Wireless Hazard Badges to Detect Nerve-Agent Simulants

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Wireless Hazard Badges for Nerve Agent Simulants

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Abstract: Human exposure to hazardous chemicals can have adverse short- and long-term health effects. In this report, we have developed a single-use wearable hazard badge that dosimetrically detects diethylchlorophosphate (DCP), a model organophosphorus cholinesterase inhibitor simulant. In so doing, we have devised a new Chemically Actuated Resonant Device (CARD) architecture that simplifies device fabrication to a single step and unambiguously relates change in chemiresistance to a wireless CARD readout. To provide selective and readily manufacturable sensor elements for this platform, we developed an ionic liquid-mediated single walled carbon nanotube based chemidosimetric scheme capable of detecting DCP across a broad dynamic range with limits of detection of 28 parts-per-billion (ppb). Furthermore, we have established a relationship between CARD readout and exposure dose, which can be generalized for any dosimeter developed with this device architecture. The device’s practical utility is demonstrated wherein an 8-hour workday time weighted average equivalent exposure of 10 ppb DCP effects an irreversible change in smartphone readout. Finally, we show that the device is selective for DCP by screening against 8 commonly encountered interferent gases and vapors.

Human exposure to hazardous chemicals in the environment, in the workplace, or in military contexts remains a critical human health concern. Furthermore, recent and continued human exposure to hazardous chemicals in ‘everyday’ environments has prompted heightened interest in chemical monitoring by citizens.[1] Acute hazardous chemical exposure is known to cause adverse human health effects ranging from mild irritation to fatality; chronic offenses can lead to cancer, allergies, and other recurring symptoms.[2] Most toxic gases are not visually detectable and can be harmful at persistent exposures below the human olfaction threshold. At present, the ability to make personalized decisions based on an exposure history is not possible. The ability to quantify a chemical hazard dose in a temporally correlated fashion would enable real-time personalized risk assessment. (Figure 1a)

Real-time, personalized situational awareness remains impractical for all but the most specialized applications: existing technological solutions are largely limited to colorimetric reagent tests such as Dräger tubes,[3] various electronic nose technologies,[4] and scaled down spectroscopy-based methods.[5] These techniques’ principal limitations are either cost, reliability, sensitivity, ease-of-use, physical size, power requirements, or all of the above. As a result, personal chemical dosimeters have not been broadly implemented. To address this need, we have developed a low cost, user-friendly, passive, reliable chemical hazard badge that collects actionable health risk data that can be transmitted wirelessly to the cloud.

Our concept was to create wearable, single-use chemical hazard badges that can be scanned periodically throughout the day. Disposable hazard badges could come in ‘packs,’ wherein a fresh tag would be peeled off at the beginning of each time period. (b) Quantification of hazardous chemical ‘dose’ with a smartphone enables facile information collection to a centralized database, via the cloud. Standardized decisions can be informed by pre-defined protective action criteria levels associated with equivalent exposure time weighted average (EE TWA) hazardous chemical concentration, such as those defined for the chemical of this study: DCP.

We targeted diethyl chlorophosphate (DCP) in our development of a prototype chemical hazard dosimeter. DCP has been studied as a target analyte for chemical sensors mainly as a chemical warfare nerve agent (NA) simulant.[7] It is also a chemical analog of cholinesterase inhibiting organophosphate pesticides.[8] Due to the fact that cholinesterase inhibiting chemicals are present in both civilian and military contexts, we believe that a DCP hazard badge could find immediate application. For chemical hazards like DCP, time-weighted-average (TWA) permissible exposure limits (PEL) are the most relevant parameter in dictating the necessity and type of protective actions to be taken (Figure 1c).

We envisioned that a chemical hazard dosimeter would allow one to instaneously assess the TWA exposure based on temporally-correlated chemical dose information. For instance, the US Department of Energy has established protective action criteria’ (PAC) levels, based on ‘concentrations of airborne hazardous materials at which protective actions are needed’ for over 3,000 hazardous substances, including DCP.[9] Accordingly, hazard badges could be designed to activate at dosage levels that induce mild, transient health effects (PAC-1), irreversible or other serious health effects that could inhibit ability to further protect oneself.
(PAC-2), or life threatening health effects (PAC-3).[9] This prioritization system would enable real-time decision-making by displaying scenario-informed options on a smartphone. Furthermore, personal exposure information could be synchronized with a cloud database[6] to expose spatio-temporal trends[10] and enable emergency decision-making by a second party in the case of incapacitation of the hazard badge-wearer.

We have previously demonstrated that two-step conversion of NFC tags into Chemically Actuated Resonant Devices (CARDs) can enable semi-quantitative, selective detection of chemical gases with a smartphone.[11] However, ultra-trace (sub-par-per-million) sensing and dosimetric detection remain challenging with our initial designs. The ideal dosimetric sensing scheme is selective and irreversible for a compound of interest, with pseudo-first order kinetics across a large dynamic range, such that accurate assessments can be made at both low- and high-dose exposures.[12] To address these challenges we report herein key improvements to both the circuit design as well as new single walled carbon nanotube (SWCNT)-based chemiresistive dosimetric materials. These improvements will have general implications in the broader context of wirelessly addressable sensor design.

We began our study by revisiting our first generation CARD platform (series-CARD, or s-CARD). In this system, the chemiresistor \( R_i \) is incorporated in series with the NFC integrated circuit (IC) in a two-step method. This method involves the disruption and reconnection of the circuit (Figure 2a). The raw chemical information that the chemiresistor collects is converted and wirelessly transmitted, mainly in the form of device resonant frequency \( f_r \) amplitude, gain (in dB).

Although the s-CARD proved successful in selectively detecting a chemically-diverse analytes at parts-per-million (ppm) levels, we noticed that its circuit structure could introduce physical constraints to the response magnitude corresponding to a certain change in the sensor resistance \( \Delta R_s \). We have systematically examined the gain readout of a series of s-CARDs with fixed resistors \( R_s \) in place of the chemiresistors. These resistors ranged from 100 \( \Omega \) to 100 k\( \Omega \), which encompassed the typical dynamic range of our CNT-based chemiresistors (1 k\( \Omega \) to 100 k\( \Omega \)). As shown in Figure 2b-1, the device resonated in all cases, and a non-monotonic change in the gain readout was observed as \( R_s \) increased (Figure 2b-1, inset). This resulted in a minimal gain difference observed between \( R_s = 1 \) k\( \Omega \) and 10 k\( \Omega \). More importantly, the non-monotonicity leads to ambiguous results when the device is operating within a large dynamic gain range.

Based on an analysis of the relative circuit component influence on overall circuit behavior, we hypothesized that the incorporation of the chemiresistor in parallel with the integrated circuit would serve to overcome these drawbacks associated with s-CARDs. Such a modification process produced a new type of CARD platform: parallel-CARD, or p-CARD. For a proof of concept, parallel fixed resistors ranging from 100 \( \Omega \) to 100 k\( \Omega \) were used to construct a p-CARDs and determine gain readouts. As shown in Figure 2b-ii, as \( R_s \) increased, the device underwent a monotonic decrease in gain and proceeded from non-resonant to resonant. The gain-log\( R_i \) relationship was linear from 1 k\( \Omega \) through 100 k\( \Omega \) (Figure 2b-ii, inset). The unambiguous linear-responsive p-CARD is ideal for highly sensitive chemodosimeter development.

The importance of practicability in the fabrication procedure of a new device structure should not be understated. In this regard, the p-CARD design is advantageous; it does not require disruption of the existing RFID circuit and is a single step to fabricate. The p-CARD is created by simple deposition of chemiresistive material to create resistance between the leads connecting the IC (Figure 2a). This non-disruptive modification method not only results in more consistent device performance but also makes p-CARDs amenable to inkjet printing and roll-to-roll manufacturing processes.[13]

With p-CARD platform in hand, we turned out attention to the development of a highly sensitive DCP-responsive dosimetric SWCNT chemiresistor[14] based on the irreversible hydrolysis of DCP.[15] To enhance the response by accelerating hydrolysis, we targeted SWCNTs in ionic liquids.[16] In addition to creating solution-phase reactivity at the SWCNT surface, ionic liquids have intrinsically low vapor pressures, making them amenable to vacuum-removal of co-solvents after dropcasting. Furthermore, ionic liquids (IL) have been shown to partially debundle SWCNTs when the two components are ground together in the solid state or when a mixture of SWCNTs and IL are sonicated together in the presence of co-solvents.[17] Despite these advantages, SWCNT/ILs are not an established chemiresistor platform.[18]

We initially tested the response of p-CARDs fabricated with SWCNT/IL composites to DCP in nitrogen (N2). We found that a combination of SWCNT and 1-butyl-3-methylimidazolium chloride (BMIMCl) showed a good, irreversible response. Previous work in our laboratory has shown that small molecule selectors incorporated into chemiresistor formulations can selectively enhance the resistive response to gas analytes.[19] By incorporating 2-(2-hydroxy-
1,1,3,3,3-hexa-fluoropropyl)-1-naphthol (HFIPN) as a hydrogen-bonding chelator/catalyst into the mixture, a 3.3x improvement in response to DCP was demonstrated (Figure 3a).

![Figure 3.](image_url) (a) When exposed to DCP (1 ppm) for 50 seconds, p-CARDs fabricated with HFIPN (blue bar, left) had a 3.3x larger magnitude of response than those fabricated without HFIPN (red bar, right). (b) Magnitude of response ($\Delta$Gain) as a function of device ‘age.’ Blue squares represent different devices. Optimized system (chemdraw inset). (c) SEM image of a typical SWCNT-wrapped microcrystal. Scale bar = 1 $\mu$m.

The significant response and irreversible enhancement associated with the BMIMCl/HFIPN-based chemiresistor was consistent with observed hydrolysis kinetics of DCP in solution (Scheme 1). We found that at r.t., DCP undergoes only minor hydrolysis after stirring in CD$_3$CN for 10 min, even in the presence of excess water (8 equiv.) as monitored by $^{31}$P NMR (Scheme 1, conditions ii: DCP: H$_2$O $\sim$ 4.8 ppm). In contrast, when DCP was added to a mixture of HFIPN and BMIMCl (a minimal amount of CD$_3$CN was added to obtain a liquid mixture) in the absence of any additional water, instantaneous hydrolysis occurred with the trace water present when operating under ambient atmosphere (conditions i). Specifically, a significant portion was hydrolyzed within a few seconds, indicated by the emerging signal of diethylphosphoric acid at $\delta$ ~ 0.5 ppm. Nearly full conversion was observed within 10 min. This rate acceleration in solution phase is well translated in the actual gas sensing process, leading to a large response magnitude.

![Scheme 1.](image_url) $^{31}$P NMR kinetics study of DCP hydrolysis.

Upon a more thorough investigation, we observed that there was a maturing process with the SWCNT/BMIMCl system, accompanied by two coinciding observations: 1) p-CARD baseline (gain) drift was effectively zero and 2) the magnitude of the response to DCP increased substantially as a function of time, reaching a maximum after $\sim$18 h (Figure 3b). Visual inspection and optical microscopy confirm time-dependent crystallization of BMIMCl at the surface of p-CARD (Figure S7). Scanning electron microscopy (SEM) revealed the formation of SWCNT-wrapped microcrystal structures (Figure 3c). We hypothesized that such structures could increase SWCNT surface area and thus lead to an enhanced response. This is consistent with our observation that p-CARDs fabricated with 1-butyl-3-methylimidazolium type ILs that are liquids at room temperature (anion = hexafluorophosphate, bromide, or iodide) did not demonstrate this behavior. Recent reports suggest solid-phase ILs hold promise for a tunable class of materials for a broad array of applications.

With the optimized system in hand, we next evaluated its performance toward various concentrations of DCP. We fabricated a series of p-CARDs that incorporated the BMIMCl/HFIPN/SWCNT-based chemiresistor. The individual device was exposed to a nitrogen flow for 100 s followed by DCP vapor until its gain readout reached saturation. The results are summarized in Figure 4a.

![Figure 4.](image_url) p-CARD DCP dosimeter performance with varying DCP concentrations: (a) Saturation plots. DCP exposure started at 100s. The
results are the averages of multiple individual devices tested \((X = 5, \text{except for PDCD} = 28 \text{ ppb where } X = 3 \text{ (inset)})\). Shaded areas indicate standard deviations. (b) Relative resistance change per minute. The upper inset shows the zoom-in for \([\text{DCP}] = 28 \text{ ppb}. \) The lower inset shows the exposure dose-normalized response determined for \(p\text{-CARDs at each concentration tested.}

Consistent magnitudes of saturation response were observed \((\Delta \text{Gain} = -1.9 \text{ dB, or } \Delta R/R_0 \sim 1400\%)\) when DCP concentration was larger than 100 parts-per-billion (ppb), while a slightly diminished overall change in gain was obtained with 28 ppb DCP \((\Delta \text{Gain} = -1.5 \text{ dB})\). From the linear region of the saturation plots, we were able to extract the relative sensor resistance change per minute as a benchmark for detection sensitivity evaluation (Figure 4b). It was found that \(R_0\) increased by over 60% after exposure to 2.4 ppm DCP for only 1 min. This high sensitivity and fast response kinetics allowed the detection of DCP at a concentration as low as 28 ppb, at a practical time scale \((0.4\%/\text{min})\).

A true test of a dosimeter is based on the response behavior across all combinations of time and concentration. Ideally the response of a dosimeter is proportional to the exposure dose, the product of analyte concentration, and exposure time \(([\text{analyte}] \cdot t)\). Simply put, a dosimeter that is exposed to a high concentration of analyte for a short time should have the same response as a dosimeter exposed to a low concentration of chemical hazard for a long time, as long as the same exposure dose is reached. It was determined across three orders of concentration magnitude that the exposure dose-normalized response (gain) of all \(p\text{-CARDs tested fell within a relatively narrow range (Figure 4b, right inset), indicating concentration-independent dosimetry of our optimized system. By taking the average exposure dose normalized response, the exposure dose dependent relationship to the change in gain of a \(p\text{-CARD can be empirically derived as:}

\[
\Delta \text{Gain} = A \int_{0}^{t} [\text{DCP}] \, dt
\]

Where \(A = -(2.5 \pm 1.2) \times 10^{-4} \text{ dB-ppb}^{-1} \text{ min}^{-1}\) and \(t\) is in minutes. This key relationship thus enables unambiguous equivalent exposure assessments based on the relative change in gain. Furthermore, when combined with knowledge of the power-threshold of binary \(p\text{-CARDs, pre-programmed} \ p\text{-CARDs that switch on and off after passing a pre-defined equivalent exposure threshold can be easily and predictably fabricated.}

Next, the \(\text{NA simulant-triggered smartphone binary switch of this system was demonstrated by a periodical exposure experiment wherein a \(p\text{-CARD was repeatedly exposed to DCP vapor (2 ppm) for 50 s followed by 170 s} \text{N}_2 \text{(Figure 5a). The device was designed to switch on when it had exceeded a PAC-1 threshold. Accordingly, with knowledge that the smartphone’s on/off threshold occurred at gain = 0.225 dB. It was unreadable by the smartphone (“off” state, indicated by green dots). The corresponding frequency-gain plot of this device \((t = 0 \text{ s})\) was nearly flat, illustrating poor device resonance within the NFC reader’s working frequency region (Figure 5b).}

As the device was subjected to the DCP exposure cycle repeatedly: 1) consistent irreversible gain readout decrease \((\text{R increase})\) was observed in every cycle, as showcased by the staircase-shape plot; 2) the amplitude of the resonance of the device increased, as indicated by the increasing depth of the minima in the frequency-gain plot; 3) After 3 cycles, corresponding to a PAC-1 TWA of 10 ppb, the device’s resonance amplitude exceeded the readability threshold and became readable by the smartphone \((\text{state “on”, indicated by red dots). [23]}

When it comes to in-field chemical hazard sensing, the sensor selectivity to the target analyte over commonly encountered interferent chemicals is critical for minimizing the occurrence of false alarms. Toward this end, a series of potential interferent chemicals that are relevant to in-field sensing environment were evaluated at elevated concentrations. Overall, the responses (AGain/\(\Delta t\)) of our \(p\text{-CARD DCP dosimeter toward NA simulants (DCP and diisopropyl fluorophosphate, DFP) at ppb or low-ppm level were at least one order of magnitude larger than those resulted from the highly concentrated vapors (100 ppm ~ 1000 ppm) of the

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Figure 5. \(p\text{-CARD DCP PAC-1 dosimeter. (a) A \(p\text{-CARD's gain (left axis, blue points) was measured while it was iteratively exposed to DCP (2 ppm in N}_2\text{(shaded bars). The equivalent exposure TWA (right axis, blue line) was calculated, and the \(p\text{-CARD was addressed with a smartphone once per cycle. Below the PAC-1 threshold, \(p\text{-CARD is unreadable, corresponding to ‘safe’ (green dots). Above the PAC-1 threshold, the \(p\text{-CARD becomes readable, corresponding to ‘dangerous’ (red dots). (b) \(p\text{-CARD radio frequency reflection spectra (S}_2\text{) measured as a function of DCP exposure, corresponding with (a).}

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interferents studied (Figure 6a). This good selectivity can be better characterized by the exposure dose-normalized responses (Figure 6b). Among the interferents tested, ketone, ester, or hydroxyl functional group containing compounds afforded detectable sensor resistance increase, presumably via hydrogen-bonding. Hydrocarbon/halogenated hydrocarbons were essentially inert to the sensor.[24] Dimethyl methylphosphonate (DMMP), a hydrogen-bond accepting NA simulant that does not react covalently under these conditions, showed a much smaller response than DCP and DFP at comparable concentrations, which is consistent with the irreversible hydrolysis proposed for the response to DCP and DFP. Additionally these other vapors do not give dosimetric responses and will likely have no effect on the determination of integrated DCP or DFP exposures.

![Figure 6](image-url)

**Figure 6.** Selectivity of p-CARD DCP dosimeter towards interferents. Change in p-CARD gain as a function of (a) exposure time (min) and (b) exposure dose (min·ppm).

In conclusion, we have developed a highly sensitive and selective disposable wireless dosimetric chemical hazard badge that can reliably detect NA simulants down to 28 ppb. This was enabled by 1) the invention of a new wirelessly addressable sensor platform, p-CARD, derived from commercial NFC tags in a single step, and 2) the identification of an SWCNT-ionic liquid-based chemiresistor that responds to the target analyte through instantaneous irreversible reactions. This badge allows the quantification of chemical hazard dose in a temporally correlated fashion and transmission of that information wirelessly, which has been demonstrated by the smartphone readability switch upon repeated exposures. The consistent dosimetric behavior of this system enables real-time hazard assessment that is relevant to widely employed chemical hazard regulation standards. We believe this system will find use in a variety of real-world cases, and the methodologies we have developed will facilitate the future evolution of wireless chemical sensors.

**Acknowledgements**

The authors would like to acknowledge the financial support of the Chemical and Biological Technologies Department at the Defense Threat Reduction Agency DTRA—CB via Grant BA12PHM123 in the “Dynamic Multifunctional Materials for a Second Skin D[MS]2” program and the Army Research Office through the institute for Soldier Nanotechnologies. We thank Marshall Craft (MIT) for building our VNA trace analysis LabView program and assisting in 3D printing of a gas sensing enclosure, Dr. Steven Koo for assisting in 3D printing of a gas sensing enclosure, Dr. Fei Yan (MIT) for discussion, and Vera Schroeder (MIT) for 3D graphic design.

**Keywords:** Wireless • Sensing • Dosimeter • Carbon Nanotubes • Ionic Liquid


[22] While we demonstrated the binary switch with the commercial NFC tags that have a threshold around -0.2 dB, we also devised a simple method to customize this parameter, which is described in the supporting information.


[24] We noted that ammonia vapor led to sensor resistance decrease, which is likely due to a deprotonation process.
We have developed a single-use, wirelessly addressable highly sensitive and selective chemical hazard badge that dosimetrically detects diethyl chlorophosphate, a nerve agent simulant, down to 28 parts-per-billion (ppb). This is enabled by the invention of a new wireless sensor platform design and a single walled carbon nanotube/ionic liquid-based chemidosimeter system. The device’s practical utility is demonstrated wherein a time weighted average (8 h) equivalent exposure of 10 ppb DCP effects an irreversible switch in smartphone readout.

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