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Experimental Design Using a Quartz Crystal Microbalance to Investigate the Transport of Explosive Vapors from Enclosed and Buried IEDs

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14. ABSTRACT

With support of the Office of Naval Research, the Naval Research Laboratory, Laboratories for Computational Physics will study the transport of explosives vapors from simulated buried improvised explosive devices (IEDs) through soil under varying conditions. Here a literature survey was conducted to aid in the design of a novel instrumental analysis method utilizing a quartz crystal microbalance (QCM) to measure the adsorption/desorption of analyte vapors (DNT and TNT) onto soil, sand, and plastic-coated sensors to validate the transport models. The QCM will provide the means to experimentally measure the adsorption/desorption properties of explosive vapors providing the necessary coefficients to necessary for the computational models.

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OBJECTIVE

With support of the Office of Naval Rearch, the Naval Research Laboratory, Laboratories for Computational Physics will study the transport of explosives vapors from simulated buried improvised explosive devices (IEDs) through soil under varying conditions. Here a literature survey was conducted to aid in the design of a novel instrumental analysis method utilizing a quartz crystal microbalance (QCM) to measure the adsorption/desorption of analyte vapors (DNT and TNT) onto soil, sand, and plastic-coated sensors to validate the transport models. The QCM is used to provide the means to experimentally measure the adsorption/desorption properties of explosive vapors providing the required coefficients for the computational models.

BACKGROUND

Motivation

Improvised explosive devices (IEDs) are weapons constructed from readily available materials and are not industrially produced. IEDs can be made from a diverse variety of materials. The explosive filler will vary depending on local availablility, with common explosive fillers including 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), as well as varying combinations of these and other additives to create different compositions [1]. Additionally, the use of homemade explosives (HMEs) in IEDs has become more frequent due to the ease of obtaining materials and information from the internet. Materials used for HMEs may include peroxide-based explosives, e.g., triacetone triperoxide (TATP) or hexamethylene triperoxide diamine (HMTD), or fuel-oxidizer mixtures, e.g., ammonium nitrate-fuel oil (ANFO) or potassium chlorate (PC) with an appropriate fuel source, which can be made from materials purchased at local stores, such as supermarkets or home improvement stores [1].

IEDs have been a major cause of American casualties in Iraq and Afghanistan for the past twenty years. From October 2001 to August 2007, IEDs caused 70% of all American combat casualties in Iraq and 50% of casualties in Afghanistan [2]. From September 2011 to October 2020 52% of deaths in Iraq and 48% of deaths in Afghanistan were caused by IEDs [3]. Although the terrorist organization associated with these tragedies was territorially defeated in 2019, landmine and IED threats still remain and research aimed to improve detection has been slow to evolve.

In this regard, Jury et al., developed a model to simulate the transport of explosive-related vapors in soil; however, the model was developed in a one-dimensional form, resulting in assumptions that may cause errors [4]. Recently, NRL's LCP&FD developed the JENRE® code. This code is capable of modeling time-accurate multispecies, chemically reacting, transport problems in complex three-dimensional geometries [5]. This technology will be used to examine the transport physics of explosive vapors through sand, soil, and containment.

Small-scale experiments using a quartz crystal microbalance (QCM) will be performed to validate certain transport terms of the model, namely the diffusion rates of explosive vapor in the gas phase and adsorption to soil surface. To accomplish this, it is necessary to understand current explosive vapor detection methods, as well as QCM in regards to explosive detection. Thus, the first portion

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of this report will provide a brief background on the differences between IEDs, landmines, and unexploded ordnances followed by current methods used to detect buried IEDs and landmines. Then, the theory of QCM and the utilization of QCMs to detect explosive vapors in the literature will be discussed. Finally, an experimental design to investigate transport of explosive vapors using a QCM is described.

Current Detection Methods for Buried IEDs and Landmines

Landmines are explosive devices designed to destroy surroundings and are typically used as defensive weapons. They can be victim-activated, triggered by a person when it is stepped on or struck, or command-activated when a person detonates a mine by remote control [6]. Landmines are typically hidden, or buried underground, making it difficult to locate and avoid the threat. Unexploded ordnances, or UXOs, are explosive munitions that have been fired, tossed, released or dropped, but failed to detonate [6]. These include, but are not limited to, artillery rounds, fuses, grenades, missiles, and bombs, while IEDs are homemade explosive devices used to destroy property or cause injuries and are often camouflaged with surroundings or buried. UXOs or abandoned munitions are often used to construct IEDs [6]. While both landmines and IEDs can be above ground or buried, they differ in that landmines are manufactured to a specific factory standard, whereas IEDs are improvised from explosive materials and almost any material sourced from industrial or agricultural domestic markets [7]. Over the years, the use of landmines became less prevalent while the use of IEDs became more frequent. Even so, the explosives used in both IEDs and landmines may be similar; thus, detection of explosive vapors above- and under- ground is important to reduce threats.

Current detection methods of explosives include canines [8, 9, 10, 11, 12] mass and ion mobility spectrometry [13, 14, 15, 16, 17], infrared (IR) absorption spectroscopy [18, 19], Raman scattering [20, 21, 22, 23], ground penetrating radar (GPR) [24, 25, 26, 27], and microcantilever and QCM sensors [28, 29, 30]. Canines are reliable, mobile detectors for many materials and are widely deployed for detection of explosives. Canine detectors use olfaction to sense chemical vapors. The majority of explosives have very low vapor pressures (for examples, see Table 1), meaning the parent molecule are not likely to be found in the vapor phase, and are thus not likely detectable by canines or other vapor detection instrumentation. Instead, a single volatile organic compound (VOC) that produces a distinct odor, also known as an odorant, or a mixture of VOCs make up the detectable vapor signature of a given detection target, such as an explosive. While an explosive may have a number of VOCs that can be found in the vapor phase, canines are known to utilize a smaller selection of odorants to identify the target of interest [10], often referred to as the odor signature or odor profile.

Table 1. Vapor pressure of common explosives at ambient temperature (25 °C).

	TNT	**PETN**	**RDX**
Vapor Pressure (Torr)	5.8×10^{-6}	1.4×10^{-8}	4.6×10^{-9}

Mass and ion mobility spectrometry are common methods selected for detection of explosives vapor due to their sensitivity and selectivity. In these methods, a vapor sample is introduced to a sample chamber where ionization occurs. In ion mobility spectrometry (IMS), sample vapors are ionized at atmospheric pressure prior to entering to the drift tube, where an electric field is applied to mobilize the ions. Drift times are associated with mass of ions, which are used to determine mass to charge ratio (*m/z*) and ultimately identify compounds by comparison to known standards [32]. In principle, mass spectrometry (MS) methods use energy from the MS source fragments and ionizes molecules, after which the fragments are separated iaccording to their *m/*z. The *m/z* of the fragments and their ratios are then be used to identify the molecule by comparison to a library. There are many types of MS that can be used for explosives detection, such as quadrupole, time-of-flight, atmospheric pressure chemical ionization (APCI), or tandem MS (MS/MS) that use differing means for ionization and separation and results in differing levels of molecule fragmentation [32]. For IMS and MS explosive detection, recent research focuses on fieldability by reducing the size and cost of instrumentation, improving ease and efficiency of sample introduction, and improving selectivity in lower fidelity instrumentation [13]. For example, Wells et al. (2008) developed a field-deployable MS method capable of detecting 250 pg and 1 ng of PETN and RDX, respectively [33], while Sanders et al. (2010) demonstrated the use of a miniaturized MS for detecting trace amounts of TNT and HMX [34]. In 2003, Marr et al. validated the use of a gas chromatography (GC) coupled with IMS-MS method to improve the detection of trace amounts of TATP and HMTD using an IMS [35]. A field-deployable example of GC-IMS-MS instrumentation for detection of nanogram levels of C4, peroxides, TNT, and other nitrates is the EGIS Defender (Thermo Scientific), which has been used in U.S. airports [32].

In principle, IR spectroscopy methods pass an IR beam through samples which results in absorption of specific wavelengths and ultimately identification of substances. A common IR method used for detecting explosives is Fourier transform infrared spectroscopy (FTIR) due its ability to scan all IR frequencies at once, opposed to individually, saving analysis time. In 2007, Hernandez-Rivera et al. reported a technique coupled with FTIR that was capable of nanogram level detection of TNT, PETN, and HMX on metal surfaces [36]. FTIR has also been used for detection of explosive residue in fingerprints, Mou et al. (2009) [19]. Here, explosives particles as small as 20 μm in fingerprints could be detected and identified using the method. Another spectroscopic method frequently used for explosive detection is Raman scattering. In Raman, a sample undergoes laser excitation, which results in vibrational transitions that are measured through analysis of scattered photons. This technique allows standoff detection, which is useful for detecting hidden explosives such as landmines or buried IEDs. Pacheco-Londono et al. (2009) demonstrated the use of Raman in combination with IR to detect milligram levels of TNT, DNT, RDX, TATP, and C4 at a distance of 7 m [20]. Another example of Raman scattering for explosives detection was established by Petterson et al. (2009). In this study, standoff identification of a range of explosives at distances of up to 55 m in realistic outdoor conditions was performed [21]. Raman has also been used for detection of PETN, TNT, and AN on the surface of nails [37].

Ground penetrating radar (GPR) has frequently been deployed for landmine and buried IED detection. In GPR, electromagnetic waves penetrate the ground, if they encounter an object the waves are reflected and the signal is scattered. The receiver detects and collects the signal, which results in an image of the buried object. In this regard, GPR is capable of locating buried explosive devices over a large span of land. The Army first used GPR for detection of landmines in the 1940s and the first commercially available device developed in 1972 [25]. More recently, Garcia-

Fernandez et al. (2019) proposed a GPR sensor for detection of landmines and IEDs. In these studies, a transmitter was placed on a vehicle, while a receiver was placed on a drone, allowing for good penetration and high resolution [38]. A combination of electromagnetic induction with GPR has been used to improve discrimination of metal fragments from live minefields [39].

Microcantilever sensors have been used for explosive vapor detection due to accuracy, sensitivity, and ability to detect trace amounts in real-time. Microcantilever sensors can be operated in dynamic or static mode. In dynamic mode, mass loading due to molecular adsorption is monitored as a variation in resonance frequency of the cantilever, while in static mode adsorption-induced surface stress is monitored as bending of a cantilever [30]. Dynamic mode is similar to the operation of surface acoustic wave or QCM transducers. Microcantilever-based sensors are typically composed of silicon wafers with a micromachined cantilever. Although microcantilever sensors are highly sensitive, they tend to lack selectivity. Selectivity can be improved by modifying the surface using self-assembled monolayers (SAMs), such as SAMs of 4-mercaptobenzoic acid [40]. These sensors were capable of detecting TNT, RDX, and PETN vapors at the parts-per-trillion level. Although all of the techniques discussed in this section were capable of detecting and identifying explosive vapors, landmines, and buried IEDs, none of them actually investigated the transport of the vapor. In fact, GPR is limited by irregularities in soil textures, roughness, and moisture [41], all of which can affect explosive vapor transportation. Understanding how and what can affect vapor transport of explosives will allow for improvement of current detection methods, as well as optimization of deployable detection resources. In this regard, small-scale experiments to validate a model being developed by NRL's LCP&FD to investigate vapor transport of explosives through soil and containment is necessary. To accomplish this, the QCM has been selected as the instrumentation of choice due to its demonstrated sensitivity, accuracy, and capability of real-time detection.

Quartz Crystal Microbalance Theory

The quartz crystal microbalance (QCM) is most commonly used as a gravimetric sensing device. The QCM consists of a quartz crystal, most commonly AT- or BT-cut quartz, with metal electrodes on either side (Fig. 1), known as a quartz crystal resonator (QCR).

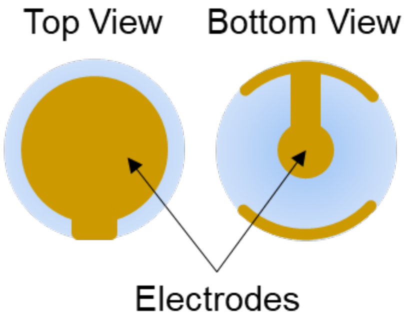

Figure 1. Schematic of QCR with gold electrodes.

The QCM is a thickness shear mode device, where elastic waves propagate through the QCR from an external voltage. The AC voltage is applied across the metal electrodes on the QCR causing the crystal to oscillate, and resulting in the generation of an acoustic shear wave, referred to as resonance frequency. This wavelength is dependent on the thickness of the crystal and expressed by the following equation:

$$f = \frac{c_q}{\lambda} = \frac{c_q}{2(d_q + d_f)} \tag{1}$$

Where f is frequency, c_q is speed of sound, λ is wavelength, d_q is thickness of the QCR, and d_f is the film thickness [42]. According to Equation 1, an increase in thickness of the QCR would result in a decrease of the resonance frequency. Thus, addition of materials onto the QCR surface would decrease the resonance frequency. This relationship is what led to Gunter Sauerbrey's discovery of the QCM as a mass detector [43]. The QCM operating principle is based on the Sauerbrey Equation (2).

$$\Delta f = -\frac{n}{c}\Delta m = -\frac{n}{c}\rho_f t_f \tag{2}$$

Where Δf is change in resonance frequency, η is harmonic number, c is mass sensitivity, which is 17.7 ngcm^{-2}Hz^{-1} for a 5 MHz AT-cut crystal as used in these studies; ρ_f is the density of the film, and t_f is film thickness [44]. Ultimately, change in mass on the QCR surface is directly related to its change is frequency, as shown in Equation 2. Therefore, change in frequency can permit an estimation of the mass of analyte adsorbed onto the surface of the QCR. As mass is added to the surface of the QCR, the resonance frequency should decrease. This is known as the ideal Sauerbrey behavior. Only rigid, uniform, and thin materials follow this behavior and would exhibit a small dissipation value. All films that do not meet these requirements would exhibit non-ideal Sauerbrey behavior and large dissipation values. Thus, resonance, thickness, and viscoelasticity of each film will affect detection response [45, 46]. Viscoelastic films, which demonstrate elastic and viscous properties, result in behavioral changes under resonant conditions as compared to rigid films. Physical changes of film materials will affect response, as shown in Figure 2 [47]. In this instance, it is possible for these films to exhibit positive frequency responses, which is a trait associated to non-ideal Sauerbrey behavior. As a result, the QCM as a transducer is fundamentally non-selective. Hence, coating materials on the surface of a QCR is a necessity to create QCM-based sensors.

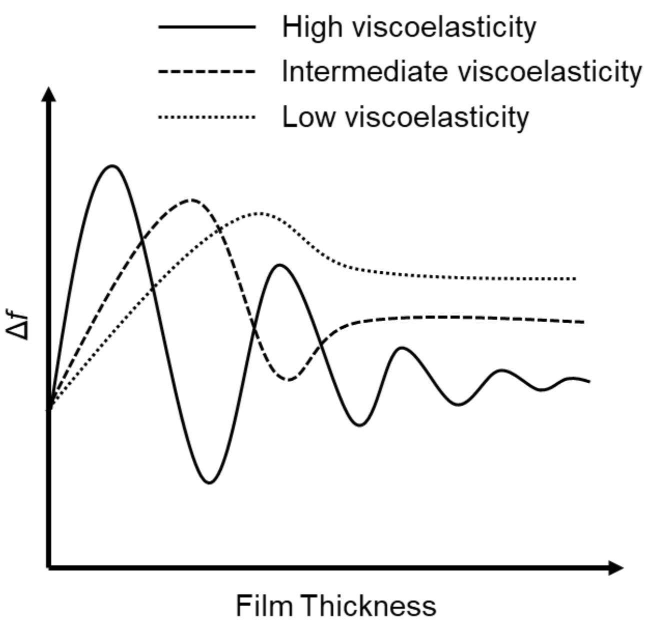

Figure 2. Schematic of frequency response based on viscoelasticity and film thickness.

Detection of IEDs and Landmines using QCMs in the Literature

In the literature, the QCM has been used to detect various explosives due to its cost-effectiveness, sensitivity, and accuracy. Hraybi et al. (2017) developed a model using the QCM to test varying environments for the detection of buried landmines [48]. In this study, experimental results provided details on how noise would affect the accuracy of QCM for explosive detection, while a computational model was used to determine future testing of buried landmines that emit low explosive vapor [48]. The QCM has also been used to validate simulations developed for detecting explosive vapor in the air [48]. Similar to microcantilever sensors, QCM-based sensors selectivity can be improved by incorporating coating materials on the QCR. For example, a QCR surface was modified using a novel polypyrrole-bromophenol blue compound for detection of explosive vapors [29]. Here, Eslami et al. was able to detect TNT, PETN, RDX, and HMX at parts-per-trillion level using the QCM-based sensors. A variety of sensors coatings have been utilized to detect a range of explosives in air and water, and in the presence of interferents [49-54]. As demonstrated by the examples above, the QCM is quite capable of detecting explosive vapors with high sensitivity and selectivity based on the coating materials used; however, there has not been an extensive amount of work completed on explosive detection in complex environments, such as buried landmines. Additionally, while the QCM has been used for detecting, discriminating, and validating models for explosives, the effects of containment or surrounding moieties, i.e. soil, have not been considered. Further described herein, the author's suggest an experimental design that utilizes a QCM will be used to validate the vapor transport model and investigate absorption/desorption of explosive vapors in the presence of soil, sand, and containment.

QCM EXPERIMENTAL DESIGN

Traditionally, QCR coatings are chosen to enhance selectivity of the sensor for detection applications. Instead, for this use of the QCM coatings are selected that represent materials that are likely to be vapor sinks, due to ad(b)sorption, during the vapor transport process, as explosive vapor moves from the buried device to the surface for detection. Coatings include those representing dirt, sand and soil, as well as containment materials, plastics and stainlesss steal, potentially used in a buried explosive device, as listed in Table 2. To simulate these environments using the QCM, sensors with respective substrates are exposed to explosive vapors, including 2,4-dinitrotoluene (DNT), a volatile component of TNT, and ammonia from ammonium nitrate (AN). The resulting data is then used to probe the ad(b)sorption properties of explosive vapors to soil or container material as it is transported to the soil surface.

Table 2. List of QCR coating materials for respective experiments.

QCR coating	Vapor sink represented
Stainless steal	Container, metal
Polystyrene	Container, plastic
Polyvinylidene fluoride (PVF)	Container, plastic
Silicon dioxide (SiO_2)	Sand
Standardized Soil (SS)	Soil

To assess ad(b)sorption of analyte vapor to the vapor sinks, a souce of analyte vapor is generated and delivered to the QCM at a controlled flow rate using a flow system comprised of two independent gas flow channels, one for explosive vapors and the other for carrier/diluent gas (ultrapure argon), as seen in Figure 3. Analyte vapor is removed from the sensor by purging the system with argon at room temperature until the baseline is recovered. It should be noted that once the QCR is inserted into the QCM chamber, it is referred to as a sensor. A schematic of the system described is shown in Figure 3.

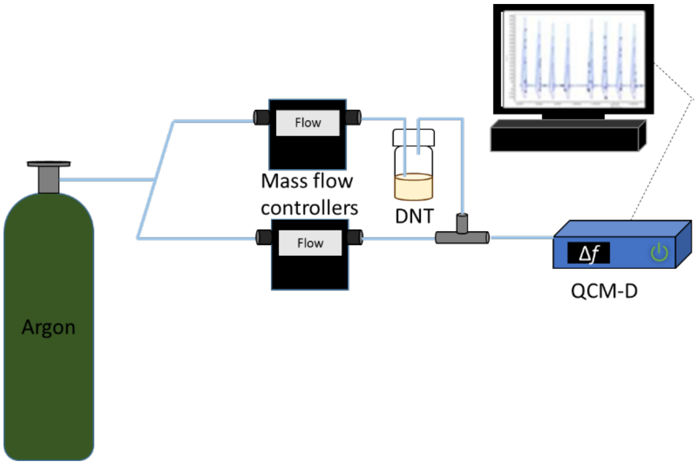

Figure 3. Schematic of QCM-D flow system.

Determine Optimal Explosive Exposure Time to Sensor

Before explosive monitoring can begin, the exposure time of explosive vapors to sensors is determined. To accomplish this, a silicon dioxide (SiO_2) QCR is inserted into the QCM-D mini chamber. After a stable baseline has been established, the SiO_2 sensor is exposed to explosive vapor (DNT and TNT) until a change in frequency is established, as noted by the plateau in figure 4. Once this equilibrium of explosive vapor to the sensor is achieved, the time and flow rate is noted and is used for further experimentation with this sensor. This same experiment is repeated with additional sensor coatings, to determine the optimal exposure time of explosive vapor to each sensor. An example sensorgram for this experiment is shown in Figure 4.

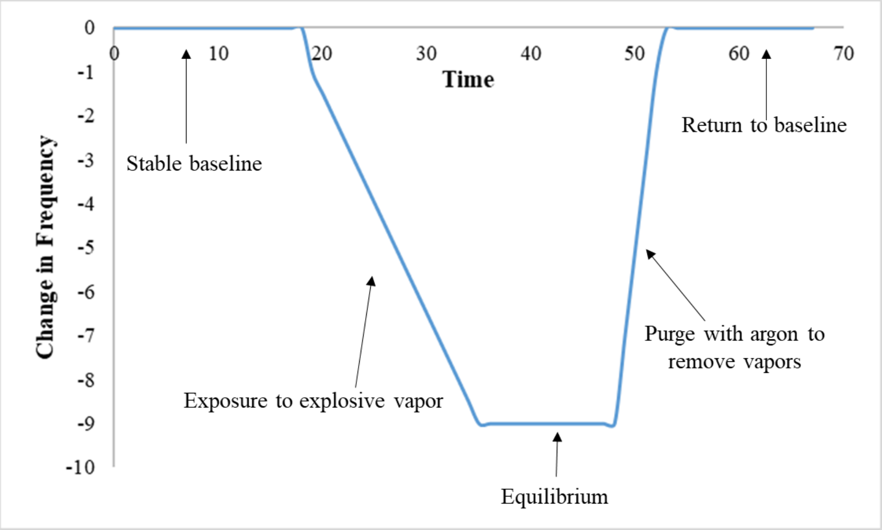

Figure 4. Example of an ideal sensorgram from establishing the initial baseline, to exposure to explosive vapor, and finally to purging the system with argon to remove explosive vapors from sensor.

Measurment of ad(b)sorption by vapor sinks

To monitor ad(b)sorption of analyte vapor to the sensor coating materials, the sensor is inserted into the QCM-D mini chamber, exposed to analyte vapor at varying concentrations with a constant flow. Sensor responses are recorded as frequency versus time and plotted as change in frequency versus concentration. A change in frequency denotes adsorption of analyte vapor onto the sensor. The change in mass is calculated using Eq. 2 representing the amount of explosive vapor adsorbed onto the surface area of the sensor. Desorption of explosive vapors after purging with argon is denoted by the return of the resonance frequency to baseline; however, if this does not occur then it is indicative of a chemical reaction (e.g., absorption) between the sensor coating and the analyte vapor. Using Eq. 2 is used to calculate the mass of vapor remaining on the sensor, and the loss due to ad(b)sorption.

SIGNIFICANCE

The model developed by Jury et al. that measures the transport of explosives vapor from a buried landmine, does not account for adsorption of vapors to solids, such as sand/soil or packaging, without the presence of liquid, i.e., only explosive vapors adsorbing to wet soil was considered. The research described herein will provide fundamental knowledge of adsorption/desorption of explosive vapors in the presence of dry soil, sand, and plastic, which are necessary for the transport the model being developed by NRL's LCP&FD to investigate vapor transport of buried explosives. The small-scale QCM experiments discussed within this report will provide ground truth for the model being developed, and aid in an overall better understanding of how the odor from a buried IED and/or landmine travels. Ultimately, the data produced from the QCM experiments will provide knowledge of the proportion of vapor lost due to ad(b)sorption to the surrounding environment. The combination of modeling and small-scale experiments will aid in the development of new detection technology and help to identify current limitations in detection of buried explosives. Following these experiments, it will be possible to incorporate microbial degradation and moisture to gain more information on how these affect transport of explosive vapor through soil, sand, and plastic containment.

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