Differentiation among peroxide explosives with an optoelectronic nose†

Zheng Li, Will P. Bassett, Jon R. Askim and Kenneth S. Suslick*

Forensic identification of batches of homemade explosives (HME) poses a difficult analytical challenge. Differentiation among peroxide explosives is reported herein using a colorimetric sensor array and handheld scanner with a field-appropriate sampling protocol. Clear discrimination was demonstrated among twelve peroxide samples prepared from different reagents, with a classification accuracy > 98%.

There is an increasingly urgent need for rapid and highly selective detection of explosives, for both civilian and military security.1,2 The ready production of homemade explosives (HMEs) and improvised explosive devices (IEDs) has become an increasing problem. Forensic identification of the source of production of HMEs poses a difficult analytical challenge, especially for in-field evaluations. Peroxide explosives, most notably triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD), have not been extensively employed as mainstream military explosives due to their high sensitivity to impact, friction and static discharge.3–6 Their ease of synthesis (Scheme 1) and difficulty of detection, however, make them explosives of choice for terrorists: both TATP and HMTD can be prepared from readily available starting materials (i.e., hydrogen peroxide, an acid catalyst, and acetone for TATP or hexamethylene-tetramine for HMTD).7,8

Peroxide explosives such as TATP or HMTD are undetectable through direct fluorescent approaches (having no chromophores) and relatively difficult to detect by standard ion mobility spectrometers.9,10 As a consequence, a large number of detection methods for TATP or HMTD have been developed in the past few years, most of which demand complex instrumentation, including electrochemical,11,12 indirect fluorescence,6,13–16 and mass spectrometry.5,17–21 Examples of readily portable detection

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Scheme 1 Reactions for the synthesis of TATP and HMTD.
Table 1 Synthesis of TATP and HMTD: nine TATP and three HMTD formulations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reactants</th>
<th>Acid catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>TATP-1</td>
<td>(CH₃)₂CO + H₂O₂</td>
<td>HCl</td>
</tr>
<tr>
<td>TATP-2</td>
<td>(CH₃)₂CO + H₂O₂</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>TATP-3</td>
<td>(CH₃)₂CO + H₂O₂</td>
<td>HNO₃</td>
</tr>
<tr>
<td>TATP-4</td>
<td>(CH₃)₂CO + Na₂CO₃·1.5H₂O₂</td>
<td>HCl</td>
</tr>
<tr>
<td>TATP-5</td>
<td>(CH₃)₂CO + Na₂CO₃·1.5H₂O₂</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>TATP-6</td>
<td>(CH₃)₂CO + Na₂CO₃·1.5H₂O₂</td>
<td>HNO₃</td>
</tr>
<tr>
<td>TATP-7</td>
<td>(CH₃)₂CO + CO(NH₂)₂·H₂O₂</td>
<td>HCl</td>
</tr>
<tr>
<td>TATP-8</td>
<td>(CH₃)₂CO + CO(NH₂)₂·H₂O₂</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>TATP-9</td>
<td>(CH₃)₂CO + CO(NH₂)₂·H₂O₂</td>
<td>HNO₃</td>
</tr>
<tr>
<td>HMTD-1</td>
<td>(CH₃)₄N + H₂O₂</td>
<td>Citric acid</td>
</tr>
<tr>
<td>HMTD-2</td>
<td>Fuel cubes + H₂O₂</td>
<td>Citric acid</td>
</tr>
<tr>
<td>HMTD-3</td>
<td>Fuel cubes + H₂O₂</td>
<td>Citric acid</td>
</tr>
</tbody>
</table>

H₂O₂: 30 wt% aqueous solution; HCHO: ~37 wt% aqueous solution; NH₃: ~29 wt% aqueous solution.
all analytes are represented by quintuplicate trials. The HCA dendrogram shows perfect discrimination among all the analytes with the exception of two confusions between TATP-4 and TATP-6; this confusion is not unexpected, given that these two samples of TATP were prepared in a very similar manner: mixing acetone, sodium percarbonate with a volatile acid (HCl or HNO₃, respectively). The effects of aging of TATP and HMTD samples were also examined and only minimally affected the sensor array response (see ESI,† Fig. S4 and S5), in spite of significant structural changes in crystal morphology (see ESI,† Fig. S6).

Principal component analysis (PCA) was performed to provide a measure of the dimensionality of the data. Given the very limited range of chemical diversity present among these analytes, relatively low dimensionality was expected and indeed observed: two dimensions account for 87% of the total variance and five dimensions are required to capture 95% of the variance (ESI,† Fig. S7). A score plot of the first two principal components (Fig. 3) shows relatively good separation among the analytes, as indicated by circling obvious clusters. All three HMTD samples were separable from TATP, and all the TATP (except TATP-4 and TATP-6) were differentiable.

A more robust and supervised classification method, support vector machine (SVM) analysis, was used to create optimized classifiers using LIBSVM, an open-source SVM library. SVM results using a leave-one-out permutation method are shown in Table S2 (see ESI†). Using SVM analysis, no errors in classification were found including all TATP samples, i.e., the error rate of predictive classification is <1.5%.

GC-MS analyses were conducted to understand the chemical composition of freshly prepared peroxides and their possible degradation during aging. Headspace volatiles were sampled using solid-phase microextraction (SPME) in a protocol which closely matched the sampling condition using handheld device. The compositions of TATP and HMTD samples as determined by SPME GC-MS are given in Table 2. TATP prepared from H₂O₂ have relatively high levels of DADP for both fresh and aged samples, and aging for 30 days yields more dimeric product DADP (see ESI,† Fig. S8 and Table S3). Fresh TATP samples prepared from percarbonate or urea peroxide are nearly pure TATP; upon aging, however, TATP prepared from urea peroxide shows a considerable amount of DADP, while TATP synthesized from percarbonate appears to have higher stability and longer shelf-life than the other TATP samples (see ESI,† Table S3). Though HMTD is much less volatile than TATP, SPME GC spectra still detect the degradation products TMA and HA (see ESI,† Fig. S8), which are primarily responsible for the sensor array responses. Good crystallinity of both TATP and HMTD samples was observed and discussed in ESI,† Fig. S8.

The limits of detection (LOD) in sample size for the bulk peroxide explosives were examined. The LOD is defined as the sample amount determined by extrapolation that provides a signal (i.e., the overall response to an analyte) at least three times as great as the noise (i.e., the standard deviation among blank controls). In general, LODs for analytes scale with volatility: higher volatility leads to greater colorimetric array response; the reactivity of the volatiles, however, also plays a critical role in array response. For three representative analytes (two TATP and one HMTD), we plotted the array response as a function of sample amount ranging from 1 to 10 mg (see ESI,† Fig. S9). Based on the extrapolated calibration curve, the LODs for three typical explosives are all determined to be at µg levels: ~90 µg for TATP-1, ~140 µg for TATP-5 and ~120 µg for HMTD-1. We emphasize that these sensor arrays are not intended for trace detection of explosives, but rather for forensic identification of the method of manufacture of a discovered HME or IED; in real world situations, intelligence information as to the explosive maker can be extremely valuable.

In field work, it is probable that there will be other odors present in the air sampled that could potentially interfere with identification of the targeted analytes. In order to gauge the specificity of the sensor array, we examined sensor array response to 10 mg of five possible interferents that are common

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Table 2 Purity of nine TATP and three HMTD samples from headspace analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fresh (1 d)</th>
<th>Aged (30 d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[TATP]/([TATP] + [DADP])%</td>
<td>79.2</td>
<td>35.8</td>
</tr>
<tr>
<td>TATP-1</td>
<td>69.0</td>
<td>47.6</td>
</tr>
<tr>
<td>TATP-2</td>
<td>66.2</td>
<td>45.5</td>
</tr>
<tr>
<td>TATP-3</td>
<td>99.1</td>
<td>96.5</td>
</tr>
<tr>
<td>TATP-4</td>
<td>98.4</td>
<td>96.7</td>
</tr>
<tr>
<td>TATP-5</td>
<td>96.3</td>
<td>93.9</td>
</tr>
<tr>
<td>TATP-6</td>
<td>95.9</td>
<td>54.1</td>
</tr>
<tr>
<td>TATP-7</td>
<td>96.5</td>
<td>53.3</td>
</tr>
<tr>
<td>TATP-8</td>
<td>96.7</td>
<td>57.7</td>
</tr>
</tbody>
</table>

*a* Calculated from integrated peak areas. TMA, trimethylamine; HA, hexamine.

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**Table 2**

Purity of nine TATP and three HMTD samples from headspace analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fresh (1 d)</th>
<th>Aged (30 d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HMTD]/([TMA] + [HA] + [HMTD])%</td>
<td>87.5</td>
<td>84.3</td>
</tr>
<tr>
<td>HMTD-1</td>
<td>88.6</td>
<td>82.9</td>
</tr>
<tr>
<td>HMTD-2</td>
<td>85.9</td>
<td>81.6</td>
</tr>
</tbody>
</table>

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**Fig. 3** Two-dimensional principal components analysis plot for quintuplicate trials of twelve preparations of peroxide explosives (number nearby each cluster represents the sample label of each corresponding peroxide) and a control; n = 65. Misclassification was only observed between TATP-4 and TATP-6.
in an airport atmosphere\textsuperscript{45} (toothpaste, sunscreen, lipstick, perfume and eye drops) as a comparison to the positive responses from two peroxides (TATP-1 and HMTD-1), as provided in ESI,\textsuperscript{1} Fig. S10. These five interferences give easily distinguishable responses from the peroxide explosives and are totally separable from the peroxides. In addition, as we have previously demonstrated,\textsuperscript{28–31} the colorimetric sensor array is very insensitive to changes in ambient humidity.

In conclusion, we have developed a colorimetric sensor array that can detect and discriminate among peroxide explosives based on their source or manufacturing details. TATP vapors undergo acid-catalysed decomposition that release detectable volatiles while the much less volatile HMTD contains detectable volatile basic impurities. Hierarchical cluster analysis, principal component analysis, and support vector machine analysis show excellent discrimination among peroxide explosives produced by a range of synthetic methods. Aging over 30 days did not affect the results, even though aging does alter the constituent and crystalline phase of TATP as confirmed by GC-MS and PXRD tests. Detection limits for both peroxides are calculated to be \( \sim 100 \mu g \). This method has significant implications in peroxide explosives identification and may prove to be a useful supplement to other available detecting technologies used in security checks and forensic evaluation of improvised explosives.

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Notes and references