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Identification of dominant odor chemicals emanating from explosives for use in developing optimal training aid combinations and mimics for canine detection

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Abstract

Despite the recent surge in the publication of novel instrumental sensors for explosives detection, canines are still widely regarded as one of the most effective real-time field method of explosives detection. In the work presented, headspace analysis is performed by solid phase microextraction (SPME)/gas chromatography–mass spectrometry (GC–MS), and gas chromatography–electron capture detection (GC-ECD), and used to identify dominant explosive odor chemicals seen at room temperature. The activity of the odor chemicals detected was determined through field trials using certified law enforcement explosives detection canines. A chemical is considered an active explosive odor when a trained and certified explosives detection canine alerts to a sample containing that target chemical (with the required controls in place). A sample to which the canine does not alert may be considered an inactive odor, but it should be noted that an inactive odor might still have the potential to enhance an active odor's effect. The results presented indicate that TNT and cast explosives share a common odor signature, and the same may be said for plasticized explosives such as Composition 4 (C-4) and Detasheet. Conversely, smokeless powders may be demonstrated not to share common odors. The implications of these results on the optimal selection of canine training aids are discussed.

Keywords: Solid phase microextraction; Explosives; Canine detection

1. Introduction

The use of canines as a method of detection of explosives is well established worldwide and those applying this technology range from police forces and military to humanitarian agencies in the developing world. Until recently, most data regarding optimal training protocols and the reliability of canine detection has been anecdotal, leading to successful challenges regarding the admissibility of evidence obtained with the assistance of canines and hampering the improvement of performance of canines as biological explosive detectors [1]. Challenges facing the field of canine detection include the limited ability to evaluate their performance with standardized calibration standards. Unlike instrumental methods, it is currently difficult to determine detection levels, perform a calibration of the canines' ability or produce scientifically valid quality control checks. In addition, there are increasingly strict requirements being applied to the admissibility of the application of detector dogs in locating items of forensic interest, highlighting the need for better a scientific understanding of the process of canine detection. This current research is targeted towards the identification of active odors for canine detection of items of forensic interest and the development of what we are calling odor mimics, or training aids that contain the odor chemicals that mimic the real substances. There are presently several theories about what is responsible for the canines' high selectivity and specificity to explosives including (i) that canines alert to the parent explosives regardless of their volatility; (ii) that canines alert to more volatile, non-explosive chemicals that are present in explosives, and which are characteristic to explosives; or (iii) both parent explosives as well as characteristic volatiles are used to accurately locate explosives. To date, there are no

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definitive peer-reviewed studies to support any of these theories. The results presented here are part of an ongoing research program aimed to improve the scientific validity of canine detection, through better understanding of the chemistry of odors emanating from forensic specimens. By identifying the key odors of items of forensic interest, in this case explosives, levels of detection and linearity ranges may be determined, and better documentation of training and deployment will serve to benefit reliability studies. In addition, identification of active odor signature chemicals aids in the selection of the fewest number of target substances needed for optimal training and facilitates the development of reliable, cost-effective non hazardous odor mimics which can be used to enhance the capabilities of detector dogs. A previous Talanta article reviewed the use of dogs as chemical detectors, and the scientific foundation and reliability of explosive detector dogs, including a comparison with analytical instrumental techniques [2]. Recent reviews of electronic noses have highlighted the current limitations of instrumental methods with Yinon concluding that electronic noses for detecting explosives have a long way to go before being field operational [3] and Gopel concluding that, for most applications, the performance of electronic noses containing sensor arrays are insufficient compared to established analytical instruments such as GC/MS [4]. A recent extensive review of instrumentation for trace detection of high explosives concluded that there is still no instrument available that simultaneously solves the problems of speed, sensitivity and selectivity required for the real time detection of explosives [5]. Overall, detector dogs still represent the fastest, most versatile, reliable real-time explosive detection device available. Instrumental methods, while they continue to improve, generally suffer from a lack of efficient sampling systems, selectivity problems in the presence of interfering odor chemicals and limited mobility/tracking ability.

2. Explosive detection technologies

There are a variety of technologies currently available and others under development. Fig. 1 illustrates some trace explosive technologies including separation techniques ranging from high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) commonly with fluorescence or electrochemical detection and gas chromatography (GC) combined with mass spectrometry (GC/MS) electron capture (GC/ECD) or luminescence detection. In addition, techniques based on mass spectrometry and ion mobility spectrometry (IMS) continue to improve [4]. Currently, the most widely deployed explosives screening technology deployed at airports is ion mobility spectrometers which rely primarily of the on detection of particles contaminated on the outside of baggage or paper tickets. Recently, a new IMS inlet has been developed which allows for the detection of odor chemicals using solid phase microextraction (SPME) sampling [6,7]. Microsensors have the potential for selective GC detectors and also as remote sensors when combined in arrays often referred to as “electronic noses”. Promising microsensors include surface acoustic wave (SAW) detectors normally coated with different semi-selective polymeric layers and microelectromechanical systems (MEMS) including microcantilever sensors. Recently, a handheld sensor based on piezoresistive microcantilevers named “SniffEx” has been demonstrated to detect PETN and RDX at levels below 10 parts per trillion within a few seconds of exposure [8]. The hope is that, in the future, hundreds of such microcantilevers, coated with suitable coatings, may be able to achieve sufficient selectivity to provide a cost-effective platform for detecting explosives in the presence of potentially interfering compounds in real environments. Other electronic nose technologies under development include the use of fiber optics and sensor beads, polymeric thin films, nanocluster metal-insulator-metal ensembles (MIME), and fluorescent polymers using amplifying chromophore quenching methods [3]. To date, there has been limited testing of these devices with noisy chemical backgrounds under operational conditions, however the handheld “FIDO” system based upon quenching chromophore amplifying fluorescent polymers (AFP) was recently field tested against certified explosive detection canines for the detection of TNT based explosives, and was reported to share similar detection capabilities with canines [9].

Optical techniques under investigation include transmission and reflectance spectophotometry including infrared (IR) detection of decomposition products including the well established EGIS system, UV–vis absorption methods including cavity ring down spectroscopy (CRDS), Raman scattering including using localized surface plasmon resonance (LSPR) and optoacoustic (OA) spectroscopy [5]. Standoff technologies under development include laser, light detection and ranging (LIDAR), differential absorption LIDAR (DIAL) and differential reflection LIDAR (DIRL) for imaging. Nonlinear optical techniques offer the potential for increased signal-to-noise ratios in sensing modes including coherent anti-Stokes Raman scattering (CARS), optical phase configuration, and coherent control of the specific states of molecules and optimize their luminescence [10]. A recent report on standoff explosive detection techniques conducted by the National Academy of Sciences concluded that it is important to use multiple orthogonal detection methods (methods that measure the properties of explosives that are not closely related) as no single technique solves the explosive detection problem [10]. Studies conducted include free-running and remote explosive scent tracing (REST) in which the odor is collected on a sorbent in the field and presented to the animal at a different location [11]. Biological explosive detectors, including detector dogs can be considered orthogonal detectors to sensors under development as they generally rely on different detection modalities. In addition to canines, other animal and plant species have been proposed as alternative methods of biological explosives detectors. A research project in Tanzania, under the support