

## Full Paper

# Explosives Detection Using Direct Analysis in Real Time (DART) Mass Spectrometry

J. Michael Nilles\*, Theresa R. Connell, Sarah T. Stokes

Excet, Inc., 8001 Braddock Road, Suite 105, Springfield, VA 22151 (USA)

H. Dupont Durst

Edgewood Chemical Biological Center, Aberdeen Proving Ground, Edgewood, MD 21040 (USA)

Received: September 28, 2009; revised version: October 28, 2009

DOI: 10.1002/prep.200900084

### Abstract

The growing use of explosives by terrorists and criminals creates a need for instrumentation which can rapidly analyze these energetic compounds, preferably on site. Direct analysis in real time (DART) is a promising technology for surface analysis with little or no sample preparation. Therefore, DART ionization is evaluated for use in detecting explosives on solid substrates and in liquid matrices. Fifteen explosives were chosen as a consequence of their common usage. Five surfaces were chosen to represent a wide range of physical properties such as composition, porosity, surface morphology, and thermal and electrical conductivity. Additionally these surfaces are commonly found in everyday surroundings. All 75 compound-surface combinations produced a clear, easily identifiable, mass spectra characteristic of the targeted analyte. Simultaneous detection of five explosives is demonstrated on these same surfaces. Lastly, rapid detection of trace contamination in common fluids is also explored.

### 1 Introduction

In recent history, use of improvised explosive devices (IEDs) has become more prevalent. However, improvised by no means implies less lethal. Although the world has borne witness to high profile, high impact bombing events for decades, the frequency of these events has increased dramatically over recent years. Starting materials for IEDs are easily accessed and simply manufactured. However, IEDs provide the possibility to identify the architect of the device. The builder of an IED will adapt the device to best utilize the materials that are available. These might include old munitions, stockpiled or cached weapons or, just as easily, household ingredients (ammonia, peroxide), batteries or even fertilizers. Adaptations and choices can create a

unique set of identifiers with regard to the device-maker. As a matter of forensic investigation, if the component or starting materials are identified, they can provide a link to the manufacturer of the device. In the aftermath of an explosive event, like an IED, rapid and accurate identification of the explosives or components used can save critical time in follow-up forensic investigations.

A prompt response is important; however tell-tale explosive compounds can remain in soil, shell fragments, or other material for long periods of time [1, 2]. In a high order explosive event much of the explosive is consumed in the blast. Any small portion that is not consumed can be blown by winds, absorbed into water and soil, or deposited on nearby surfaces. Low order or inefficient explosive events can produce much more residual material. In all cases, these residual quantities deposited on or absorbed in nearby surfaces can be of forensic value in post-blast analysis. These residual amounts can also create environmental hazards because many explosive formulations are toxic [3].

While there appears to be an upsurge in use of explosive mixtures of inorganic salts and peroxide-based explosives, the vast majority of explosives in use will likely remain organic nitro-based explosives. Although they are inherently unstable, low vapor pressure compounds, there are numerous methodologies capable of detecting them. Most widespread is the use of ion mobility spectrometry [4]. This technique provides for small, low cost, portable devices. Though it is a rapid and sensitive technique, low resolution leads to higher frequencies of false positives and negatives. Other methods include liquid chromatography-mass spectrometry [5–7], capillary electrophoresis [8], solid phase micro-extraction [9], gas chromatography-mass spectrometry [10, 11]. However, these techniques involve extensive sample preparation and/or significant analysis time. Another

\* Corresponding author; e-mail: mike.nilles@us.army.mil

er technique, desorption electrospray ionization [12], uses a solvent spray which might damage or distort items under investigation. Multi- and single-photon ionizations have been explored with some success, however these devices require expensive and delicate laser systems.

Direct analysis in real time (DART) is an atmospheric pressure ionization method that offers several advantages for the analysis of explosives on surfaces. It is a rapid technique, capable of providing analytical results in seconds [13]. Speed is useful in time critical situations, such as immediately following a blast, and for high throughput demands, such as airport screening. Compounds are ionized directly from the surface facilitating detection of residues, coatings and adsorbed species, without wipes, extractions, or sprayed solvent. Fundamentally, DART is a non-contact technique reducing the risk of sample cross contamination, toxic waste, and sample loss.

DART is, in effect, a non-destructive technique. Samples are not ground up or dissolved in solvents, which preserves the integrity of the original sample; this is significant when quantities are limited. This unique advantage permits other complementary investigations when time and conditions permit. Often pieces of debris contain a variety of components. For example, a piece of window frame may contain glass, wood, metal, and foam rubber. An analyst using DART is able to evaluate each of these components independently such that complications with sample non-homogeneity are largely mitigated.

Previous work validates the use of the DART technique to identify everything from chemical warfare agents [13–17], to pharmaceuticals [18–23], to drugs of abuse [13–15, 24–26], to biocides [24, 27, 28]. Additional applications include analysis of soft drinks [29], inks [30], flavors and fragrances [31], flame retardants and accelerants [32, 33], metabolites and other bio-molecules [24, 34] as well as a host of other compounds [35–39]. There have been reports that cursorily investigate the use of DART to identify a few explosives on even fewer surfaces [13–15]. But, its suitability as a fast, first line screening technique is better demonstrated by an in depth presentation of multiple explosives on multiple surfaces and in several liquid matrices.

## 2 Experimental

### 2.1 Chemicals

To demonstrate detection across a broad number of explosive compounds, a large selection of explosive standards were obtained. Dinitroethylene glycol (EGDN) [628-96-6], dinitropropylene glycol (PGDN) [6423-43-4], *n*-methyl-2,4,6-tetranitrobenzenamine (Tetryl) [479-45-8], pentaerythritol tetranitrate (PETN) [78-11-5], mononitroglycerine (MNG) [624-43-1], dinitroglycerine (DNG) [623-87-0], and trinitroglycerine (TNG) [9010-02-0] standards with concentrations of 1 mg mL<sup>-1</sup> were purchased from Cerilliant. 1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (HMX) [2691-41-0], 1,3,5-trinitro-1,3,5-triazacyclohexane

(RDX) [121-82-4], 2,4-dinitrotoluene (DNT) [121-14-2], 2-amino 4,6-dinitrotoluene (Amino-DNT) [35572-78-2], 2,4,6-trinitrotoluene (TNT) [118-96-7], 1,3-dinitrobenzene (DNB) [99-65-0], and 1,3,5-trinitrobenzene (TNB) [99-35-4] standards with concentrations of 1 mg mL<sup>-1</sup> were purchased from AccuStandard. 2,4,6-Trinitrophenol (Picric Acid) [88-89-1] was purchased from Sigma–Aldrich at 1% concentration by weight and diluted to 1 mg mL<sup>-1</sup>.

### 2.2 Ion Source and Mass Spectrometer

The DART ion source (Ionsense Inc., Saugus, MA, USA) has been described previously in detail [13]. In this study, the discharge electrode was set to 5000 V, producing excited-state species in a helium gas stream. It is hypothesized that these excited state helium atoms through Penning ionization of oxygen and other atmospheric gases produce low energy electrons [40, 41]. These low energy electrons in turn ionize the sample or a dopant such as the dichloromethane used in this study. DART/sample/orifice distances remained at 7 mm for this study. Gas flow typically remained at 3 L min<sup>-1</sup> and gas temperature ranged from 150 °C to ~225 °C. Users typically have to tune these parameters to achieve optimal sensitivity.

High accuracy mass measurements are achieved using a JEOL AccuTOF<sup>TM</sup> (JEOL USA, Peabody, MA, USA) time-of-flight mass spectrometer. The mass spectrometer is operated at a resolving power greater than 6000 (FWHM definition) at mass 609. The mass-to-charge ratio ( $m/z$ ) scale is calibrated using neat polyethylene glycol (PEG 600 CAS# 25322-68-3) applied to a glass capillary. A concentrated iodine [7553-56-2] solution is used to verify instrument performance on a daily basis. When necessary, a mass drift correction is made using a 1% solution of PEG 600. In this way, ion masses are determined to an accuracy of 0.002 u or better. These accurate mass identifications were made using the included JEOL Mass Center software. In this study, the mass spectra were typically collected from  $m/z$  150 to 400 u and the polarity of both the ion source and mass spectrometer are set for anion production and detection.

As a matter of good laboratory practices, periodically a blank substrate was analyzed between sample analyses to assure that there was no sample carry over; none was observed. An instrument standard was run immediately following each sample within the same data file. Analyzing a standard with each run not only reliably validates instrument performance, but it allows for highly accurate mass reporting. As such, false positives are highly unlikely.

### 2.3 Deposition Procedure

The surfaces: glass, Great Stuff<sup>TM</sup> polyurethane foam, steel, wood, and asphalt shingle were selected to represent a wide range of physical and chemical properties. Because the ion source did not have an opening large enough to allow objects much larger than 7 mm, asphalt shingle and polyur-

ethane foam were cut into thin strips 3–5 mm in width. For glass, steel and wood, standard melting point capillaries, mild steel paperclips, and toothpicks were used, respectively. Although there is a significant limitation on the size and shapes of samples which can be analyzed, it is hoped that engineering improvement can be made to the DART to allow for analyses of flat surfaces.

We crafted a procedure to deposit the explosives on the surfaces designed to best mimic deposition after an explosion. An actual explosive event would likely deposit residue in a dried form, not in a solvent. Rather than spike the surfaces directly with a wet explosive solution, we dried 2  $\mu\text{L}$  aliquots of each standard on an aluminium foil surface, resulting in a 2  $\mu\text{g}$  deposition. The explosive residue was then transferred to the surface being evaluated by abrasive contact (rubbing). The solid surface was then analyzed by DART. Although this was perhaps not the most optimal or quantitative transfer [42], it was felt that it was important to simulate how the material would be applied in a real-world event. Identification on relevant surfaces is the thrust of this investigation and as such the 2  $\mu\text{g}$  deposition supplied a more than adequate response, such that even a poor transfer would be detectable.

For the liquid samples used in this study the standards referenced above were diluted in diesel fuel, creek water, and sea water to a concentration of 100  $\text{ng mL}^{-1}$ . The diesel fuel was collected from a commercial gas pump; the creek water was obtained from a local creek that drains through an active cattle farm; the sea water was collected from the Atlantic Ocean in Ocean City, Maryland. These were analyzed by dipping the closed end of a glass melting point capillary in them followed by insertion into the DART beam.

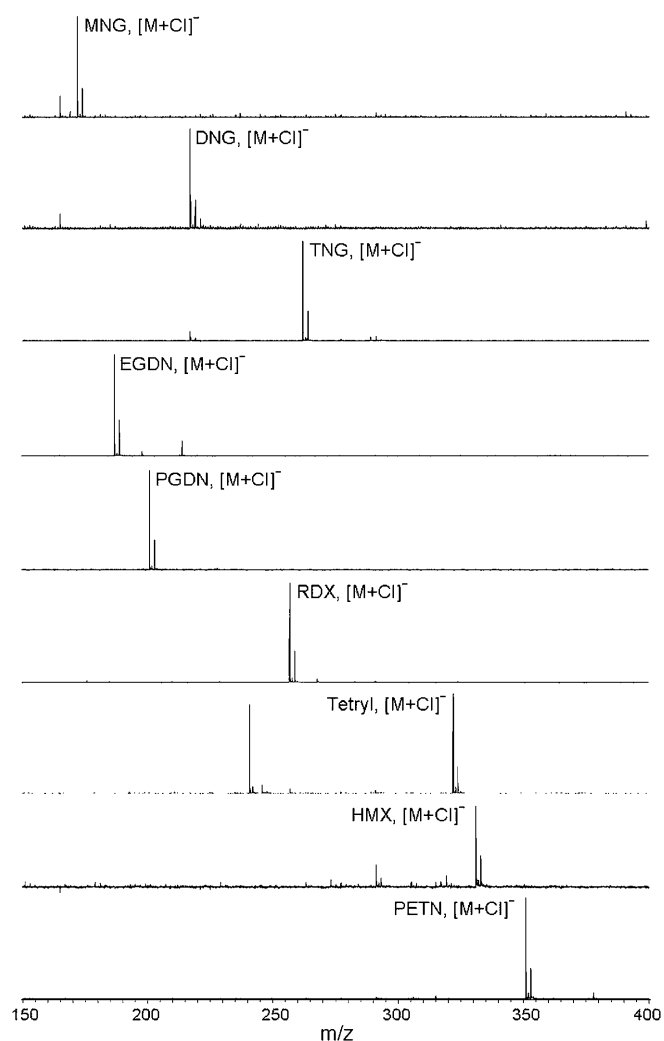
### 3 Results and Discussion

The goal of this study was to evaluate the DART technique with a variety of explosives (15) on an array of surfaces (5) that might be found in a blast area following an explosion. These surfaces: glass, Great Stuff polyurethane foam, steel, wood, and asphalt shingle were selected to represent a wide range of physical properties such as composition, porosity, surface morphology, thermal, and electrical conductivity. The explosives were purposefully chosen for their ease of appropriation, widespread use as starting material, or component material of IEDs. They include: trinitroglycerin (as well as mono- and dinitroglycerin), EGDN, PGDN, RDX, Tetryl, HMX, PETN, trinitrotoluene (as well as di- and 2 amino-dinitrotoluene), trinitrobenzene (as well as dinitrobenzene), and Picric Acid. This particular sample set also exhibits a wide range of thermal instabilities and volatilities.

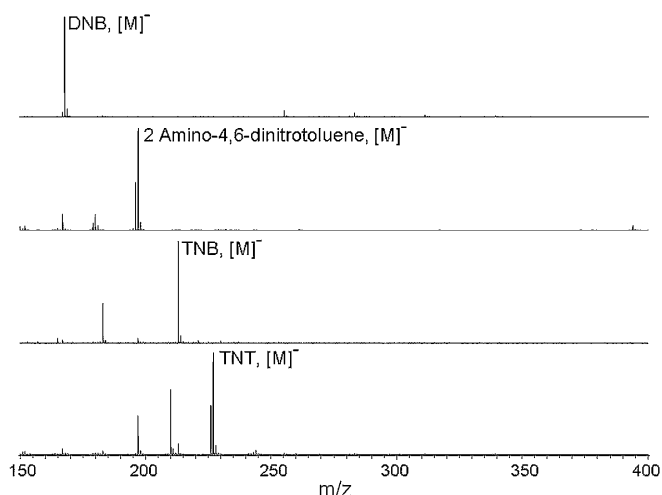
All 15 explosives were detected and they are identified through analysis on all 5 surfaces. Having generated a plethora of spectral data, a single representative spectrum is illustrated in Figures 1–3 for each compound. Complete, non-background subtracted spectra of all 15 explosives on 5

separate surfaces are provided in the Supporting Information data section. The spectra are typically clean, regardless of the surface. With few exceptions there is very little background complication and no interferant prevents identification of the target analyte on any of the surfaces evaluated. Due to ubiquitous plasticizers and other volatile organics in the Great Stuff Foam<sup>TM</sup>, these spectra possessed the most background noise. Still, the explosives were detected and identified without difficulty.

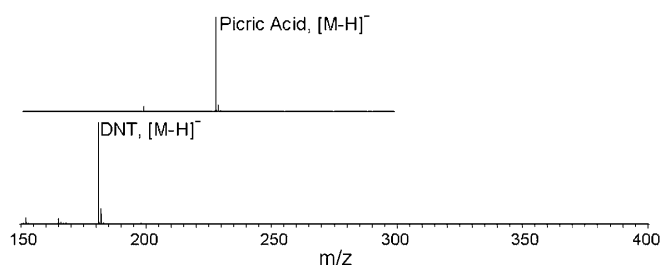
In general, these compounds can be differentiated by the preferential ion produced. The majority of the explosives analyzed were best detected in the presence of a dopant, such as dichloromethane, which readily provides a chloride adduct (Figure 1). However, if no dopant is available, the instrument can be tuned to produce  $\text{NO}_2^-$  ions which will also readily adduct with the anion. But many explosives possess one or more nitro groups, which can confuse identification. Therefore, the instrument conditions were optimized to produce minimal  $\text{NO}_2^-$  ions, relying instead on



**Figure 1.** Representative mass spectra of MNG, DNG, TNG, EGDN, PGDN, RDX, Tetryl, HMX, and PETN. All readily form the chloride adduct.



**Figure 2.** Representative mass spectra of DNB, Amino-DNT, TNB, and TNT.



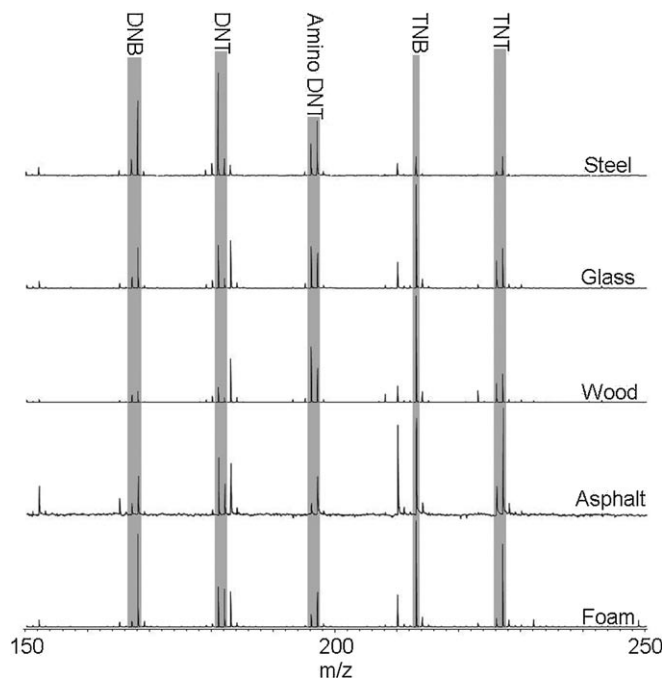
**Figure 3.** Representative mass spectra of Picric Acid and DNT.

the presence of the chlorinated dopant. Nevertheless, small peaks corresponding to  $[M + \text{NO}_2]^-$  and/or  $[M + \text{NO}_3]^-$  can still be seen in the spectra of DNG, TNG, EGDN, RDX, HMX, PETN, and several of the Supporting Information figures. DART is a soft ionization technique. Which means that the intensity of peaks representing fragment ions, if any, is usually very much less than that of the peak representing the precursor ion, with one notable exception. Tetryl readily loses  $\text{NO}_2$  to produce the *N*-methyl-2,4,6 trinitroaniline fragment ion that has  $m/z$  241.021. This fragment anion often has an abundance greater than the  $[M + \text{Cl}]^-$  ion of Tetryl.

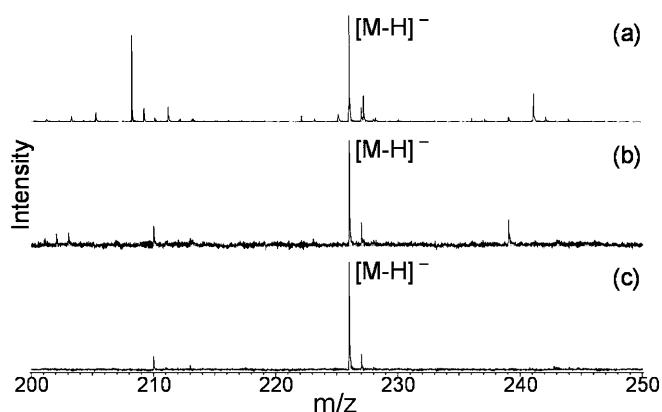
Several explosive compounds preferentially formed molecular anions  $[M]^-$  (Figure 2) and a few underwent proton loss forming deprotonated molecules,  $[M - \text{H}]^-$  (Figure 3). With the exception of TNB, all were observed to form both to a greater or lesser degree. Interestingly, the compounds which formed molecular ions were more likely to produce fragment ions, though still relatively low in abundance. Low-intensity peaks representing ions of the well characterized losses of NO and OH are frequently observed in spectra of these compounds [43]. Notably, the TNT spectra contain a small peak at the exact mass of trinitrobenzene (molecular anion), this is ascribed to impurity in the TNT standard.

In the above studies (Figures 1–3) each explosive compound was analyzed individually. However, ion source conditions for detection of these compounds were generally similar and quite flexible. For those explosives which add an anion (charge carrier), one set of conditions can be used. For those that deprotonate or form molecular anions, a second set of conditions can be used. Figure 4 illustrates a case of selecting one set of conditions, showing five explosive compounds that are detected simultaneously on each of the five different surfaces. Again in all cases except TNB, both  $M^-$  and  $[M - \text{H}]^-$  were observed in varying amounts. Additionally, the fragments TNB-NO, TNT-NO, and TNT-OH can be seen at 183.004, 197.020, and 210.015, respectively.

In addition to adsorption on solid surfaces, residual explosive can be dissolved by liquids. Bodies of water near an event can absorb explosive or rain can flush explosive from surfaces to streams, in the form of run-off terminating in tributaries, bays or oceans. Energetic compounds may be immersed in incendiary liquids to enhance their effect, thus making diesel fuel a fluid of interest as well. To demonstrate detection in real world liquid matrices we have included the analytical results of TNT evaluations in diesel fuel, dirty creek water, and sea water. Figure 5 illustrates TNT detection at the  $100 \text{ ng mL}^{-1}$  level in diesel fuel, local creek water, and sea water.



**Figure 4.** Simultaneous detection of DNB, DNT, Amino-DNT, TNB, and TNT on each surface. These five were chosen because there is clear separation in the mass spectra. The figure is intended to show that one can detect all five energetic compounds on all five surfaces not to imply any quantitative comparison.



**Figure 5.** Mass spectra of TNT in (a) diesel fuel (b) creek water and (c) sea water.  $[\text{TNT} - \text{OH}]^-$  also appears in each spectrum.

#### 4 Conclusion

All 75 compound-surface combinations produced clear, easily identifiable, mass spectra. Although the number of surfaces tested was necessarily limited, those chosen possess diverse physical and chemical properties. It may also be important to note, the surfaces were used as is, not cleaned or pre-prepared. Even though this study focused on nitro based explosives, it is interesting to note that although they are of the same compound class, they differ in preferential ion formed ( $[\text{M} + \text{Cl}]^-$ ,  $[\text{M}]^-$ ,  $[\text{M} - \text{H}]^-$ ).

Identification of analytes using the DART/AccuTOF process is less cumbersome than many alternative techniques which produce, and even rely on, cluttered and fragmented ion patterns for identification. Ion fragments are always possible, particularly with thermally unstable compounds. However, the DART technique produces a remarkably soft ionization, generally meaning that fragmentation is not the norm. Compound identification is straightforward and typically more reliable than identifying a fragmentation pattern. The documented speed of operation [13–15] coupled with this relative ease of analyte identification suggests that it might be useful on site after an explosive event or used as a screening method in airports, subways, port authorities, etc.

The DART methodology is rapid and straightforward; however, there are additional characteristics which could be exploited. The technique is capable, without sample preparation, of evaluating irregular pieces of debris, soil, or other oddly shaped inhomogeneous samples. It is non-destructive to the original sample, which may be of benefit for follow up investigations. Furthermore, because the samples do not make contact with the ion source or spectrometer, contamination, and maintenance are minimal.

This particular exploration is a peripheral look at a range of possibilities (e.g., explosives on surfaces, and in real world fluids). It is not intended to be an all inclusive list or a final statement on explosives detection capability. There is existing data demonstrating the successful use of DART to detect many compound classes, on numerous surfaces and

fluid types. Given the growing demand for rapid and accurate explosive detection, this technology certainly merits further investigation.

#### 5 References

- [1] R. R. Kunz, K. C. Gregory, D. Hardy, J. Oyler, S. A. Ostazeski, A. W. Fountain, III, Measurement of Trace Explosive Residues in a Surrogate Operational Environment: Implications for Tactical Use of Chemical Sensing in C-IED Operations, *Anal. Bioanal. Chem.* **2009**, 395, 1618.
- [2] J. C. Lynch, J. M. Brannon, J. J. Delfino, Dissolution Rates of Three High Explosive Compounds: TNT, RDX, and HMX, *Chemosphere* **2002**, 47, 725.
- [3] J. Yinon, *Toxicity and Metabolism of Explosives*, CRC Press, Boca Raton **1990**, p. 176.
- [4] E. J. Davis, P. Dwivedi, M. Tam, W. F. Siems, H. H. Hill, High-Pressure Ion Mobility Spectrometry, *Anal. Chem.* **2009**, 81, 3270.
- [5] R. Schulte-Ladbeck, P. Kolla, U. Karst, Trace Analysis of Peroxide-Based Explosives, *Anal. Chem.* **2003**, 75, 731.
- [6] A. Crowson, M. S. Beardah, Development of an LC/MS method for the Trace Analysis of Hexamethylenetriperoxidediamine (HMTD) *Analyst* **2001**, 126, 1689.
- [7] L. Widmer, S. Watson, K. Schlatter, A. Crowson, Development of an LC/MS Method for the Trace Analysis of Triacetone Triperoxide (TATP), *Analyst* **2002**, 127, 1627.
- [8] J. P. Hutchinson, C. J. Evenhuis, C. Johns, A. A. Kazarian, M. C. Breadmore, M. Macka, E. F. Hilder, R. M. Guijt, G. W. Dicinoski, P. R. Haddad, Identification of Inorganic Improvised Explosive Devices by Analysis of Postblast Residues Using Portable Capillary Electrophoresis Instrumentation and Indirect Photometric Detection with a Light-Emitting Diode, *Anal. Chem.* **2007**, 79, 7005.
- [9] P. Guerra, H. Lai, J. R. Almirall, Analysis of the Volatile Chemical Markers of Explosives Using Novel Solid Phase Micro-extraction Coupled to Ion Mobility Spectrometry, *J. Sep. Sci.* **2008**, 31, 2891.
- [10] M. E. Sigman, C. D. Clark, R. Fidler, C. L. Geiger, C. A. Clausen, Analysis of Triacetone Triperoxide by Gas Chromatography/Mass Spectrometry and Gas Chromatography/Tandem Mass Spectrometry by Electron and Chemical Ionization, *Rapid Commun. Mass Spectrom.* **2006**, 20, 2851.
- [11] G. A. Eiceman, J. Gardea-Torresdey, F. Dorman, E. Overton, A. Bhushan, H. P. Dharmasena, Gas Chromatography, *Anal. Chem.* **2006**, 78, 3985.
- [12] I. Cotte-Rodriguez, H. Hernandez-Soto, H. Chen, R. G. Cooks, In Situ Trace Detection of Peroxide Explosives by Desorption Electrospray Ionization and Desorption Atmospheric Pressure Chemical Ionization, *Anal. Chem.* **2008**, 80, 1512.
- [13] R. B. Cody, J. A. Laramée, H. D. Durst, Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions, *Anal. Chem.* **2005**, 77, 2297.
- [14] J. A. Laramée, R. B. Cody, Chemi-Ionization and Direct Analysis in Real Time (DART<sup>TM</sup>) Mass Spectrometry, in: M. L. Gross, R. M. Caprioli (Eds.), *The Encyclopedia of Mass Spectrometry*, Vol. 6, Ionization Methods, Elsevier, Amsterdam **2007**, p. 377.
- [15] J. A. Laramée, R. B. Cody, J. M. Nilles, H. D. Durst, Forensic Application of DART (Direct Analysis in Real Time) Mass Spectrometry, in: R. D. Blackledge (Ed.), *Forensic Analysis on the Cutting Edge: New Methods for Trace Evidence Analysis*, Wiley-Interscience, Hoboken, NJ **2007**, p. 175.
- [16] J. A. Laramée, H. D. Durst, T. R. Connell, J. M. Nilles, Detection of Chemical Warfare Agents on Surfaces Relevant to Homeland Security by Direct Analysis in Real-Time Spectrometry, *Am. Lab.* **2008**, 40, 16.

- [17] J. M. Nilles, T. R. Connell, H. D. Durst, Quantitation of Chemical Warfare Agents Using the Direct Analysis in Real Time (DART) Technique, *Anal. Chem.* **2009**, *81*, 6744.
- [18] F. M. Fernández, R. B. Cody, M. D. Green, C. Y. Hampton, R. McGready, S. Sengaloundeth, N. J. White, P. N. Newton, Characterization of Solid Counterfeit Drug Samples by Desorption Electrospray Ionization and Direct-analysis-in-real-time Coupled to Time-of-flight Mass Spectrometry, *ChemMedChem* **2006**, *1*, 702.
- [19] F. M. Fernandez, M. D. Green, P. N. Newton, Prevalence and Detection of Counterfeit Pharmaceuticals: A Mini Review, *Ind. Eng. Chem. Res.* **2008**, *47*, 585.
- [20] P. N. Newton, F. M. Fernandez, A. Plancon, D. C. Mildenhall, M. D. Green, L. Ziyong, E. M. Christophel, S. Phanouvong, S. Howells, E. McIntosh, P. Laurin, N. Blum, C. Y. Hampton, K. Faure, L. Nyadong, C. W. R. Soong, B. Santoso, W. Zhiguang, J. Newton, K. Palmer, A Collaborative Epidemiological Investigation into the Criminal Fake Artesunate Trade in South East Asia, *PLoS Med.* **2008**, *5*, e32.
- [21] P. N. Newton, C. Y. Hampton, K. Alter-Hall, T. Teerwarakulpana, S. Prakongpan, R. Ruangveerayuth, N. J. White, N. P. J. Day, M. B. Tudino, N. Mancuso, F. M. Fernández, Characterization of "Yaa Chud" Medicine on the Thailand–Myanmar Border: Selecting for Drug-resistant Malaria and Threatening Public Health, *Am. J. Trop. Med. Hyg.* **2008**, *79*, 662.
- [22] C. Petucci, J. Diffendal, D. Kaufman, B. Mekonnen, G. Terefenko, B. Musselman, Direct Analysis in Real Time for Reaction Monitoring in Drug Discovery, *Anal. Chem.* **2007**, *79*, 5064.
- [23] J. P. Williams, V. J. Patel, R. Holland, J. H. Scrivens, The Use of Recently Described Ionization Techniques for the Rapid Analysis of Some Common Drugs and Samples of Biological Origin, *Rapid Commun. Mass Spectrom.* **2006**, *20*, 1447.
- [24] R. B. Cody, J. A. Laramée, J. M. Nilles, H. D. Durst, Direct Analysis in Real Time (DART<sup>TM</sup>) Mass Spectrometry, *JEOL News* **2005**, *40*, 8.
- [25] M. J. Bennett, R. R. Steiner, Detection of Gamma-Hydroxybutyric Acid in Various Drink Matrices via AccuTOF-DART, *J. Forensic Sci.* **2009**, *54*, 370.
- [26] R. R. Steiner, R. L. Larson, Validation of the Direct Analysis in Real Time (DART) Source for Use in Forensic Drug Screening, *J. Forensic Sci.* **2009**, *54*, 617.
- [27] J. Schurek, L. Vaclavik, H. Hooijerink, O. Lacina, J. Poustka, M. Sharman, M. Caldow, M. W. F. Nielen, J. Hajslova, Control of Strobilurin Fungicides in Wheat Using Direct Analysis in Real Time Accurate Time-of-Flight and Desorption Electrospray Ionization Linear Ion Trap Mass Spectrometry, *Anal. Chem.* **2008**, *80*, 9567.
- [28] L. Vaclavik, J. Schurek, T. Cajka, J. Hajslova, Direct Analysis in Real Time–Time-of-Flight Mass Spectrometry: Analysis of Pesticide Residues and Environmental Contaminants, *Chem. Listy* **2008**, *102*, s324.
- [29] T. Cajka, L. Vaclavik, K. Riddellova, J. Hajslova, GC–TOF-MS and DART–TOF-MS: Challenges in the Analysis of Soft Drinks, *LC-GC Eur.* **2008**, *21*, 250.
- [30] R. W. Jones, R. B. Cody, J. F. McClelland, Differentiating Writing Inks Using Direct Analysis in Real Time Mass Spectrometry, *J. Forensic Sci.* **2006**, *51*, 915.
- [31] O. P. Haeffliger, N. Jeckelmann, Direct Mass Spectrometric Analysis of Flavors and Fragrances in Real Applications Using DART, *Rapid Commun. Mass Spectrom.* **2007**, *21*, 1361.
- [32] T. Cajka, L. Vaclavik, K. Riddellova, J. Hajslova, DART–TOFMS: A Challenging Approach in Rapid Monitoring of Brominated Flame Retardants in Environmental Matrices, *Organohalogen Compd.* **2008**, *70*, 922.
- [33] C. M. Coates, S. Coticone, P. D. Barreto, A. E. Cobb, R. B. Cody, J. C. Barreto, Flammable Solvent Detection Directly from Common Household Materials Yields Differential Results: An Application of Direct Analysis in Real-Time Mass Spectrometry, *J. Forensic Identif.* **2008**, *58*, 624.
- [34] J. Y. Yew, R. B. Cody, E. A. Kravitz, Cuticular Hydrocarbon Analysis of an Awake Behaving Fly Using Direct Analysis in Real-Time Time-of-Flight Mass Spectrometry, *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 7135.
- [35] K. Kpegba, T. Spadaro, R. B. Cody, N. Nesnas, J. A. Olson, Analysis of Self-Assembled Monolayers on Gold Surfaces Using Direct Analysis in Real Time Mass Spectrometry, *Anal. Chem.* **2007**, *79*, 5479.
- [36] C. Y. Pierce, J. R. Barr, R. B. Cody, R. F. Massung, A. R. Woolfitt, H. Moura, H. A. Thompson, F. M. Fernandez, Ambient Generation of Fatty Acid Methyl Ester Ions from Bacterial Whole Cells by Direct Analysis in Real Time (DART) Mass Spectrometry, *Chem. Commun.* **2007**, *8*, 807.
- [37] N. J. Smith, M. A. Domin, L. T. Scott, HRMS Directly From TLC Slides. A Powerful Tool for Rapid Analysis of Organic Mixtures, *Org. Lett.* **2008**, *10*, 3493.
- [38] T. M. Vail, P. R. Jones, O. D. Sparkman, Rapid and Unambiguous Identification of Melamine in Contaminated Pet Food Based on Mass Spectrometry with Four Degrees of Confirmation, *J. Anal. Toxicol.* **2007**, *31*, 304.
- [39] JEOL AccuTOF mass spectrometer with DART application notes, at <http://www.jeol.com/HOME/tabid/36/Default.aspx>.
- [40] L. Song, A. B. Dykstra, H. Yao, J. E. Bartmess, Ionization Mechanism of Negative Ion – Direct Analysis in Real Time: A Comparative Study with Negative Ion-Atmospheric Pressure Photoionization, *J. Am. Soc. Mass Spectrom.* **2009**, *20*, 42.
- [41] L. Song, A. D. Wellman, H. Yao, J. E. Bartmess, Negative Ion-Atmospheric Pressure Photoionization: Electron Capture, Dissociative Electron Capture, Proton Transfer, and Anion Attachment, *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 1789.
- [42] R. T. Chamberlain, *Dry Transfer Method for the Preparation of Explosives Test Samples*, US Patent 6,470,730, **2002**, The USA as represented by the Secretary of Transportation, Washington D.C., USA.
- [43] R. C. Dorey, W. R. Carpert, Synthesis and High-Resolution Mass-Spectral Analysis of Isotopically Labeled 2,4,6-Trinitrotoluene, *J. Chem. Eng. Data* **1984**, *29*, 93.

# Acknowledgements

We thank the Defense Threat Reduction Agency, the Joint Science and Technology Office (JSTO), and the DoD Chemical and Biological Defense Program for their support. We also thank Dr. Fred Berg, Augustus W. Fountain, and David Tevault for their advice and support and Robert Juliano for his assistance. This document is UNCLASSIFIED and is cleared for unlimited public release.