

1 An electroanalytical methodology to detect 2 explosive residues using a gelled ionic liquid based 3 field-deployable device

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9 Abstract

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

22 Keywords

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

25

26 1. Introduction

27 Global terrorism is an increasing threat in today's world, requiring the development of new techniques
28 for the detection of explosives. Common explosive compounds include 2,4,6-trinitrotoluene (TNT),
29 2,4-dinitrotoluene (DNT) and other nitroaromatics. Such compounds are often used by terrorists as
30 they can cause large amounts of damage but are relatively easy to prepare using procedures found on
31 the internet and with commercially available chemicals. The prevention of terrorist activities relies
32 upon fast, on-scene detection. Current detection methods include gas and liquid chromatography
33 coupled with mass spectrometry [1, 2], ion mass spectrometry [3], Raman spectroscopy [4],
34 spectrophotometry [5], and electrogenerated chemiluminescence [6]. Many of these detection
35 techniques require specialist equipment, which can be expensive to acquire. Additionally, many
36 techniques are not easily portable, leading to lengthy delays in analysis due to the requirement of
37 evidence collection, storage and transportation. Electrochemistry is emerging as an alternative
38 detection method due to its low power requirements, ease of use and instrument portability [7, 8].
39 Electrochemical sensor devices are commercially available in small lightweight options, and offer a
40 viable alternative to detect explosive compounds onsite with high specificity and sensitivity.[7, 9, 10]
41 Low-cost, disposable electrodes, can be produced in bulk quantities, and software with a simple user-
42 interface can be developed. Such systems require only very low volumes of solvent (e.g. microliters)
43 to connect the electrodes, reducing the cost, equilibration time, and environmental footprint.

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

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

67 Explosive compounds have also been detected directly by dissolving in RTIL solvents. For example,
68 Xiao et al. studied the effect of changing the RTIL structure to tailor the physiochemical properties to
69 the redox processes of various explosives, resulting in discriminatory electrochemical sensing for
70 different analytes.[23] RTILs have also been employed in a hybrid electrochemical colorimetric sensor
71 to detect vapour phase TNT, DNT and picric acid with detection limits in the ppb range and with good
72 selectivity.[6] Castro et al. recently used a graphite sheet as both the collecting device and working

73 electrode for the detection of TNT from bank notes, as well as bare and gloved hands.[24] Screen
74 printed electrodes have been used as a collection and detection device, involving the mechanical
75 transfer of trace solid onto the electrode.[25] These works both required the use of an aqueous-based
76 electrolyte after the sampling step, and the resulting liquid handling reduced the robustness and field
77 portability of the technique. To overcome this, a ‘Forensic Finger’ was developed by Bandokar et al.
78 for the detection of gunshot residue (GSR) and DNT powder residues using screen printed electrodes
79 and an ionogel electrolyte.[26] The technique offered integrated sampling and analysis using a spill-
80 less solvent, showing noteworthy sensitivity and selectivity towards GSR and DNT, and demonstrating
81 the promise of such a robust system. It noted that TNT and other similar explosive molecules may
82 degrade and undergo thermal-[27] and bio-[28] decomposition while being transported back to the
83 lab, hence the ability to detect TNT directly in the field will be of significant benefit. Therefore, the
84 development of techniques and materials for field sampling is highly crucial in forensic applications.

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

98

99 2. Experimental

100 2.1. Chemicals and Reagents

101 The RTIL trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P_{14,6,6,6}][NTf₂]) was kindly
102 donated by Prof. Chris Hardacre (University of Manchester, UK). Poly(methyl methacrylate) (PMMA)
103 was obtained from Merck with average molecular weights (M_w) of $\sim 3,000$ g mol⁻¹, $\sim 15,000$ g mol⁻¹, and
104 $\sim 120,000$ g mol⁻¹. Acetone (CHROMASOLV for HPLC, $\geq 99.9\%$, Merck) was used as a casting solvent for
105 the gel polymer electrolyte. 2,4,6-Trinitrotoluene (TNT, 1000 $\mu\text{g mL}^{-1}$ in acetonitrile) was purchased
106 from Cerillant Corporation (Round Rock, Texas, USA). Ultrapure water (resistance = 18.2 M Ω cm,
107 prepared by an ultrapure laboratory water purification system from Millipore Pty Ltd, North Ryde,
108 NSW, Australia) was used to rinse the electrodes. A 0.5 M stock solution of H₂SO₄ (prepared with
109 ultrapure water and 95-98 % wt. H₂SO₄ from Ajax Finechem, WA, Australia) was used for activation of
110 the thin-film electrodes. Oxygen (O₂, $>99.5\%$) and nitrogen (N₂, $>99.99\%$) gases were purchased from
111 Coregas, WA, Australia. Glass microfiber filters (Whatman, Grade GF/C, Merck) were cut down to 3
112 mm squares to use as a “swab” to pick up explosive residue. Premium heavy-duty aluminium foil was
113 purchased from Confoil (Victoria, Australia).

114 2.2. Instrumental

115 For laboratory-based electrochemical experiments, a PGSTAT101 Autolab potentiostat (Metrohm,
116 Gladsville, NSW, Australia) interfaced to a PC operating Nova 1.11 software was employed. For the
117 outdoor experiments, a PalmSens4 potentiostat (PalmSens, Houten, The Netherlands), interfaced to

118 an Android tablet operating the PSTouch software, was used. The optimized parameters for square
119 wave voltammetry (SWV) experiments were: frequency of 25 Hz, amplitude of 25 mV, step potential
120 of 4 mV.[21] The temperature inside the laboratory was measured to be 22(±1) °C, and the
121 electrochemical cell was placed inside a custom-made aluminium Faraday cage. The temperature for
122 the outdoor experiments was measured at 36.0(±1) °C, and these experiments were open to the air,
123 i.e. not placed in a glass cell or in a Faraday cage.

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

134 2.3. Preparation of Gel-Polymer Electrolyte Cocktail

135 Gel-polymer electrolyte cocktails (PMMA mixed with RTIL in acetone) were prepared using a similar
136 method as reported previously,[30] with mass ratios of 30, 40, 50 % $m_{\text{pol.}}/m_{\text{tot.}}$ examined, where $m_{\text{pol.}}$
137 is the mass of the polymer (in g) and $m_{\text{tot.}}$ is the total mass (polymer and RTIL, in g). A 40 %
138 $m_{\text{pol.}}/m_{\text{tot.}}$ was chosen for all measurements due to the highest currents and fastest responses observed
139 from this mixture, while still maintaining the non-flowing property of a gel. Furthermore, different
140 ratios of casting solvent (acetone) were tested to observe response time changes compared to gel
141 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
142 for all measurements as it was found to be the most optimal (see section 2.4.3). To obtain a thin film
143 of GPE, 5 μL of the cocktail was drop-casted on the planar electrode device, resulting in a thickness of
144 $37 \pm 1 \mu\text{m}$. Film thicknesses were characterised using a confocal microscope (WITec (alpha300 series),
145 Ulm, Germany) by manually focusing at the base and top of the deposited GPEs with the 100 \times
146 magnification lenses. More than 10 measurements were taken at different spots above the working
147 electrode area, and the measured thicknesses were then averaged.

148 2.4. Electrochemical Experiments

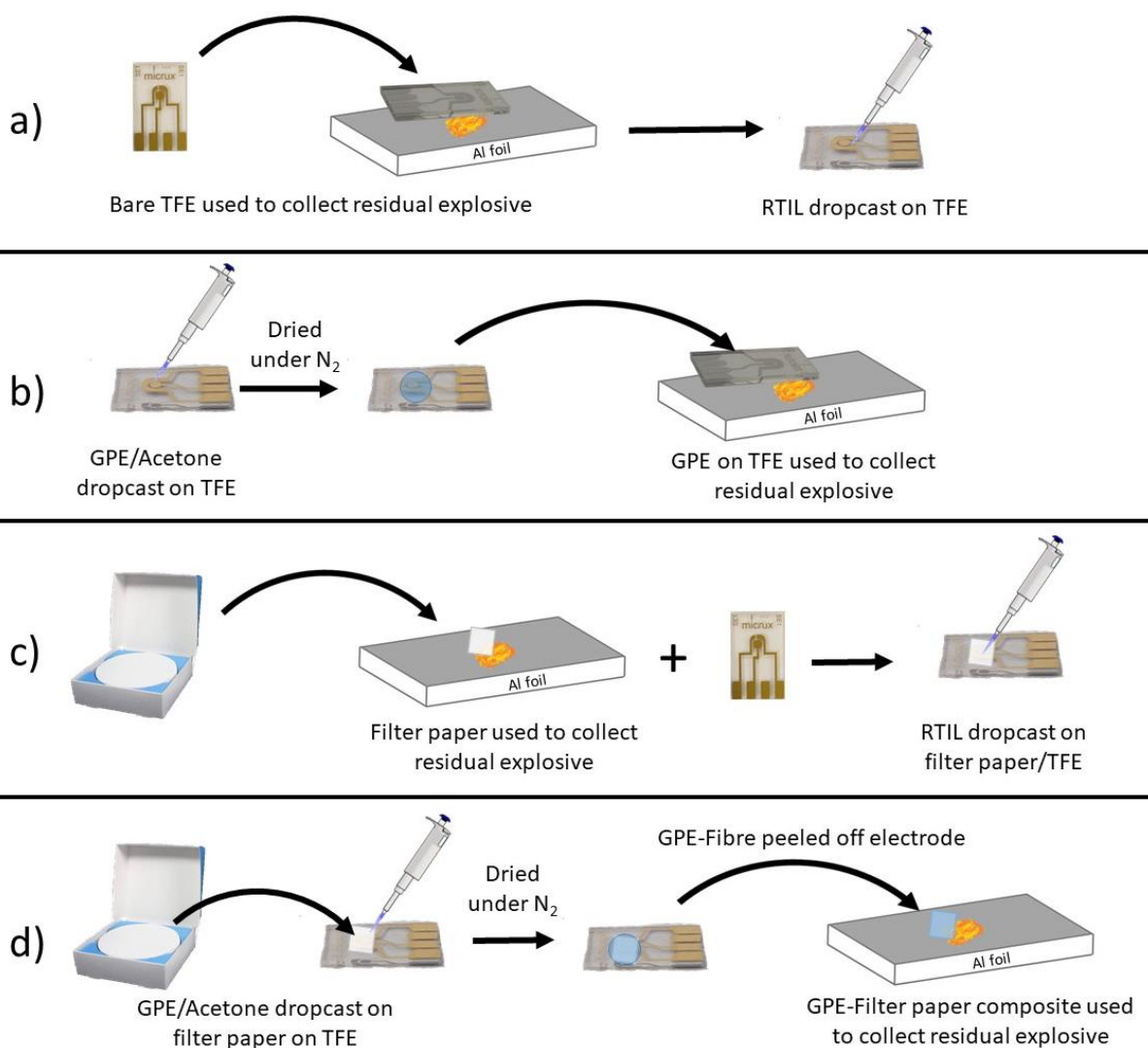
149 2.4.1. Explosive Sampling Experiments

150 TFEs with gold working (disk-shaped, 1 mm diameter, corresponding to a surface area of 0.785 mm²),
151 reference, and counter electrodes were obtained from MicruX Technologies, Oviedo, Spain (ED-SE1-
152 Au). An electrode adaptor supplied by MicruX was employed to connect the TFE to the potentiostat.
153 All TFEs were electrochemically activated by performing at least 15 cyclic voltammetry (CV) cycles
154 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
155 activated, the TFE was removed from the adaptor, washed with ultrapure water, and dried under a
156 stream of nitrogen before use.

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

161 The different substrates to collect the explosive were: (a) a bare TFE, placed face down onto the
162 sample, (b) a TFE covered with a GPE, placed face down in the sample, (c) a 3 mm square of filter paper
163 that is used to collect the sample, before attaching swab side down onto the electrode, and (d) a 3 mm

164 square of filter paper covered with GPE that is used to collect the sample, before attaching swab side
 165 down onto the electrode (Figure 1). All substrates were pressed down onto the sample (the TNT
 166 contaminated Al surface), and this is repeated again at least 4 times at different spots within the area
 167 of contamination, to sample a wide area where the explosive residue was present. After swabbing,
 168 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
 169 the electrolyte required for electrochemical sensing. For methods (b) and (d), the pre-made GPE or
 170 GPE-soaked filter paper were used, which also serve as the electrolyte. All samples were then allowed
 171 to purge under dry N_2 for at least 20 minutes for the laboratory-based experiments to remove oxygen
 172 and moisture. The experiments performed in the open air are described in more detail below. Due to
 173 the use of the gold quasi-reference electrode built into the TFE, the voltammetry scans were started
 174 from the open circuit potential (OCP), as measured by the potentiostat. All voltammetry scans
 175 collected in this study were scanned in the negative potential direction. The potential axes were then
 176 manually shifted so that the OCP was at 0 V for presentation of results. Baseline correction was also
 177 applied to the GPE samples by choosing a flat current section prior to the TNT peaks and subtracting
 178 the extrapolated linear current.



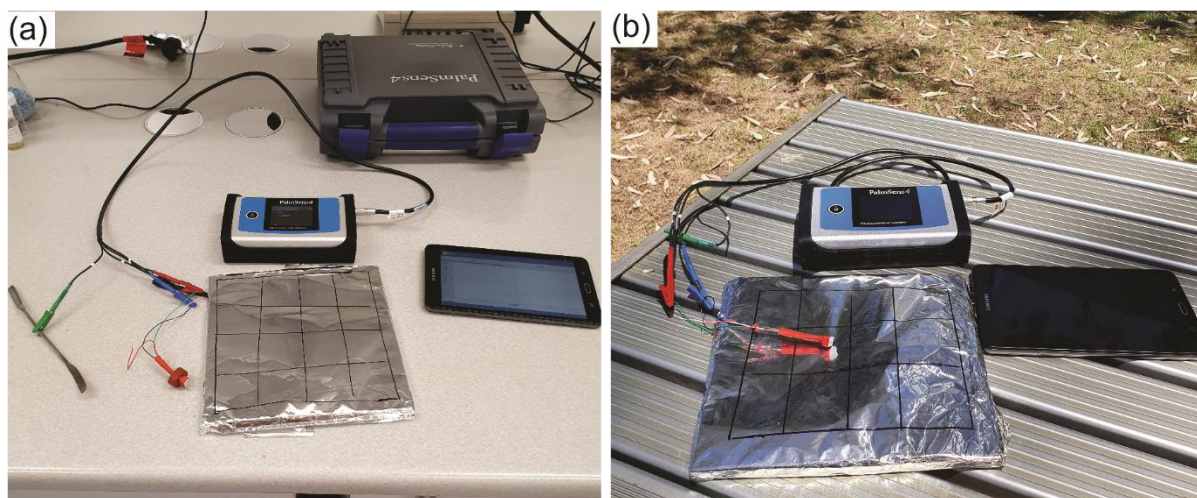
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180 *Figure 1: Schematic of the four techniques used to collect residual solid explosive from foil using either the pure RTIL*
 181 *$[\text{P}_{14,6,6,6}][\text{NTf}_2]$ or the GPE (40 % wt. PMMA and $[\text{P}_{14,6,6,6}][\text{NTf}_2]$), and with or without glass microfiber filter paper squares*
 182 *(3 mm square).*

183 **2.4.2. Field Simulated Explosive Sensing Experiments**

184 The most user-friendly and robust technique (b) was further explored in different environmental
185 conditions. Three conditions were compared: ideal lab conditions (dry N₂ atmosphere at 1000 sccm),
186 ambient lab conditions (22.3 °C, 39 % RH, no gas flow) and outside in a hot, dry environment in the
187 Australian summer (36.0 °C, 21 % RH, no gas flow). The experimental set-up for the latter two
188 conditions is shown in Figure 2. The sensor devices were prepared in the laboratory by drop casting
189 5 µL of the GPE cocktail onto the electrode, followed by drying under N₂ for 10 minutes to allow the
190 casting solvent (acetone) to evaporate. For sensing in ambient conditions, the GPE-modified TFE was
191 allowed to first equilibrate in the external environment for ~30 minutes before an “environmental
192 blank” voltammogram was recorded. The TFE was then pressed and swabbed on residual TNT and left
193 flat on the table for 30 minutes, to allow for partitioning of the explosive into the viscous GPE, before
194 a detection voltammogram was recorded.

195



196

197 *Figure 2: Photos showing the experimental set-up employed for sampling method b (GPE thin film on gold TFE) in ambient*
198 *air. (a) Under normal lab conditions (22.3 °C, 39 % RH) and (b) under field-simulated conditions outside of the lab (36 °C,*
199 *21 % RH).*

200 2.4.3. Influence of GPE thickness on the timescale for TNT detection

201 The thickness of the GPE dictates the length of time before a signal can be detected (i.e. development
202 time, T_{dev}) because the TNT particles collected at the surface of the GPE need time to diffuse and reach
203 the WE to be electrochemically detected. Different GPE thicknesses were investigated to optimise the
204 T_{dev} of the sensor, by diluting the polymer with different amounts of casting solvent before being drop-
205 casted onto the TFE. It was found that the thinnest film tested – with 55 % $m_{acetone}/m_{tot}$ as a casting
206 solvent and resulting in a thickness of $6.1 \pm 0.8 \mu\text{m}$ – gave a T_{dev} of ca. 5 minutes. However, these
207 samples gave a poor signal-to-noise ratio due to its low conductivity resulting in high resistance effects
208 between the working and counter electrodes. Although this response time is ideal for field testing, the
209 low currents would be susceptible to being swamped by electromagnetic noise if measurements are
210 conducted outside of a Faraday cage. The thickest film of $37.1 \pm 1.1 \mu\text{m}$ using 40 % $m_{acetone}/m_{tot}$
211 resulted in a T_{dev} of more than one hour. Since a more reasonable TNT peak current could be achieved
212 at ca. 30 minutes whilst maintaining a good signal-to-noise ratio for the GPE with a thickness of
213 $20.1 \pm 0.4 \mu\text{m}$ using 45 % $m_{acetone}/m_{tot}$, this system was thus selected for further field testing with a
214 30 minute T_{dev} .

215 2.5. Safety Considerations

216 Nitroaromatic compounds such as TNT are hazardous substances and should be handled by trained
217 individuals inside a fume cupboard. A laboratory coat, enclosed shoes, safety glasses and Viton gloves
218 should be worn, and hands should be properly washed with soapy water after handling. These

219 compounds are shock sensitive and may detonate under high temperatures or pressures. It is essential
220 to store and work with minimal amounts where possible, and avoid conditions that may lead to
221 detonation at all times.

222

223 3. Results and Discussion

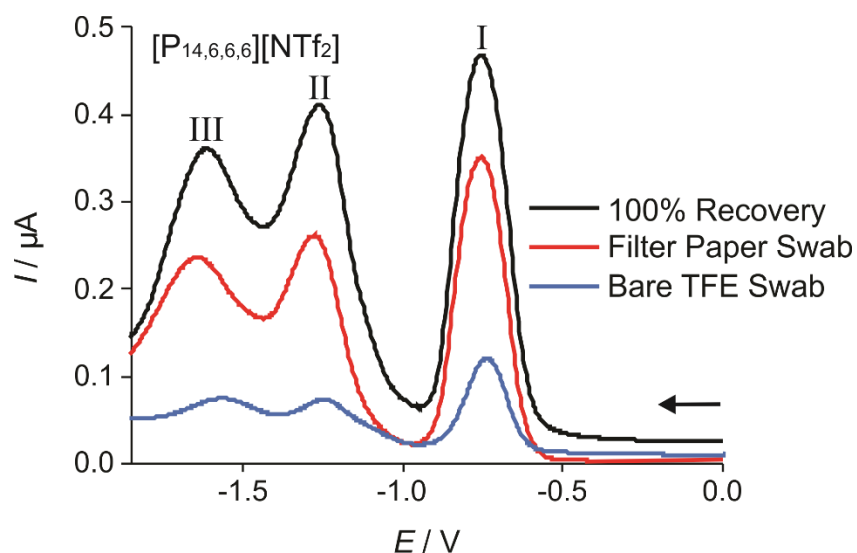
224 3.1. Collection of explosive residue from a non-porous surface

225 To detect trace solid explosives using electrochemical techniques, the material must first be collected
226 and transported to the working electrode surface. For this, we used a simple “swabbing” technique
227 (see experimental section for more details). Four different substrates were investigated as collection
228 materials: (a) a bare gold thin-film electrode (TFE), (b) a RTIL-polymer GPE coated TFE, (c) a piece of
229 glass microfibre filter paper, and (d) a glass microfibre filter paper-GPE composite. The different
230 methods are shown in Figure 1, and are described in more detail in the experimental section.
231 Aluminium foil was used as a non-porous surface contaminated with a known amount of solid TNT
232 residue, which enables the assessment of different collection substrates without the influence of
233 different surfaces (e.g. clothing, plastics, metal); we plan to examine these in future work. The four
234 techniques were designed for their ease of execution – straight forward, and requiring minimal
235 preparation and training for personnel using the devices in the field.

236 The RTIL [P_{14,6,6,6}][NTf₂] was chosen as the electrolyte due to its non-volatility and hydrophobicity,
237 which is beneficial for the intended field applications of this work. It was used directly from the bottle
238 and dropped on the electrode in methods (a) and (c), or mixed with a cheap, widely commercially
239 available polymer – poly(methyl methacrylate) (PMMA) – to form a gel-polymer electrolyte (GPE) in
240 methods (b) and (d) (see discussion later).

241 Glass microfibre filter paper was first investigated as a collection material. Its porosity was intended
242 to act similar to that of existing fabric swabs – used currently for explosives detection in airports – as
243 it can capture and trap large amounts of explosive material within the fibres. To test the uptake ability
244 of the filter paper, a comparison between the filter paper-collected TNT sample and the bare electrode
245 was made, with square wave voltammetry (SWV) used to analyse the current responses. SWV is a very
246 sensitive technique, since non-Faradaic current is reduced due to the method of current sampling,
247 which occurs at the end of the forward pulse and at the end of the backward pulse.[31] Figure 3 shows
248 SWV for the reduction of TNT collected using the bare TFE as a swab (blue line) and the filter paper as
249 a swab (red line), both using a droplet of the pure RTIL as the electrolyte. Three reduction peaks are
250 present – labelled as peaks I, II and III – suggesting that TNT has been successfully transferred to the
251 electrode and detected in both cases. We note that there was no obvious effect on the shape of the
252 voltammetry caused by the presence of the glass filter paper in the pure RTIL. The bare TFE itself is,
253 surprisingly, found to be quite effective in picking up the explosive particles, producing well-defined
254 current responses. However, a three times higher current response is observed with the porous filter
255 paper swab, suggesting that this is a more efficient method to collect explosive residue compared to
256 the bare TFE. The fibrous and flexible nature of the filter paper may also allow the effective collection
257 of explosive particles on uneven surfaces compared to the solid, hard, and flat surface of the bare TFE.

258 Also shown in Figure 3 is the current response expected for 100 % recovery – where the explosive
259 standard in acetonitrile was drop-casted directly onto the TFE surface before applying the RTIL –
260 showing a ca. 75 % recovery with the filter paper, and ca. 25 % recovery with the TFE. It is noted that
261 there was a large variation in the current response for the bare TFE swab on multiple electrodes,
262 indicating that the amount of solid adhered to the electrode surface is inconsistent with subsequent
263 sampling. However, the difference was relatively small (~12 % variance in current) for the glass filter
264 paper swab, suggesting a good reproducibility for this method. We also attempted to use conventional
265 hardened ashless cellulose filter paper (Whatman, Grade 540, Merck), but found that the presence of
266 the cellulose fibre led to additional peaks and reduced electrochemical windows in the absence of
267 TNT.



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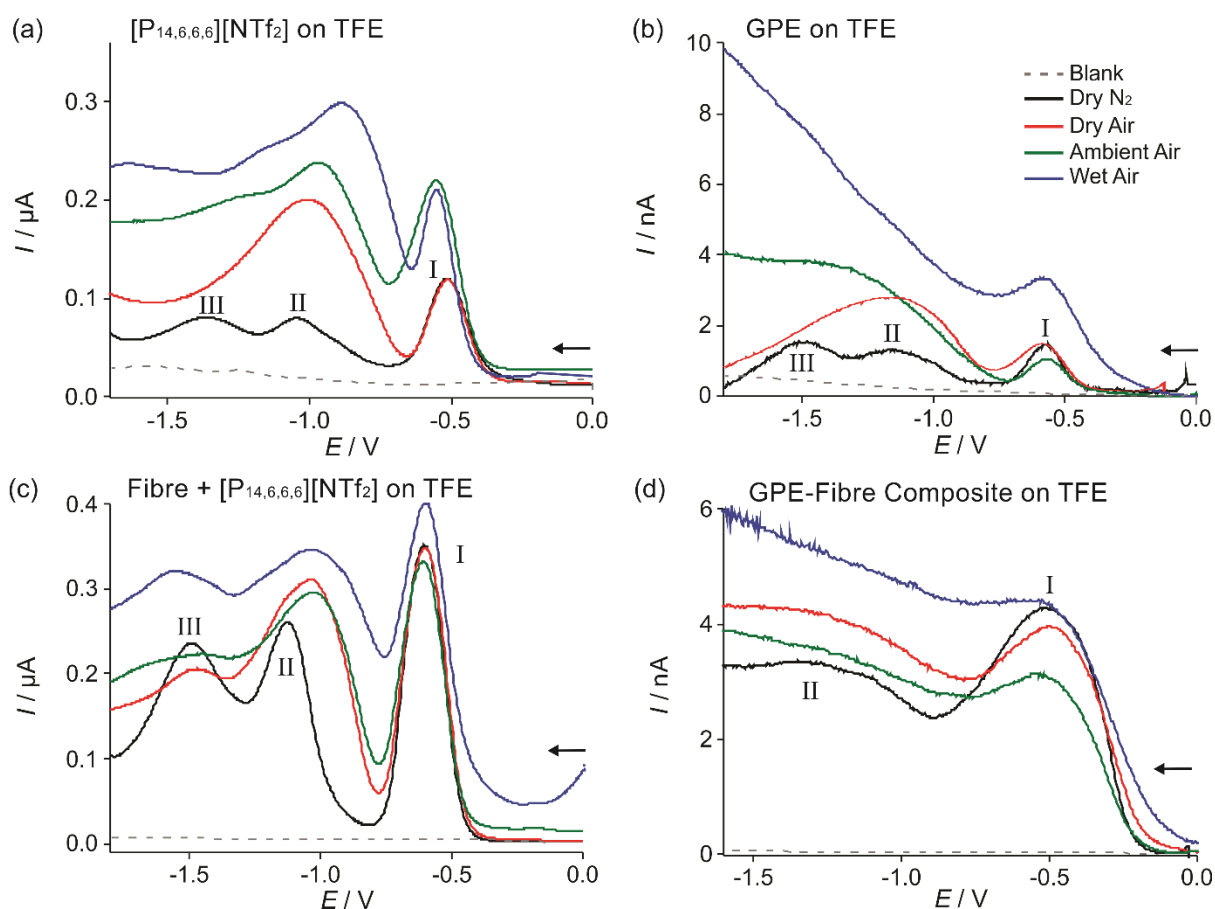
269 *Figure 3: Square wave voltammetry (SWV) on Au TFEs for the reduction of TNT recovered from aluminium foil by sampling*
 270 *with a bare TFE (blue line) and a 3 mm square of filter paper (red line). A standard reference solution (1 μL , 1 mg mL^{-1}) drop*
 271 *cast directly on the electrode is also shown (black line). All samples employed 2 μL of $[\text{P}_{14,6,6,6}][\text{NTf}_2]$ as the electrolyte on the*
 272 *planar electrode. The potential was corrected so that the OCP was at 0 V.*

273 To make the sensor more robust for use in the field, a non-flowing gel-polymer electrolyte (polymer
 274 mixed with RTIL) was also used. The polymer acts as a gelling agent to increase viscosity and reduce
 275 flow of the RTIL, while the RTIL provides ionic conductivity; the gel itself can also be used as a collection
 276 material. Notably, this particular GPE mixture (PMMA with $[\text{P}_{14,6,6,6}][\text{NTf}_2]$) has been explored in our
 277 previous work for the sensing of TNT in contaminated water samples.[21] A mixing ratio of
 278 40 % polymer : RTIL (by mass) was chosen for this work since it remained in a gelled state with no
 279 visible liquid flow. Different molecular weights of PMMA ($M_w = 3,000, 15,000$ and $120,000 \text{ g mol}^{-1}$)
 280 were employed to observe the effect on the current signal and stability of the GPE film. Good signal-
 281 to-noise was achieved with a M_w of $\sim 3,000 \text{ g mol}^{-1}$, however when the TFE was gently pressed on the
 282 residual explosive, the “sticky” GPE adhered to the foil and some detached from the electrode.
 283 Conversely, when a M_w of $120,000 \text{ g mol}^{-1}$ was used, signal-to-noise was poor and no TNT signals could
 284 be observed even after 3 hours, probably due to the long chain polymer hindering the partitioning of
 285 TNT in the gel.[32] An intermediate M_w of $\sim 15,000 \text{ g mol}^{-1}$ was chosen for this work because a response
 286 for TNT could be achieved within 30 minutes of sampling while no visible transfer of GPE to the foil
 287 occurred upon pressing.

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

304 3.2. Square Wave Voltammetry for TNT detection using different swabbing methods

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



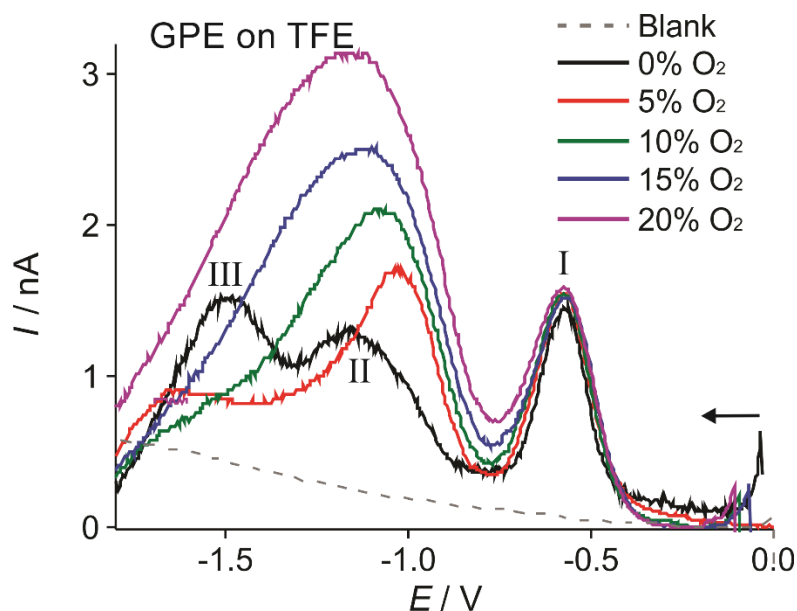
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 319 *Figure 4: Square wave voltammetry (SWV) on a gold thin film electrode (1 mm diameter) for the reduction of TNT collected*
 320 *via different techniques; (a) bare TFE with neat [P_{14,6,6,6}][NTf₂], (b) GPE (40 % wt. PMMA and [P_{14,6,6,6}][NTf₂]) film on TFE, (c)*
 321 *glass filter paper used as swab with neat [P_{14,6,6,6}][NTf₂] and (d) glass filter paper soaked in GPE used as swab. Each technique*
 322 *was exposed to the absence and presence of moisture in air or nitrogen.*

323 For TNT sensing in real environments, it is highly desirable if common impurities such as oxygen and
 324 moisture do not have a significant impact on the sensing signal. Figure 4 shows the response in
 325 different atmospheric environments, revealing how the current changes in the presence of air and
 326 moisture. The red line is the response in dry air (6 RH %), showing that peak I (the detection signal) is
 327 mostly unaffected compared to the dry N₂ environment. Peaks II and III are significantly larger in the
 328 presence of air for all collection methods, primarily due to the influence of oxygen reduction that
 329 overlaps with peaks II and III for TNT reduction, which is consistent with our previous observations.[16]

330 However, the response in ambient air (green line, 35 RH %) and wet air (blue line, 85 RH %) is more
 331 variable, affecting the current of peak I more significantly. Since the reaction mechanism changes from
 332 a one-electron reduction in RTILs [14] to a six-electron reduction in water [17], this is not unexpected.
 333 The current increase is ca. 2 times compared to dry air in the neat RTIL (Figure 4a) and the GPE (Figure
 334 4b). However, the collection methods involving the glass fibre filter paper show a smaller influence of
 335 water, suggesting that the filter paper may – at least partially – inhibit water from reaching the
 336 electrode surface. Despite the difference in current in the presence of moisture, the shapes and
 337 positions of peak I are quite similar, and hence it is envisioned that these low-cost miniaturised sensors
 338 could be deployed as a preliminary “detector” in the field to identify surfaces where TNT is present,
 339 with its concentration later determined by other methods once the identified samples are transferred
 340 back in the lab. Provided the swabbing is carried out in a consistent manner, the relative currents from
 341 separate devices can qualitatively inform investigators about how the explosive residue is distributed
 342 around a crime scene.

343 3.3. Detection of TNT using the most robust sensor – method (b) – in field simulated environments

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

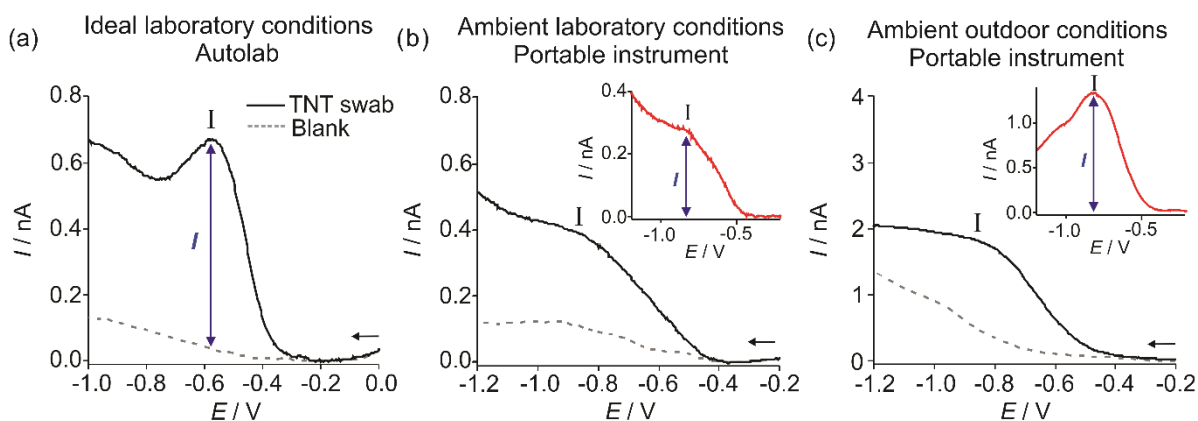


354
 355 *Figure 5: Square wave voltammetry (SWV) on a gold thin film electrode (1 mm diameter) for the reduction of TNT collected*
 356 *using method (b), with the GPE (PMMA:[P_{14,6,6}][NTf₂]) drop-casted film on TFE used as swab. The graphs show the effect of*
 357 *addition of different concentrations of oxygen (0, 5, 10, 15, 20 % vol.) in the background environment. The dotted line shows*
 358 *the blank scan in the absence of TNT and at 0% O₂.*

359 To enable the detection of explosives directly at the scene, the sensor and instrumentation must be
 360 portable and able to provide a detection signal within a reasonably short period of time. Therefore, a
 361 hand-held potentiostat (from PalmSens, connected to an android tablet) was used in different
 362 atmospheric conditions to determine the field applicability of the detector. The experimental set-up
 363 is shown in Figure 2 for the experiments performed: (a) in the laboratory and (b) outside in a real

364 environment. The whole measurement set-up can be contained within a small carry case and easily
365 moved between detection sites. Importantly, being carried out in a real environment, no gas or air
366 flow was employed in these field-simulated experiments, thus negating the requirement to use a gas
367 cylinder at the detection site. It was also noted that there were no issues with measuring low currents
368 at the sub nanoamp level using the portable potentiostat.

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



376

377 *Figure 6: Square wave voltammetry (SWV) obtained with a 30 minute “development time” on a gold thin film electrode (1 mm*
378 *diameter) for the reduction of TNT collected using GPE (40 % wt. PMMA and $[P_{14,6,6,6}][NTf_2]$) film on a TFE in different*
379 *environments: (a) inside the lab and purged under dry N_2 for 30 min (22 °C, 6 % RH) on a lab-based potentiostat, (b) inside*
380 *the lab and allowed to develop in ambient conditions (22 °C, 39 % RH) for 30 min with a portable potentiostat and (c) outside*
381 *the lab and allowed to develop in ambient conditions (36 °C, 21 % RH) with a portable potentiostat. The inset graphs show*
382 *the background subtracted voltammetry, with the peak current signal for TNT peak I indicated by the arrows.*

383 Under ideal lab conditions (Figure 6a, 22 °C, 6 % RH, flowing N_2 stream), peak I was clearly visible,
384 indicating that TNT is detected. The signal was ca. 50 % smaller compared to Figure 5, because of the
385 shorter (30 minute) T_{dev} employed. Using the portable potentiostat in ambient conditions (Figure 6b,
386 22 °C, 39 % RH), the background currents were slightly larger due to the presence of ambient
387 atmospheric contaminants, therefore the voltammetry was background subtracted as shown in the
388 inset to Figure 6b. The TNT detection signal was much broader compared to ideal lab conditions,
389 possibly due to the additional background contaminants from the ambient air samples, and the peak
390 current is ca. 40 % of that observed from the ideal lab experiments. The TNT response in the inset to
391 Figure 6b shows a clear signal that indicates that TNT is present. Similar results were observed for the
392 detection in ambient outdoor conditions (Figure 6c, 36 °C, 21 % RH), but the current was larger and
393 more well defined compared to ambient lab conditions, likely due to the higher temperatures of the
394 outside environment lowering the viscosity of the GPE and improving diffusion.[33] A more well-
395 defined peak is obvious in the background-subtracted data (inset to Figure 6c) with a reasonably high
396 current observed for TNT detection.

397 This technique shows a clear signal for a mass of 1 μ g of TNT, spread over an area of \sim 2 cm diameter.
398 A typical surface particulate sampling is ca. 100 μ g in a fingerprint [34], so this is well within the
399 required range for detection. We note that it is not possible to perform quantitative measurements
400 using this methodology, since the method of collection results in different amounts of trace explosive
401 adhering to the gel. However, repeat trials consistently showed an obvious reduction peak for TNT,

402 allowing for its qualitative identification. The current signal can then be converted to estimate the
403 amount of solid TNT that partitioned in the gel.

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

414 4. Conclusions

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

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433 Highlights

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

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