (see above) that was placed inside different gloves revealed that different materials would led odors pass through at very different time scales (from hours for natural rubber to many days for nitrile gloves). It appears advisable to always use nitrile gloves. The permeability of a given material to different scents can be quite different and so there may be odors that pass through these nitrile gloves much quicker than vanillin. However, the trend between the different materials should be similar for all chemicals so that one can assume that nitrile gloves are the best choice among the commercially available gloves for all types of odors.

How to create a scent copy of an item that contains the target odor

For training and operational purposes it might be helpful to create a scent copy that can easily be transported and stored. There are various demands that a material used to create a scent copy should fulfill: a) it should sorb a rather high amount of the scent(s) so that it is not quickly depleted from the scent by fresh air (e.g. when presenting to a dog), b) after the copy process is complete the scent concentration produced by the copy in the surrounding air should be should be comparable to the original scent item that was copied (note: for thermodynamic reasons the air concentration produced by the copy can usually never be higher compared to the original item although there are some tricks to overcome this rule) and -what is more important- c) if there is a scent pattern (i.e. the combination of several scents that make up the individual target odor) than the composition of this pattern should be copied correctly. The latter can be a difficult task because different scents contributing to a pattern will typically have different sorption properties. In order to fulfill the demands b) and c) the equilibration time needed for the scents to diffuse from the original item to the material used for the copy should be short and the sorption capacity of the material should be low which stands in contradiction to demand a) and therefore requires some kind of compromise. Wrapping film made from LDPE – a cheap material found in each house hold should fulfill these demands to a high degree when used to wrap the original scent item tightly with a single layer. Here is not enough room to give full account of the reasoning that leads to this suggestion but some thoughts may justify its plausibility. Wrapping film closely attached to the original item allows for a quick scent transfer between original and copy: the maximal possible surface area for diffusion of scent molecules from the original scent item into the wrapping film is used and the diffusion distance is minimized because of tight wrapping and because the film itself is very thin (10-15 µm) so that diffusion within the film also proceeds rather quickly. A quick scent transfer is not only convenient but it helps to establish a sorption equilibrium between original and the copy for the scents which is a must if a scent pattern is to be copied. Among all plastic materials LDPE belongs to those with the highest diffusion velocities for organic molecules [5] which again allows for rather quick equilibration. The sorption capacity per volume of polyethylene is pretty high but due to the thin nature of the film and its high surface area only a small amount of film is needed so that there is still a good chance that the original item is not depleted significantly from the odor(s). Additional positive side effects are that the film can easily be stored in glass jars and that it does not suck up moisture in contact with wet materials. Examples of possible application can be: a) if a scent item of a suspect or a missing person is required for the work of a mantrailer dog and the only available item is an armchair or the steering wheel of a car or any other item that cannot be easily carried away then scent copies are wanted. All these immobile items can easily be wrapped or covered with wrapping film which can then be used to help the dog when it is under way (Note:) b) training of human remains detection dogs is often hampered by the fact that human remains are not easily available and cannot easily be deployed in realistic environments for training. However, it might be quite feasible -by cooperating with pathological institutes- to acquire and store pieces of wrapping film that had previously been wrapped around the leg or an arm of a dead body overnight. These pieces of wrapping film can then be deployed for training indoors and outdoors without raising unwanted publicity. (Despite its convenience, this wrapping film should of course not become a dominant training item. For all detection dogs it is important to be trained in very versatile scenarios that cover all kinds of realistic operational conditions.) As stated above, copying a scent pattern requires complete equilibration between the source and the copy which can take time if odors with low volatility are involved. A single sheet of LDPE wrapping film with a thickness of 12.5 µm should require about 20 minutes for equilibrating with the odors in the surrounding air assuming a typical diffusion coefficient of 1E-9 cm^2/sec. This is pretty short. However, if the kinetics of the odor transfer between a source and the film is not limited by diffusion in the film but by diffusion through the air as is the case for chemicals with low volatility (e.g. most explosives) then the time to equilibration can be much longer than these 20 minutes and will differ from odor to odor. Still the wrapping film would be first choice because the air space between the odor source and the film can be minimized but it might be impossible to achieve complete equilibrium within an hour or less as it might be required for operational reasons, e.g. for mantrailing.

It appears that police units often use gauze bandage for creating scent copies with the argument that this material is sterile. However, sterile does not mean ´free of odor. Sterile items can only be assumed to be free of microorganisms, a feature that is irrelevant for the sampling of scent. In fact the same misconception can be found when it comes to the cleaning of materials that are used in training and operational procedures. Sterilization of an item does by no means imply that odors are removed. In fact, sterilization of glass or metal surfaces will largely remove adsorbed odors but sterilization of plastic items will hardly change the amount of absorbed odors at all.

What controls the concentration of an odor in the air?

To answer this question it is important to understand that there are two principally different situations with all the possible gradual transitions between them:

1) If the scent emerging from a source is quickly diluted by fresh air that is passing by then the air concentration will quickly drop with increasing distance (in the mm range [6]) from the source and the air concentration will be determined by the following factors: a) concentration of the scent in/on the source item, b) the ´volatility´ of the scent from the source, c) the surface area of the scent source because this determines the volatilization rate of the scent (usually this is proportional to the amount of source material), d) the volume flow rate and turbulence of fresh air passing by the source and e) possibly the diffusion velocity of the scent within the material of the scent source. The latter matters if the scent source had been exposed to fresh air for a while so that its surface has already been depleted from the scent.

   Search dogs will usually encounter this very complex situation in their operations and training. A high and predictable air concentration will only exist within a few mm of the actual scent source while further away only concentration pulses exist due to inevitable aerodynamic turbulences (see d) above)[6]. Concentration in these pulses is just as unpredictable as are time and location of the occurrence of these pulses. It is interesting to note that the sniffing strategy of dogs i.e. sampling small volumes of air at a high frequency is perfectly adapted to this situation. The high frequency guarantees that every now and then just by chance a concentration pulse is sampled and high concentrations are encountered by the dog. Taking long deep breathes would be much less efficient because then the high concentration in the pulses would be diluted with much uncontaminated air.

2) The other extreme occurs if the scent source is located in a closed environment with no access of fresh air. In this case the scent source can eventually equilibrate with the surrounding air and all materials within this closed room and build up the maximally possible

air concentration throughout the whole room or container. When the equilibrium state is reached no concentration gradient will exist in the air of such a room, i.e close to the odor source the air concentration is the same as at maximal distance to the source. Concentration pulses do not exist under these conditions. The time needed until complete odor equilibration in a closed room can be very long depending on the volatility of the odors and the sorptive capacity of the materials in this closed room. This equilibrium air concentration itself only depends on the first two factors from above: a) concentration of the scent in/on the source item and b) the ´volatility´ of the scent from the source.

Of course, if the capacity of the scent source is so small that it quickly becomes depleted then this will strongly affect the air concentration in both cases above. In practice it may not always be easy to distinguish between both cases. Here are some examples: i) Outdoors one will typically have the first situation with fresh air diluting the scent that comes from the source. However, if the scent source is outdoors but hidden in a crevice, a bin or a pipe with only one opening then air movement within this crevice, bin or pipe will be very restricted and the inside-air can equilibrate with the scent source. Only when the scent gets to the outside it is quickly diluted by fresh air in an uncontrollable way. Ii) A dead body in a closed living room may equilibrate with the rest of the room rather quickly with respect to some typical volatile odors (e.g. cadaverin and putrescin) so that a maximum air concentration is reached and no concentration gradient exists within the room (which may make it difficult for a dog to locate the body if it is out of sight). To the contrary, a small scent source with a less volatile scent in the same room may need days or weeks to equilibrate with the complete air room and during that equilibration time we have a type 1 situation.

Diluting scent samples

The work with detection dogs inevitably brings up the question of how sensitive dogs are, i.e. how small can an odor concentration be that a dog would still indicate correctly. Hence, dog handlers will try to dilute their training samples in order to find out. However, there are various pitfalls to observe: the available air concentration may not only depend on the scent concentration in/on the source material (see discussion of situation 1 above). And diluting a sample is also not trivial. For example, diluting a blood sample with water will not lower the equilibrium air concentration of any odors emanating from the mixture just according to the volumetric mixture ratio. Instead the air concentration that is achieved from 1:1 blood/water mixture may only be a few percent lower than in equilibrium with the non-diluted blood. This is not intuitive but is the inevitable effect of proteins and lipids in the blood that act as buffers to the blood odors and that release sorbed odor molecules as soon as the liquid is diluted with water [7]. A good quantitative control of a scent can be achieved if the scent source is placed in a closed container from which the scent can only exit by a diffusion controlled process as shown in Fig.1. Here the air inside the container will reach a constant and maximal concentration sometime after the scent source was placed inside. The concentration at the outlet of the tube that becomes available to a dog then depends on the geometric dimensions of the tube and the inside air concentration. Doubling the length of the tube will lower the concentration at the outlet to half, lowering the diameter of the tube by a factor 2 will lower the cross sectional area and thus the transport rate and the concentration by a factor of 4, and vice versa of course. Due to air turbulences this device can, of course, only control the air concentration directly at the opening of the tube (see discussion above).

The well controlled permeability of LDPE bags can also be used to provide controlled air concentrations in the vicinity of the source as discussed in a patent by Furton et al.[4] .

In summary, this technical note tries to convey some state-of-the-art knowledge on the physico-chemical behavior of scents in general that should proof helpful in the training and deployment of search dogs. This text is not complete and it does not cover more specific questions whose answer would require a detailed analysis of the complete scenario including the specific type of odors that are relevant.

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Figure Capture

Fig. 1: A sample container with a diffusion device for controlled delivery rate of an odor