An electroanalytical methodology to detect explosive residues using a gelled ionic liquid based field-deployable device

Catherine E. Hay, Junqiao Lee, and Debbie S. Silvester

Curtin Institute for Functional Molecules and Interfaces, School of Molecular and Life Sciences, Curtin University, GPO Box U1987, Perth, 6845, WA, Australia

* DSS Correspondence: d.silvester-dean@curtin.edu.au; Tel.: +61-8-9266-7148

* JL Correspondence: junqiaolee81@gmail.com

Abstract

A simple and robust, low-cost device is proposed for the combined sampling and detection of the trace solid explosive 2,4,6-trinitrotoluene (TNT) from a non-porous surface. Four different substrates were investigated to collect explosive residue – a bare thin-film electrode, glass microfiber filter paper, a gel-polymer electrolyte (GPE), and a GPE-filter paper composite. The GPE contained the hydrophobic room temperature ionic liquid (RTIL) trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)-imide ([P_{14,6,6,6}][NTf_2]) and the polymer poly(methyl methacrylate) (PMMA). A simple “swabbing” technique was used to sample explosive residue on all substrates. Square wave voltammetry was performed to determine the effects of oxygen and moisture on the current response. The most robust method for use in the field – a GPE drop-casted on a TFE – was applied in real environments using a hand-held portable potentiostat. The prototype device was able to detect TNT with a 30 minute development time in different ambient environmental conditions. The portability, ease of use and low-cost of the sensor device makes this a viable platform for the rapid onsite detection of explosives.

Keywords

Explosives; detection; sensing; 2,4,6-trinitrotoluene; TNT; electrochemistry; square wave voltammetry; planar device.
1. Introduction

Global terrorism is an increasing threat in today’s world, requiring the development of new techniques for the detection of explosives. Common explosive compounds include 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and other nitroaromatics. Such compounds are often used by terrorists as they can cause large amounts of damage but are relatively easy to prepare using procedures found on the internet and with commercially available chemicals. The prevention of terrorist activities relies upon fast, on-scene detection. Current detection methods include gas and liquid chromatography coupled with mass spectrometry [1, 2], ion mass spectrometry [3], Raman spectroscopy [4], spectrophotometry [5], and electrogenerated chemiluminescence [6]. Many of these detection techniques require specialist equipment, which can be expensive to acquire. Additionally, many techniques are not easily portable, leading to lengthy delays in analysis due to the requirement of evidence collection, storage and transportation. Electrochemistry is emerging as an alternative detection method due to its low power requirements, ease of use and instrument portability [7, 8].

Electrochemical sensor devices are commercially available in small lightweight options, and offer a viable alternative to detect explosive compounds onsite with high specificity and sensitivity. [7, 9, 10] Low-cost, disposable electrodes, can be produced in bulk quantities, and software with a simple user-interface can be developed. Such systems require only very low volumes of solvent (e.g. microliters) to connect the electrodes, reducing the cost, equilibration time, and environmental footprint.

Room temperature ionic liquids (RTILs) are salts that are liquid at room temperature comprised of bulky cations and anions, and have been suggested as alternative non-volatile solvent/electrolyte systems for electrochemical experiments. [11] The redox behaviour of nitroaromatic explosives such as TNT in RTILs has been the subject of a number of recent studies. [12-16] Three distinct reduction signals were observed for TNT in eight RTILs using cyclic voltammetry (CV), corresponding to the reduction of each of the three nitro groups. [14] A one-electron reduction step followed by dimerization to form azo or azoxy compounds at higher concentrations, was proposed for the first reduction peak. [14] This is in contrast to the mechanism in aqueous solvents, where three successive six electron, six proton reduction peaks are observed (total of 18 e\(^-\) and 18 H\(^+\)). [17] The electrochemical behaviour of other nitroaromatics, such as 2,4-dinitrotoluene (DNT), has also been studied in RTILs, displaying two peaks and a similar one-electron reduction and dimerization behaviour for the first peak. [18]

Various groups have used electrochemical methods to detect explosive compounds dissolved in aqueous solutions. Wang et al. developed voltammetric sensors using disposable screen printed electrodes, showing a wide linear range and detection limit of 200 parts-per-billion (ppb) for TNT in phosphate buffer solution. [19] Microfabricated capillary electrophoresis chips have also been used for the detection of TNT in buffer solutions with determination provided in less than 130 s, and with detection limits ranging from 24 to 36 µg/L. [20] Yu et al. used a gel polymer electrolyte (hydrophobic polymer and RTIL mixture) for the direct sensing of TNT in water. [21] The unique ability of TNT to preconcentrate into the RTIL enabled the extraction of TNT from water into the gel through a liquid/liquid partitioning step. [6] It was observed that wet and dry samples showed different CV responses – since the reaction mechanism is altered in the presence of water – therefore, drying techniques needed to be employed for reliable signals. [22]

Explosive compounds have also been detected directly by dissolving in RTIL solvents. For example, Xiao et al. studied the effect of changing the RTIL structure to tailor the physiochemical properties to the redox processes of various explosives, resulting in discriminatory electrochemical sensing for different analytes. [23] RTILs have also been employed in a hybrid electrochemical colorimetric sensor to detect vapour phase TNT, DNT and picric acid with detection limits in the ppb range and with good selectivity. [6] Castro et al. recently used a graphite sheet as both the collecting device and working
electrode for the detection of TNT from bank notes, as well as bare and gloved hands.[24] Screen printed electrodes have been used as a collection and detection device, involving the mechanical transfer of trace solid onto the electrode.[25] These works both required the use of an aqueous-based electrolyte after the sampling step, and the resulting liquid handling reduced the robustness and field portability of the technique. To overcome this, a ‘Forensic Finger’ was developed by Bandokar et al. for the detection of gunshot residue (GSR) and DNT powder residues using screen printed electrodes and an ionogel electrolyte.[26] The technique offered integrated sampling and analysis using a spillless solvent, showing noteworthy sensitivity and selectivity towards GSR and DNT, and demonstrating the promise of such a robust system. It noted that TNT and other similar explosive molecules may degrade and undergo thermal-[27] and bio-[28] decomposition while being transported back to the lab, hence the ability to detect TNT directly in the field will be of significant benefit. Therefore, the development of techniques and materials for field sampling is highly crucial in forensic applications.

In the present work, we employ a low-cost commercially available thin-film electrode (TFE) as both a collection device and sensing surface for the detection of residual solid TNT. Different sampling substrates are tested, including a glass microfiber filter paper to provide a porous substrate to collect and concentrate trace amounts of explosives. Here, we introduce a new gelled electrolyte (methacrylate-polymer and phosphonium-RTIL) based swabbing material, employed as a spillless alternative to RTILs, as well as acting as a moderately ‘sticky’ surface to enhance sample collection efficiency. We also explored combining filter paper and the gelled electrolyte to form a composite material to improve the mechanical stability and robustness of the material, allowing the material to be used as a free-standing film. The effect of oxygen and moisture on the voltammetric response of the sensor is examined to understand the performance of these systems in the field, i.e. outside of ideal laboratory conditions. Finally, a promising field portable system using a handheld potentiostat and a low-cost sensor device is developed, showing clear responses under various atmospheric environments.

2. Experimental

2.1. Chemicals and Reagents

The RTIL trihexyltetradecylphosphonium bis(trifluoromethylsulfonylimide ([P$_{16,6,6,6}$][NTf$_2$]) was kindly donated by Prof. Chris Hardacre (University of Manchester, UK). Poly(methyl methacrylate) (PMMA) was obtained from Merck with average molecular weights ($M_w$) of ~3,000 g mol$^{-1}$, ~15,000 g mol$^{-1}$, and ~120,000 g mol$^{-1}$. Acetone (CHROMASOLV for HPLC, ≥99.9%, Merck) was used as a casting solvent for the gel polymer electrolyte. 2,4,6-Trinitrotoluene (TNT, 1000 μg mL$^{-1}$ in acetonitrile) was purchased from Cerillant Corporation (Round Rock, Texas, USA). Ultrapure water (resistance = 18.2 MΩ cm, prepared by an ultrapure laboratory water purification system from Millipore Pty Ltd, North Ryde, NSW, Australia) was used to rinse the electrodes. A 0.5 M stock solution of H$_2$SO$_4$ (prepared with ultrapure water and 95-98 % wt. H$_2$SO$_4$ from Ajax Finechem, WA, Australia) was used for activation of the thin-film electrodes. Oxygen (O$_2$, >99.5 %) and nitrogen (N$_2$, >99.9 %) gases were purchased from Coregas, WA, Australia. Glass microfiber filters (Whatman, Grade GF/C, Merck) were cut down to 3 mm squares to use as a “swab” to pick up explosive residue. Premium heavy-duty aluminium foil was purchased from Confoil (Victoria, Australia).

2.2. Instrumental

For laboratory-based electrochemical experiments, a PGSTAT101 Autolab potentiostat (Metrohm, Gladsvile, NSW, Australia) interfaced to a PC operating Nova 1.11 software was employed. For the outdoor experiments, a PalmSens4 potentiostat (PalmSens, Houten, The Netherlands), interfaced to
an Android tablet operating the PSTouch software, was used. The optimized parameters for square
wave voltammetry (SWV) experiments were: frequency of 25 Hz, amplitude of 25 mV, step potential
of 4 mV.[21] The temperature inside the laboratory was measured to be 22(±1) °C, and the
electrochemical cell was placed inside a custom-made aluminium Faraday cage. The temperature for
the outdoor experiments was measured at 36.0(±1) °C, and these experiments were open to the air,
i.e. not placed in a glass cell or in a Faraday cage.

For laboratory experiments in the presence of air and moisture, measurements were conducted in:
(a) dry air (6 % relative humidity, RH), passed through a regular air scrubber-filtration system supplied
by the laboratory, and (b) ambient air, at ~35 % RH. For experiments at ~85 % RH, highly humidified
air was generated by vigorously bubbling air through a container of water prior to feeding through the
environmental glass cell. A constant flow rate of 1000 standard cubic centimeters per minute (scm)
was used for all experiments. All ambient air studies were performed with no air flow through the
electrochemical cell (i.e. static conditions) to simulate a natural environment. Humidity
measurements were recorded using a humidity pen 800012 from SPER Scientific, Arizona, USA, with
a measurement range between 20-95 % RH. Oxygen gas was diluted with nitrogen using a gas mixing
system as described in detail previously.[29]

2.3. Preparation of Gel-Polymer Electrolyte Cocktail

Gel-polymer electrolyte cocktails (PMMA mixed with RTIL in acetone) were prepared using a similar
method as reported previously,[30] with mass ratios of 30, 40, 50 % \(m_{\text{pol}}/m_{\text{tot}}\) examined, where \(m_{\text{pol}}\)
is the mass of the polymer (in g) and \(m_{\text{tot}}\) is the total mass (polymer and RTIL, in g). A 40 %
\(m_{\text{pol}}/m_{\text{tot}}\) was chosen for all measurements due to the highest currents and fastest responses observed
from this mixture, while still maintaining the non-flowing property of a gel. Furthermore, different
ratios of casting solvent (acetone) were tested to observe response time changes compared to gel
thickness. Mass ratios of 40, 45 and 50 % \(m_{\text{acetone}}/m_{\text{tot}}\) were tested, and 45 % \(m_{\text{acetone}}/m_{\text{tot}}\) was chosen
for all measurements as it was found to be the most optimal (see section 2.4.3). To obtain a thin film
of GPE, 5 µL of the cocktail was drop-casted on the planar electrode device, resulting in a thickness of
37 ± 1 µm. Film thicknesses were characterised using a confocal microscope (WITec alpha300 series,
Ulm, Germany) by manually focusing at the base and top of the deposited GPEs with the 100 ×
magnification lenses. More than 10 measurements were taken at different spots above the working
electrode area, and the measured thicknesses were then averaged.

2.4. Electrochemical Experiments

2.4.1. Explosive Sampling Experiments

TFEs with gold working (disk-shaped, 1 mm diameter, corresponding to a surface area of 0.785 mm²),
reference, and counter electrodes were obtained from MicruX Technologies, Oviedo, Spain (ED-SE1-
Au). An electrode adaptor supplied by MicruX was employed to connect the TFE to the potentiostat.
All TFEs were electrochemically activated by performing at least 15 cyclic voltammetry (CV) cycles
between 1.1 V and -1.2 V at 1 V s⁻¹ in 10 µL of 0.5 M H₂SO₄, until the activation CVs converged. Once
activated, the TFE was removed from the adaptor, washed with ultrapure water, and dried under a
stream of nitrogen before use.

A “swabbing” method was employed using four different sampling substrates, as outlined in Figure 1.
For each sampling technique, 1 µL of explosive standard (TNT at 1000 µg mL⁻¹) was dropped onto
aluminium foil and the acetonitrile was allowed to evaporate to leave ca. 1 µg of trace solid explosive
spread over an approximately circular area (diameter = 1.5 cm).

The different substrates to collect the explosive were: (a) a bare TFE, placed face down onto the
sample, (b) a TFE covered with a GPE, placed face down in the sample, (c) a 3 mm square of filter paper
that is used to collect the sample, before attaching swab side down onto the electrode, and (d) a 3 mm
square of filter paper covered with GPE that is used to collect the sample, before attaching swab side
down onto the electrode (Figure 1). All substrates were pressed down onto the sample (the TNT
contaminated Al surface), and this is repeated again at least 4 times at different spots within the area
of contamination, to sample a wide area where the explosive residue was present. After swabbing,
2 μL of $[\text{P}_{14,6,6,6}][\text{NTf}_{2}]$ was drop cast onto the electrode in methods (a) and (c) in Figure 1 to provide
the electrolyte required for electrochemical sensing. For methods (b) and (d), the pre-made GPE or
GPE-soaked filter paper were used, which also serve as the electrolyte. All samples were then allowed
to purge under dry $\text{N}_2$ for at least 20 minutes for the laboratory-based experiments to remove oxygen
and moisture. The experiments performed in the open air are described in more detail below. Due to
the use of the gold quasi-reference electrode built into the TFE, the voltammetry scans were started
from the open circuit potential (OCP), as measured by the potentiostat. All voltammograms scans
collected in this study were scanned in the negative potential direction. The potential axes were then
manually shifted so that the OCP was at 0 V for presentation of results. Baseline correction was also
applied to the GPE samples by choosing a flat current section prior to the TNT peaks and subtracting
the extrapolated linear current.

**Figure 1**: Schematic of the four techniques used to collect residual solid explosive from foil using either the pure RTIL
$[\text{P}_{14,6,6,6}][\text{NTf}_{2}]$ or the GPE (40 % wt. PMMA and $[\text{P}_{14,6,6,6}][\text{NTf}_{2}]$), and with or without glass microfiber filter paper squares
(3 mm square).

2.4.2. Field Simulated Explosive Sensing Experiments
The most user-friendly and robust technique (b) was further explored in different environmental conditions. Three conditions were compared: ideal lab conditions (dry N\textsubscript{2} atmosphere at 1000 sccm), ambient lab conditions (22.3 °C, 39 % RH, no gas flow) and outside in a hot, dry environment in the Australian summer (36.0 °C, 21 % RH, no gas flow). The experimental set-up for the latter two conditions is shown in Figure 2. The sensor devices were prepared in the laboratory by drop casting 5 µL of the GPE cocktail onto the electrode, followed by drying under N\textsubscript{2} for 10 minutes to allow the casting solvent (acetone) to evaporate. For sensing in ambient conditions, the GPE-modified TFE was allowed to first equilibrate in the external environment for ~30 minutes before an “environmental blank” voltammogram was recorded. The TFE was then pressed and swabbed on residual TNT and left flat on the table for 30 minutes, to allow for partitioning of the explosive into the viscous GPE, before a detection voltammogram was recorded.

Figure 2: Photos showing the experimental set-up employed for sampling method b (GPE thin film on gold TFE) in ambient air. (a) Under normal lab conditions (22.3 °C, 39 % RH) and (b) under field-simulated conditions outside of the lab (36 °C, 21 % RH).

2.4.3. Influence of GPE thickness on the timescale for TNT detection

The thickness of the GPE dictates the length of time before a signal can be detected (i.e. development time, $T_{\text{dev}}$) because the TNT particles collected at the surface of the GPE need time to diffuse and reach the WE to be electrochemically detected. Different GPE thicknesses were investigated to optimise the $T_{\text{dev}}$ of the sensor, by diluting the polymer with different amounts of casting solvent before being drop-casted onto the TFE. It was found that the thinnest film tested – with 55 % $m_{\text{acetone}}/m_{\text{tot}}$ as a casting solvent and resulting in a thickness of $6.1 \pm 0.8 \mu m$ – gave a $T_{\text{dev}}$ of ca. 5 minutes. However, these samples gave a poor signal-to-noise ratio due to its low conductivity resulting in high resistance effects between the working and counter electrodes. Although this response time is ideal for field testing, the low currents would be susceptible to being swamped by electromagnetic noise if measurements are conducted outside of a Faraday cage. The thickest film of $37.1 \pm 1.1 \mu m$ using 40 % $m_{\text{acetone}}/m_{\text{tot}}$ resulted in a $T_{\text{dev}}$ of more than one hour. Since a more reasonable TNT peak current could be achieved at ca. 30 minutes whilst maintaining a good signal-to-noise ratio for the GPE with a thickness of $20.1 \pm 0.4 \mu m$ using 45 % $m_{\text{acetone}}/m_{\text{tot}}$, this system was thus selected for further field testing with a 30 minute $T_{\text{dev}}$.

2.5. Safety Considerations

Nitroaromatic compounds such as TNT are hazardous substances and should be handled by trained individuals inside a fume cupboard. A laboratory coat, enclosed shoes, safety glasses and Viton gloves should be worn, and hands should be properly washed with soapy water after handling. These
Compounds are shock sensitive and may detonate under high temperatures or pressures. It is essential to store and work with minimal amounts where possible, and avoid conditions that may lead to detonation at all times.
3. Results and Discussion

3.1. Collection of explosive residue from a non-porous surface

To detect trace solid explosives using electrochemical techniques, the material must first be collected and transported to the working electrode surface. For this, we used a simple “swabbing” technique (see experimental section for more details). Four different substrates were investigated as collection materials: (a) a bare gold thin-film electrode (TFE), (b) a RTIL-polymer GPE coated TFE, (c) a piece of glass microfibre filter paper, and (d) a glass microfibre filter paper-GPE composite. The different methods are shown in Figure 1, and are described in more detail in the experimental section.

Aluminium foil was used as a non-porous surface contaminated with a known amount of solid TNT residue, which enables the assessment of different collection substrates without the influence of different surfaces (e.g. clothing, plastics, metal); we plan to examine these in future work. The four techniques were designed for their ease of execution – straightforward, and requiring minimal preparation and training for personnel using the devices in the field.

The RTIL \(\text{[P}_{24,6,6,6}\text{]}\text{[NTf}_{2}\text{]}\) was chosen as the electrolyte due to its non-volatility and hydrophobicity, which is beneficial for the intended field applications of this work. It was used directly from the bottle and dropped on the electrode in methods (a) and (c), or mixed with a cheap, widely commercially available polymer – poly(methyl methacrylate) (PMMA) – to form a gel-polymer electrolyte (GPE) in methods (b) and (d) (see discussion later).

Glass microfiber filter paper was first investigated as a collection material. Its porosity was intended to act similar to that of existing fabric swabs – used currently for explosives detection in airports – as it can capture and trap large amounts of explosive material within the fibres. To test the uptake ability of the filter paper, a comparison between the filter paper-collected TNT sample and the bare electrode was made, with square wave voltammetry (SWV) used to analyse the current responses. SWV is a very sensitive technique, since non-Faradaic current is reduced due to the method of current sampling, which occurs at the end of the forward pulse and at the end of the backward pulse.\([31]\)

Figure 3 shows SWV for the reduction of TNT collected using the bare TFE as a swab (blue line) and the filter paper as a swab (red line), both using a droplet of the pure RTIL as the electrolyte. Three reduction peaks are present – labelled as peaks I, II and III – suggesting that TNT has been successfully transferred to the electrode and detected in both cases. We note that there was no obvious effect on the shape of the voltammetry caused by the presence of the glass filter paper in the pure RTIL. The bare TFE itself is, surprisingly, found to be quite effective in picking up the explosive particles, producing well-defined current responses. However, a three times higher current response is observed with the porous filter paper swab, suggesting that this is a more efficient method to collect explosive residue compared to the bare TFE. The fibrous and flexible nature of the filter paper may also allow the effective collection of explosive particles on uneven surfaces compared to the solid, hard, and flat surface of the bare TFE.

Also shown in Figure 3 is the current response expected for 100 % recovery – where the explosive standard in acetonitrile was drop-casted directly onto the TFE surface before applying the RTIL – showing a ca. 75 % recovery with the filter paper, and ca. 25 % recovery with the TFE. It is noted that there was a large variation in the current response for the bare TFE swab on multiple electrodes, indicating that the amount of solid adhered to the electrode surface is inconsistent with subsequent sampling. However, the difference was relatively small (\(\pm 12 \text{ % variance in current}\)) for the glass filter paper swab, suggesting a good reproducibility for this method. We also attempted to use conventional hardened ashless cellulose filter paper (Whatman, Grade 540, Merck), but found that the presence of the cellulose fibre led to additional peaks and reduced electrochemical windows in the absence of TNT.
Figure 3: Square wave voltammetry (SWV) on Au TFEs for the reduction of TNT recovered from aluminium foil by sampling with a bare TFE (blue line) and a 3 mm square of filter paper (red line). A standard reference solution (1 µL, 1 mg mL\(^{-1}\)) drop cast directly on the electrode is also shown (black line). All samples employed 2 µL of \([P_{14,6,6,6}][NTf_2]\) as the electrolyte on the planar electrode. The potential was corrected so that the OCP was at 0 V.

To make the sensor more robust for use in the field, a non-flowing gel-polymer electrolyte (polymer mixed with RTIL) was also used. The polymer acts as a gelling agent to increase viscosity and reduce flow of the RTIL, while the RTIL provides ionic conductivity; the gel itself can also be used as a collection material. Notably, this particular GPE mixture (PMMA with \([P_{14,6,6,6}][NTf_2]\)) has been explored in our previous work for the sensing of TNT in contaminated water samples.\[21\] A mixing ratio of 40% polymer : RTIL (by mass) was chosen for this work since it remained in a gelled state with no visible liquid flow. Different molecular weights of PMMA (\(M_w = 3,000, 15,000\) and 120,000 g mol\(^{-1}\)) were employed to observe the effect on the current signal and stability of the GPE film. Good signal-to-noise was achieved with a \(M_w\) of \(\sim3,000\) g mol\(^{-1}\), however when the TFE was gently pressed on the residual explosive, the “sticky” GPE adhered to the foil and some detached from the electrode. Conversely, when a \(M_w\) of 120,000 g mol\(^{-1}\) was used, signal-to-noise was poor and no TNT signals could be observed even after 3 hours, probably due to the long chain polymer hindering the partitioning of TNT in the gel.\[32\] An intermediate \(M_w\) of \(\sim15,000\) g mol\(^{-1}\) was chosen for this work because a response for TNT could be achieved within 30 minutes of sampling while no visible transfer of GPE to the foil occurred upon pressing.

In technique (b), the GPE-covered electrode device was simply turned upside down and swabbed on the sample, then placed flat (upright) on the bench. This method was found to be the most user-friendly as it involves direct sampling with the device, and does not require any sample preparation or solvent pipetting by the user, which may be inconvenient when employed in the field. In technique (d), the filter paper was first placed on the electrode and the GPE cocktail was drop-casted to leave a GPE-fibre composite. The composite was peeled off and used as a free-standing film to swab explosive material, then placed swipe-side down on the electrode to drastically reduce the \(T_{dev}\) for the users. However, poor conductivity was observed with the free-standing composite when it was placed back on the electrode due to insufficient re-adhesion of the film back onto the TFE. Therefore, 5 µL of acetone was drop cast to redissolve the GPE and provide better adhesion back to the electrode surface. This led to some variation in the results from different preparations and hence may not be the most ideal method for use in the field. The fibrous and flexible nature of the filter paper affords significant advantage when sampling uneven surfaces in contrast with the use of bare TFE. Furthermore, here, the malleable gel-like property of the GPE also allows particles on uneven surfaces to be picked up, while the sticky nature of the GPE ensures effective collection and retention of particles during swabbing.
3.2. Square Wave Voltammetry for TNT detection using different swabbing methods

Figure 4 shows SWV for the reduction of TNT using the four collection methods described in Figure 1. The black lines show the response in a dry nitrogen environment, revealing the three expected reduction peaks [14] for all methods, and the dashed lines show the blank response in the absence of TNT. We note that the definition of peaks II and III were observed to improve over time and with successive scans, and the scans shown (Figure 4) are when the voltammetry converged, typically after ca. 1.5 hours. The currents are much lower in the GPE (nA, nanoamp scale) (Figure 4a and 4c) compared to the pure RTIL (µA, microamp scale) (Figure 4b and 4d) – as expected due to the higher viscosity of the GPE – but regardless, the peaks in the GPE are clearly distinguishable from the blank. Compared to the neat RTIL, the shape of the peaks in the GPE are broader and less well defined (particularly peaks II and III in the GPE-fibre composite) – likely due to the higher viscosity and poorer conductivity of the GPE. Consistent with the results in Figure 3, the current for peak I is generally ~2.5 times higher in the GPE-Fibre composite compared to the GPE alone, again, suggesting that the GPE-fibre composite material is able to collect more explosive residue.

![Figure 4: Square wave voltammetry (SWV) on a gold thin film electrode (1 mm diameter) for the reduction of TNT collected via different techniques; (a) bare TFE with neat [P_{14,6,6,6}][NTf_2], (b) GPE (40 % wt. PMMA and [P_{14,6,6,6}][NTf_2]) film on TFE, (c) glass filter paper used as swab with neat [P_{14,6,6,6}][NTf_2] and (d) glass filter paper soaked in GPE used as swab. Each technique was exposed to the absence and presence of moisture in air or nitrogen.](image)

For TNT sensing in real environments, it is highly desirable if common impurities such as oxygen and moisture do not have a significant impact on the sensing signal. Figure 4 shows the response in different atmospheric environments, revealing how the current changes in the presence of air and moisture. The red line is the response in dry air (6 RH %), showing that peak I (the detection signal) is mostly unaffected compared to the dry N₂ environment. Peaks II and III are significantly larger in the presence of air for all collection methods, primarily due to the influence of oxygen reduction that overlaps with peaks II and III for TNT reduction, which is consistent with our previous observations.[16]
However, the response in ambient air (green line, 35 RH %) and wet air (blue line, 85 RH %) is more variable, affecting the current of peak I more significantly. Since the reaction mechanism changes from a one-electron reduction in RTILs [14] to a six-electron reduction in water [17], this is not unexpected. The current increase is ca. 2 times compared to dry air in the neat RTIL (Figure 4a) and the GPE (Figure 4b). However, the collection methods involving the glass fibre filter paper show a smaller influence of water, suggesting that the filter paper may – at least partially – inhibit water from reaching the electrode surface. Despite the difference in current in the presence of moisture, the shapes and positions of peak I are quite similar, and hence it is envisioned that these low-cost miniaturised sensors could be deployed as a preliminary “detector” in the field to identify surfaces where TNT is present, with its concentration later determined by other methods once the identified samples are transferred back in the lab. Provided the swabbing is carried out in a consistent manner, the relative currents from separate devices can qualitatively inform investigators about how the explosive residue is distributed around a crime scene.

3.3. Detection of TNT using the most robust sensor – method (b) – in field simulated environments

Upon evaluating the four different collection methods, it was determined that method (b) was the most user-friendly due to its simplicity and spill-less nature which allows it to be used in the field by personnel with minimal training. This method also gave reasonably good current responses towards TNT detection, despite the high resistance of the electrolyte. To investigate in more detail at how oxygen influences the current response, different concentrations of oxygen were added into the cell, and the voltammetry was recorded. Figure 5 shows the systematic increase in current for peaks II and III as oxygen is introduced into the cell, eventually merging into one large broad peak as the oxygen content becomes higher and dominates the TNT peaks. Of analytical interest is that peak 1 remains relatively unaffected by the presence of oxygen and hence may be used for the detection of TNT in solid samples in real air environments, as we will next demonstrate.

![Square wave voltammetry (SWV) on a gold thin film electrode (1 mm diameter) for the reduction of TNT collected using method (b), with the GPE (PMMA:[P14,6,6,6][NTf2]) drop-casted film on TFE used as swab. The graphs show the effect of addition of different concentrations of oxygen (0, 5, 10, 15, 20 % vol.) in the background environment. The dotted line shows the blank scan in the absence of TNT and at 0 % O2.](image)

To enable the detection of explosives directly at the scene, the sensor and instrumentation must be portable and able to provide a detection signal within a reasonably short period of time. Therefore, a hand-held potentiostat (from PalmSens, connected to an android tablet) was used in different atmospheric conditions to determine the field applicability of the detector. The experimental set-up is shown in Figure 2 for the experiments performed: (a) in the laboratory and (b) outside in a real
environment. The whole measurement set-up can be contained within a small carry case and easily moved between detection sites. Importantly, being carried out in a real environment, no gas or air flow was employed in these field-simulated experiments, thus negating the requirement to use a gas cylinder at the detection site. It was also noted that there were no issues with measuring low currents at the sub nanoamp level using the portable potentiostat.

Figure 6 shows SWV for TNT reduction in (a) ideal conditions in the laboratory under a stream of dry nitrogen, (b) ambient conditions in the laboratory using a portable hand-held potentiostat, and (c) ambient conditions in an outdoor environment using a portable hand-held potentiostat. The samples were left flat on the table for 30 minutes \( T_{\text{dev}} \) after swabbing the sample to allow the TNT to penetrate into the GPE and diffuse to the electrode. We note that longer \( T_{\text{dev}} \) resulted in higher currents – due to the partitioning and diffusion of more TNT particles through the GPE to reach the electrode surface – but that 30 minutes was chosen for practicality in the field.

Under ideal lab conditions (Figure 6a, 22 °C, 6 % RH, flowing N\(_2\) stream), peak I was clearly visible, indicating that TNT is detected. The signal was ca. 50 % smaller compared to Figure 5, because of the shorter (30 minute) \( T_{\text{dev}} \) employed. Using the portable potentiostat in ambient conditions (Figure 6b, 22 °C, 39 % RH), the background currents were slightly larger due to the presence of ambient atmospheric contaminants, therefore the voltammetry was background subtracted as shown in the inset to Figure 6b. The TNT detection signal was much broader compared to ideal lab conditions, possibly due to the additional background contaminants from the ambient air samples, and the peak current is ca. 40 % of that observed from the ideal lab experiments. The TNT response in the inset to Figure 6b shows a clear signal that indicates that TNT is present. Similar results were observed for the detection in ambient outdoor conditions (Figure 6c, 36 °C, 21 % RH), but the current was larger and more well defined compared to ambient lab conditions, likely due to the higher temperatures of the outside environment lowering the viscosity of the GPE and improving diffusion.[33] A more well-defined peak is obvious in the background-subtracted data (inset to Figure 6c) with a reasonably high current observed for TNT detection.

This technique shows a clear signal for a mass of 1 \( \mu \)g of TNT, spread over an area of ~2 cm diameter. A typical surface particulate sampling is ca. 100 \( \mu \)g in a fingerprint [34], so this is well within the required range for detection. We note that it is not possible to perform quantitative measurements using this methodology, since the method of collection results in different amounts of trace explosive adhering to the gel. However, repeat trials consistently showed an obvious reduction peak for TNT,
allowing for its qualitative identification. The current signal can then be converted to estimate the amount of solid TNT that partitioned in the gel.

On assessing the results from the hand-held potentiostat (PalmSens), we observed that the instrumentation performed just as well as a conventional bench-top potentiostat (Autolab). Overall, these results show that TNT can be detected using a simple swabbing method followed by a 30 minute $T_{dev}$. Although there is a large variation in signal due to a number of factors (amount of TNT collected, $T_{dev}$, temperature, humidity, etc.) that effectively limits the precise quantification of the explosive, we propose that this method can be employed as a simple preliminary test to detect and identify if, and where, TNT is present at the scene; the amount of explosive can then be quantified using other methods, if required. Future work plans to investigate the detection of TNT from real post-explosive examples in mixed analyte environments in collaboration with appropriate law enforcement agencies, and residue deposited on different substrates.

4. Conclusions

Four techniques were used to collect and detect TNT using a low-cost, miniaturised planar electrode device. Fibrous filter paper was found to be effective in the collection of higher amounts TNT residue at the electrode, improving the SWV current response. The response in dry, ambient and wet air environments was examined for all samples, revealing differences in current in the presence of air and moisture, but overall the peak shape remained the same. Out of the four methods tested, the thin-film electrode coated with a thin-layer of gel-polymer electrolyte was determined to be the most user-friendly for field-based detection. The GPE covered electrode was then employed in ambient environments using a portable potentiostat to assess its capabilities for the detection of TNT in the field. The sensor was able to collect and detect solid TNT with only a 30 minute development time, producing currents clearly distinguishable from the blank. The setup is robust, disposable, low-cost, highly portable, and convenient with simple sample preparation. The results demonstrate that our GPE/TFE system is a viable candidate for the onsite forensic detection of TNT in real environments.

Acknowledgements

DSS thanks the Australian Research Council for funding through a Future Fellowship (FT170100315). CEH acknowledges a scholarship from the Australian Government Research Training Program (RTP). The authors thank Prof. Christopher Hardacre for the kind donation of the tetraalkylphosphonium ionic liquid. The authors acknowledge the Curtin Institute for Functional Molecules and Interfaces (CIFMI) for financial assistance in purchasing the portable potentiostat.

Highlights

- A simple swabbing technique is used to collect residual solid explosives on a planar electrode device
- Four substrates were used as collection materials to enable transportation of TNT to the electrode surface for detection (138)
- An ionic liquid gel-polymer electrolyte on a gold thin-film electrode is suggested the most user-friendly platform
- Current signals for TNT were observed in ideal lab conditions, ambient lab conditions and outdoors in hot, dry conditions. (138)
References


15


