

A Colorimetric Sensor Array for Detection of Triacetone Triperoxide Vapor

Hengwei Lin and Kenneth S. Suslick*

Department of Chemistry, University of Illinois at Urbana–Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received August 25, 2010; E-mail: ksuslick@illinois.edu

Abstract: Triacetone triperoxide (TATP), one of the most dangerous primary explosives, has emerged as an explosive of choice for terrorists in recent years. Owing to the lack of UV absorbance, fluorescence, or facile ionization, TATP is extremely difficult to detect directly. Techniques that are able to detect generally require expensive instrumentation, need extensive sample preparation, or cannot detect TATP in the gas phase. Here we report a simple and highly sensitive colorimetric sensor for the detection of TATP vapor with semiquantitative analysis from 50 ppb to 10 ppm. By using a solid acid catalyst to pretreat a gas stream, we have discovered that a colorimetric sensor array of redox sensitive dyes can detect even very low levels of TATP vapor from its acid decomposition products (e.g., H_2O_2) with limits of detection (LOD) below 2 ppb (i.e., $<0.02\%$ of its saturation vapor pressure). Common potential interferences (e.g., humidity, personal hygiene products, perfume, laundry supplies, volatile organic compounds, etc.) do not generate an array response, and the array can also differentiate TATP from other chemical oxidants (e.g., hydrogen peroxide, bleach, *tert*-butylhydroperoxide, peracetic acid).

Triacetone triperoxide (TATP), a high-powered primary explosive first synthesized in 1895,¹ has become well-known during the past decade as an explosive of choice for terrorists.² Due to its extreme sensitivity, TATP does not have any practical engineering or military applications. It has been used, however, in at least three major terrorist acts in the past 10 years,^{2b} in part because TATP is easy to prepare from readily available chemicals (i.e., acid catalyzed reaction of acetone with hydrogen peroxide)³ but difficult to detect.⁴ While several techniques for TATP detection have been developed in recent years⁵ and there are several commercial products available,⁶ these methods generally require expensive and generally nonportable instrumentation,⁷ need extensive sample preparation,⁸ are qualitative or have poor limits of detection,⁵ or are limited to liquid or solid samples and cannot detect TATP vapor.⁹ Hence, the development of an inexpensive, portable, and easy-to-use device for the field detection of TATP remains a high priority. Particularly, on-site detection of TATP vapor would have significant advantages for rapid screening.

In recent years, our group has developed a colorimetric sensor array methodology¹⁰ that has been applied successfully for the identification of a wide range both of toxic industrial gases and vapors¹¹ and of organic analytes in aqueous liquids.¹² Herein, we describe a colorimetric sensor array for the sensitive and selective detection of the vapor phase of TATP. Owing to the lack of UV absorbance, fluorescence, or facile ionization, TATP is extremely difficult to detect directly: indeed, even redox sensitive dyes are not very responsive to TATP vapor. By using a solid acid catalyst to pretreat a gas stream, we have discovered that a colorimetric sensor array can detect even very low levels of TATP vapor from its acid decomposition products¹³ (e.g., H_2O_2) with limits of

detection (LOD) below 2 ppb (i.e., $<0.02\%$ of its saturation vapor pressure) (Figure 1 and Supporting Information (SI) Figure S1).

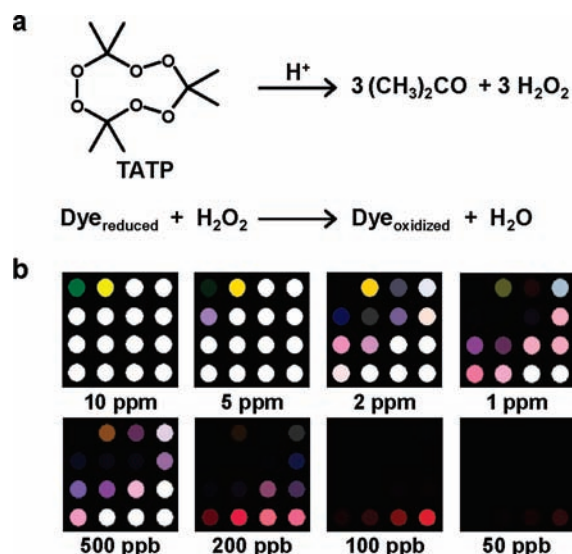


Figure 1. (a) Acid catalyzed decomposition of TATP. (b) Color difference maps of TATP vapor at concentrations specified after 5 min (top row) and 10 min (bottom row) of exposure at 50% relative humidity and 298 K. For display purposes, the color range of these difference maps is expanded from 4 to 8 bits per color (RGB range of 4–19 expanded to 0–255). The identity of the nanoporous pigments and a full database of the color differences are given in Supporting Information Tables S1 and S2.

We have extensively tested a colorimetric sensor array against a wide range of TATP vapor concentrations, using a solid acid catalyst to decompose the TATP in a gas flow to H_2O_2 . After screening several possible acid catalysts, we chose Amberlyst-15, the acid form of a sulfonated highly cross-linked polystyrene ion-exchange polymer;¹⁴ see SI for experimental details and cautions. Using an ordinary flatbed scanner, digital images of an array were acquired before and after exposure to TATP vapor at various concentrations. The red, green, and blue values of each spot in the array were measured before and after TATP vapor exposure, and color difference maps were generated. These difference maps provide a pattern that effectively identifies different concentrations of TATP vapor, as shown in Figure 1b. This colorimetric array is capable of semiquantitative detection of TATP vapor well below 50 ppb. For comparison, the array response to TATP vapor without the use of an acid catalyst is nearly a 100-fold less (SI Figure S3), and therefore prior redox sensitive dyes have not previously proved useful for the detection of TATP vapor.⁹

TATP vapor concentrations were confirmed by in-line analysis in real time using an FT-IR multigas analyzer (SI Figure S4). The amount of catalyst required was optimized (Figure 2); Amberlyst-15 proved to be extremely efficient in the decomposition of TATP

vapor, and the observed amount of acetone corresponded to the stoichiometry expected from TATP decomposition (3:1). These results indicate that Amberlyst-15 is an excellent solid-acid catalyst for TATP vapor decomposition because negligible amounts of TATP vapor or its decomposition products were adsorbed.

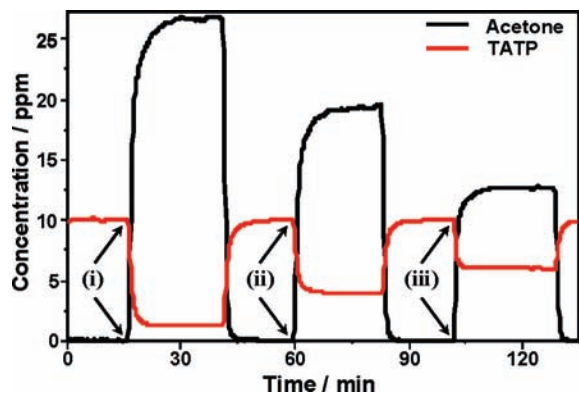


Figure 2. Decomposition of TATP vapor by a solid-acid Amberlyst-15 catalyst. At $t = 0$, a gas stream containing 10 ppm of TATP vapor is initiated; no acetone is observed. At $t = 15$ min (i), a small Teflon tube containing 20 mg of Amberlyst-15 was inserted quickly into the gas stream, and TATP and acetone were monitored: TATP concentration immediately drops and acetone concentration increases with the expected stoichiometry. At $t = 40$ min, the catalyst tube was removed, and TATP returned rapidly to 10 ppm and acetone to 0 ppm. This process was repeated with (ii) 10 mg and (iii) 5 mg of catalyst: as the amount of catalyst was decreased, so did the extent of TATP decomposition.

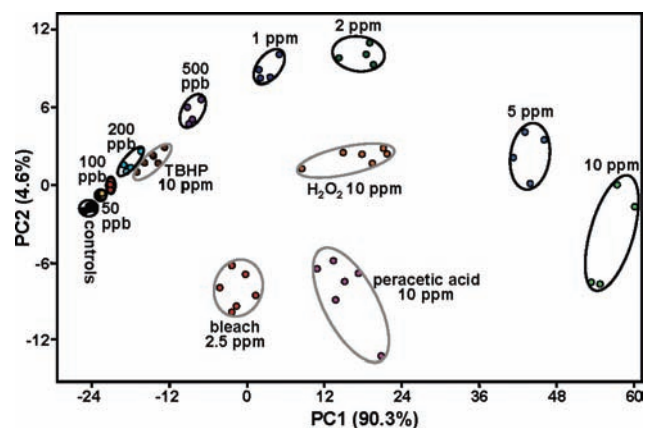


Figure 3. Two-dimensional principal component analysis (PCA) plot. TATP vapor at different concentrations, other peroxides (encircled in gray ellipsoids), and controls for changes in humidity (50% RH and 50% vs 10% RH and 50% vs 90% RH). TBHP = *tert*-butylhydroperoxide.

To measure the array response at different concentrations of TATP, principal component analysis (PCA)¹⁵ was performed and a two-dimensional plot was obtained (Figure 3) with excellent separation even at low concentrations. In addition, the array's response to changes in relative humidity was negligible, clustering inseparably with the controls.

We next examined the relationship between the total Euclidean distances of the color changes (i.e., square root of the sums of the squares of the Δ RGB values) of the array as a function of TATP vapor concentration. As shown in Figure 4, after a 5 min exposure time, the total Euclidean distance tracks monotonically with increasing TATP vapor concentration from 50 ppb to 10 ppm. When the data were examined, a linear response was obtained for lower concentrations (Figure 4 inset). An extrapolated limit of detection based on $3 \times S/N$ of the three largest color changes was 2 ppb

after 10 min of exposure, i.e., $<0.02\%$ of its saturated vapor concentration at room temperature (~ 69 ppm at 25°C).¹⁶

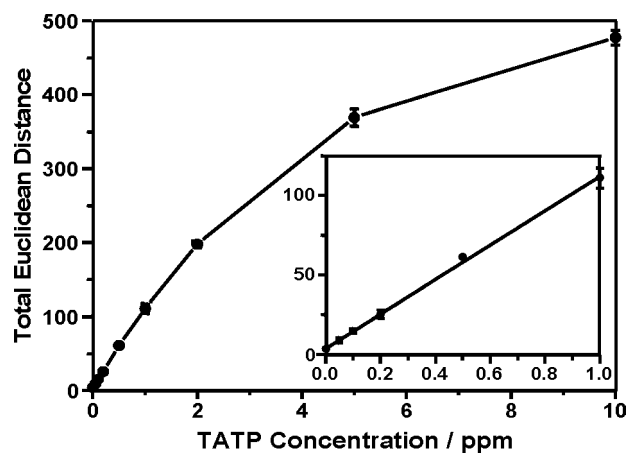


Figure 4. Total Euclidean distance of the array plotted versus concentration of TATP vapor after 5 min of exposure. Inset shows concentration vs total Euclidean distance plot for the lower concentrations with a linear fit. The average of three trials is shown with error bars. The Euclidean distance is simply the total length of the 48-dimensional color-difference vector, i.e. the total array response.

As shown in SI Figure S5, one may also use hierarchical cluster analysis (HCA) to analyze the color change patterns of the array. Dendrograms are based on the clustering of the array response data in the 48 dimensional Δ RGB color space (i.e., 16 changes in red, green, and blue values). In quadruplicate trials at different concentrations of TATP vapor, there were no misclassifications out of 44 trials, even at the lowest concentrations (50 ppb).

In real world applications, interferences, including changes in humidity, can be highly problematic. With the indicators used in this sensor array, however, only strong oxidants will elicit any response, and therefore the array should be immune to interference from nearly all common chemicals, vapors, or odorants. We have examined a wide range of relevant potential interferences (18 in total) and also the effects of humidity on our sensor array and found no significant response (SI Figure S6). Common potential interferences might include personal care products typically found in travelers' baggage: e.g., mouthwash, body wash, toothpaste, shampoo, perfume, lotion, liquor, vinegar, laundry supplies, and various volatile organic compounds (e.g., acetone, ethyl acetate, benzene, toluene, and petroleum ether, which are possible volatile components in paints, finger nail polish, etc.). Arrays were exposed at room temperature to these interferences at 5% and 10% of their saturated vapor at 50% RH for 10 min: importantly, none of these interferences invoked any significant response from the sensor array. In addition, no change in the array was observed after 10 min of exposure to a relative humidity (RH) range from 10 to 90% RH compared to 50% RH. The specificity of this colorimetric sensor array for TATP was rationally planned: the array components were chosen to be responsive only to strong oxidants, and thus, our array is indeed insensitive to the presence of nearly all odorants, VOCs, and common potential interferences, or to changes in humidity.

In addition, the shelf life stability and reproducibility are of the utmost importance if these arrays are to be used in practical applications. Exposure of the array to air has no effect for a period of several days. Additional investigations showed that the response of the array to TATP vapor was unaffected by the presence or absence of O_2 in the gas flow. For long-term storage, the arrays are best kept under N_2 , and we observe very little change over 2 months in their response to 1 ppm or 10 ppm TATP vapor (SI

Figure S7); practically no variation was observed in the color difference maps, and a tight clustering of data collected regardless of array age was obtained. In addition, three separate printing batches of arrays gave nearly identical results for tests at 1 ppm and 10 ppm TATP vapor (SI Figure S8), which demonstrates excellent reproducibility for printing of the arrays and their response to TATP.

Finally, it should be noted that our array can also distinguish TATP from H₂O₂ or other volatile oxidants (e.g., hypochlorite bleach, peracetic acid, and *tert*-butyl hydroperoxide). As clearly shown in Figures 3 and S9, there is no confusion in the array response among TATP, H₂O₂, Clorox bleach, peracetic acid, or *tert*-butyl hydroperoxide in sextuplicate trials at 10 ppm. Furthermore, we note that Amberlyst-15 does not affect the array response to H₂O₂ or the other oxidants but dramatically changes the array response to TATP vapor (due to its acid catalyzed decomposition), which provides additional discrimination between TATP vapor and other oxidants (SI Figure S9).

While the laboratory studies reported here made use of inexpensive flatbed scanners for imaging, we have recently constructed a fully functional prototype hand-held device, as shown in SI Figure S10, which has a 3-fold improved *S/N* compared to the flatbed scanners. Combined with a low dead volume cartridge (SI Figure S11), a hand-held device could present a rapid, inexpensive, and highly sensitive method for portable monitoring of TATP vapor, e.g., for screening of luggage.

In conclusion, we have created a simple, disposable colorimetric sensor array that is capable of sensitive and semiquantitative detection of the vapor phase of the primary explosive TATP with limits of detection below 0.02% of its saturation vapor pressure. The array is highly selective for TATP, is unaffected by changes in humidity or by the presence of many common potential interferents, and can differentiate TATP from other chemical oxidants.

Acknowledgment. This work was supported through the NIH Genes, Environment and Health Initiative through Award U01ES016011.

Supporting Information Available: Experimental details, Figures S1–S11, and Tables S1–S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Wolfenstein, R. *Chem. Ber.* **1895**, *28*, 2265–2269.
- (2) (a) Naughton, P. *Times Online*, July 15, 2005. <http://www.timesonline.co.uk/tol/news/uk/article544334.ece>. (b) TATP has been used during various recent terrorist acts, including in (i) Richard Reid's shoe bomb on American Airlines Flight 63 (Cooper, R. T. *Los Angeles Times*, December 29, 2001, p A12. <http://articles.latimes.com/2001/dec/29/news/mn-18822>); (ii) the July 7th 2005 London bombings. (Townsend, M. The real story of 7/7. *The Observer*, May 7, 2006. <http://www.guardian.co.uk/2006/may/07/theobserver.uknews>); and (iii) the attempted bombing in Northwest Airlines Flight 253 on Christmas Day, December 25, 2009 ("Indictment in U.S. v. Abdulmutallab". January 6, 2010. http://www.cbsnews.com/htdocs/pdf/Abdulmutallab_Indictment.pdf (retrieved January 10, 2010).
- (3) Laine, D. F.; Roske, C. W.; Cheng, I. F. *Anal. Chim. Acta* **2008**, *608*, 56–60.
- (4) Dubnikova, F.; Kosloff, R.; Zeiri, Y.; Karpas, Z. *J. Phys. Chem. A* **2002**, *106*, 4951–4956.
- (5) (a) Schulte-Ladbeck, R.; Vogel, M.; Karst, U. *Anal. Bioanal. Chem.* **2006**, *386*, 559–565. (b) Burks, R. M.; Hage, D. S. *Anal. Bioanal. Chem.* **2009**, *395*, 301–313.
- (6) (a) ACRO Security Technologies: ACRO-P.E.T. . (b) Mistral Security Inc. www.mistralgroup.com/SEC_explosives.asp. (c) Bauer, C.; Sharma, A.; Willer, U.; Burgmeier, J.; Braunschweig, B.; Schade, W.; Blaser, S.; Hvozdzara, L.; Müller, A.; Holl, G. *Appl. Phys. B* **2008**, *92*, 327–333. (d) Santillan, J.; Brown, C.; Jalenak, W. *Proc. SPIE* **2007**, *6540*, 65400P. (e) Staples, E. In *Electronic Noses & Sensors for the Detection of Explosives*; Gardner, J.; Yinon, J., Eds.; Kluwer: Dordrecht, 2004.
- (7) (a) Schulte-Ladbeck, R.; Kolla, P.; Karst, U. *Anal. Chem.* **2003**, *75*, 731–735. (b) Wilson, P. F.; Prince, B. J.; McEwan, M. *J. Anal. Chem.* **2006**, *78*, 575–579. (c) Schulte-Ladbeck, R.; Edelman, A.; Quintás, G.; Lendl, B.; Karst, U. *Anal. Chem.* **2006**, *78*, 8150–8155. (d) Cotte-Rodríguez, I.; Hernández-Soto, H.; Chen, H.; Cooks, R. G. *Anal. Chem.* **2008**, *80*, 1512–1519. (e) Lindley, R.; Normand, E.; Howieson, I.; McCulloch, M.; Black, P.; Lewis, C.; Foulger, B. *Proc. SPIE* **2007**, *6741*, 67410P. (f) Lindley, R.; Normand, E.; McCulloch, M.; Black, P.; Howieson, I.; Lewis, C.; Foulger, B. *Proc. SPIE* **2008**, *7119*, 71190K.
- (8) (a) Schulte-Ladbeck, R.; Karst, U. *Anal. Chim. Acta* **2003**, *482*, 183–188. (b) Malashikhin, S.; Finney, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 12846–12847.
- (9) (a) Germain, M. E.; Knapp, M. J. *Inorg. Chem.* **2008**, *47*, 9748–9750. (b) Lu, D.; Cagan, A.; Munoz, R. A. A.; Tangkuaram, T.; Wang, J. *Analyst* **2006**, *131*, 1279–1281. (c) Sella, E.; Shabat, D. *Chem. Commun.* **2008**, 5701–5703. (d) Aplett, A.; Kiran, B.; Malka, S.; Materer, N.; Piquette, A. *Ceram. Trans.* **2005**, *172*, 29–35.
- (10) (a) Rakow, N. A.; Suslick, K. S. *Nature* **2000**, *406*, 710–713. (b) Suslick, K. S.; Bailey, D. P.; Ingison, C. K.; Janzen, M.; Kosal, M. E.; McNamara, W. B., III; Rakow, N. A.; Sen, A.; Weaver, J. J.; Wilson, J. B.; Zhang, C.; Nakagaki, S. *Quim. Nova* **2007**, *30*, 677–681.
- (11) (a) Janzen, M. C.; Ponder, J. B.; Bailey, D. P.; Ingison, C. K.; Suslick, K. S. *Anal. Chem.* **2006**, *78*, 3591–3600. (b) Lim, S. H.; Feng, L.; Kemling, J. W.; Musto, C. J.; Suslick, K. S. *Nature Chem.* **2009**, *1*, 562–567. (c) Feng, L.; Musto, C. J.; Kemling, J. W.; Lim, S. H.; Suslick, K. S. *Chem. Commun.* **2010**, *46*, 2037–2039. (d) Feng, L.; Musto, C. J.; Suslick, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 4046–4047.
- (12) (a) Zhang, C.; Suslick, K. S. *J. Am. Chem. Soc.* **2005**, *127*, 11548–11549. (b) Musto, C. J.; Lim, S. H.; Suslick, K. S. *Anal. Chem.* **2009**, *81*, 6526–6533.
- (13) Armitt, D.; Zimmermann, P.; Ellis-Steinborner, S. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 950–958.
- (14) Amberlyst-15 is manufactured by Rohm and Haas and available from Sigma-Aldrich.
- (15) Jolliffe, I. T. *Principal Component Analysis*; Springer-Verlag: New York, 2002.
- (16) Oxley, J. C.; Smith, J. L.; Shinde, K.; Moran, J. *Propellants, Explos., Pyrotech.* **2005**, *30*, 127–130.

JA107419T