Cyclic Organic Peroxides Characterization by Mass Spectrometry and Raman Microscopy

Alvaro J. Pena-Quevedo, James A. Laramee, H. Dupont Durst, Samuel P. Hernandez-Rivera

Triacetone triperoxide and hexamethylene triperoxide diamine are among the most used and most studied non-nitro based high explosives. Still, there are other peroxides which do not have reported methods for their detection. Direct Analysis in Real Time is an emerging ambient pressure ionization technique in mass spectrometry (MS). This contribution presents the analysis, characterization and detection of triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) using DART. Although typical experiments are done using helium, adding a small amount of ammonium hydroxide improved the detection.

Benzoyl peroxide, cyclic organic peroxides, DART, hexa-methylene triperoxide diamine (HMTD), triacetone triperoxide (TATP), TATP-d18, triacetone triperoxide (TATP), time-of-flight–mass spectrometry (TOF–MS).
ABSTRACT

Triacetone triperoxide and hexamethylene triperoxide diamine are among the most used and most studied non-nitro based high explosives. Still, there are other peroxides which do not have reported methods for their detection. Direct Analysis in Real Time is an emerging ambient pressure ionization technique in mass spectrometry (MS). This contribution presents the analysis, characterization and detection of triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) using DART. Although typical experiments are done using helium, adding a small amount of ammonium hydroxide improved the detection limit to 30 ppb. This study also presents the detection and identification of benzoyl peroxide, tricyclopentanone triperoxide and tetramethylene diperoxide dicarbamide (TMDD) by MS and Raman microscopy. TATP showed a single peak at m/z 240.144 [M + NH4+] with the peaks at m/z 223.118 [M + H]+ or 222.110 [M+] completely absent. Deuterium enriched (TATP-d18) was analyzed for comparison. These presented a similar peak at m/z 258.267 [TATP-d18 + H]. HMTD showed a peak at m/z 209.078 [M + H]+ and small adduct peak at m/z 226.103 [M + H]+ that allowed its detection in standard solution and lab made samples. TMDD showed several peaks with a base peak at m/z 101.033, molecular peak at m/z 237.081 [M + H]+ and a strong ammonium adduct at m/z 254.108 [M + NH4+] + H+. All samples were analyzed by Raman Microscopy in order to characterize them and to confirm the MS results.
Continuation for Block 13

ARO Report Number 58949.37-PH-REP
Cyclic Organic Peroxides Characterization by M...

Block 13: Supplementary Note
© 2011. Published in IEEE Sensors Journal, Vol. Ed. 0 11, (4) (2011), (, (4). DoD Components reserve a royalty-free, nonexclusive and irrevocable right to reproduce, publish, or otherwise use the work for Federal purposes, and to authorize others to do so (DODGARS §32.36). The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

Approved for public release; distribution is unlimited.
Cyclic Organic Peroxides Characterization by Mass Spectrometry and Raman Microscopy

Alvaro J. Peña-Quevedo, James A. Laramee, H. Dupont Durst, and Samuel P. Hernández-Rivera

Abstract—Triacetone triperoxide and hexamethylene triperoxide diamine are among the most used and most studied non-nitro based high explosives. Still, there are other peroxides which do not have reported methods for their detection. Direct Analysis in Real Time is an emerging ambient pressure ionization technique in mass spectrometry (MS). This contribution presents the analysis, characterization and detection of triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) using DART. Although typical experiments are done using helium, adding a small amount of ammonium hydroxide improved the detection limit to 30 ppb. This study also presents the detection and identification of benzoyl peroxide, tricyclopentanone triperoxide and tetramethylene diperoxide dicarbamide (TMDD) by MS and Raman microscopy. TATP showed a single peak at m/z 240.144 [M + NH₄]⁺ with the peaks at m/z 223.118 [M + H]⁺ or 222.110 [M]⁺ completely absent. Deuterium enriched (TATP – d₁₈) was analyzed for comparison. These presented a similar peak at m/z 258.267 [TATP – d₁₈ + NH₄]⁺. HMTD showed a peak at m/z 209.078 [M + H]⁺ and small adduct peak at m/z 226.103 [M + NH₄]⁺ that allowed its detection in standard solution and lab made samples. TMDD showed several peaks with a base peak at m/z 101.033, molecular peak at m/z 237.081 [M + H]⁺ and a strong ammonium adduct at m/z 254.108 [M + NH₄]⁺. All samples were analyzed by Raman Microscopy in order to characterize them and to confirm the MS results.

Index Terms—Benzoyl peroxide, cyclic organic peroxides, DART, hexa-methylene triperoxide diamine (HMTD), triacetone triperoxide (TATP), TATP – d₁₈, triacetone triperoxide (TATP), time-of-flight–mass spectrometry (TOF–MS).

I. INTRODUCTION

W IDESPREAD use of organic peroxides in terrorist acts has required government security agencies to evaluate new technologies for the detection of these compounds [1], [2].

Manuscript received May 18, 2009; accepted May 18, 2009. Date of publication September 23, 2009; date of current version February 11, 2011. This work was supported in part by the Center for Chemical Sensors Development and the Department of Chemistry at the University of Puerto Rico-Mayaguez is sponsored by the Defense of Defense, University Research Initiative-Multi-disciplinary University Research Initiative (URI-MURI) Program under Grant DAAD19-02-1-0257 and by the U.S. Department of Homeland Security under Award 2008-ST-061-ED0001. A. J. Peña-Quevedo is with the Department of Chemistry, University of Puerto Rico-Mayaguez, Mayaguez, Puerto Rico 00681 (e-mail: alvarojp@gmail.com). J. A. Laramee is with EAI Corporation, Abingdon, MD 21009 (e-mail: james.a.laramee@us.army.mil). H. D. Durst is with Edgewood Chemical Biological Center, Aberdeen Proving Grounds, MD 21010 USA (e-mail: horatio.d.durst@us.army.mil). S. P. Hernández-Rivera is with the Center for Sensors Development, Department of Chemistry, University of Puerto Rico-Mayaguez, Mayaguez, Puerto Rico 00681 (e-mail: sp_hernandez_uprm@yahoo.com). Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/JSEN.2010.2057730

In 1983, the first forensic analysis and characterization of TATP by electron ionization (EI) and chemical ionization (CI) mass spectrometry (MS) [5] was reported. Characterization of HMTD by x-ray analysis to determine its structure was published in 1985 [6]. Later, in 1988, HMTD was fully characterized by nuclear magnetic resonance (NMR), Raman and infrared (IR) spectroscopies [7]. One of the first HMTD mass spectra was presented in 2000 [8]. In the same year, gas chromatography–mass spectrometry (GC–MS) based methodologies for TATP and diacetone diperoxide (DADP) detection at picogram levels were presented [9]. In 2001, a method for HMTD detection was described using high performance liquid chromatography–mass spectrometry (HPLC–MS) [10]. Later in the same year, the shoe-bomber case further motivated peroxide-based explosives detection [11]. In 2002, detection methods for TATP were described using HPLC separation, post column derivatization, MS analysis [12], and direct HPLC–MS analysis [13]. GC-electron capture detector (ECD) was used to observe TATP and HMTD decomposition products and these studies included essential thermal properties for further analysis by other techniques [14]–[16]. In addition, a theoretical proposition of a method for detection using metal cations was presented [17]. In 2003, a method for detection of TATP in air was developed [18]. This work was followed by a method to detect TATP using ion mobility spectrometry (IMS) [19]. A year later, TATP trace detection methods for GC–MS were performed using headspace analysis [20] and Solid Phase Micro Extraction [21]. Also in 2004, a method for TATP and HMTD analysis using HPLC–MS–MS was presented [22]. In 2005, methods for acetone peroxide analysis using GC–MS, GC–FTIR and Raman microscopy were discussed [23].

Due to novel advances in MS, 2006 witnessed a significant increment in studies of peroxide detection. A selected-ion flow-tube mass spectrometer was developed for TATP detection that provided 10 ppb detection levels [24]. The introduction of desorption electrospray ionization (DESI) was very useful for atmospheric pressure analysis of acetone peroxides reaching 15 ng detection limit but at a signal-to-noise ratio of only 20 [25]. Also, laser desorption–MS was used to analyze TATP, 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) with 40 ppb detection levels [26]. Methodologies for TATP, HMTD, and other peroxides were developed using IMS, direct insertion probe MS and Raman scattering microscopy in pure form and...
spiked with metal salts that could be present in the crude products [27], [28]. Later in the same year, several methodologies for TATP detection were compared: GC–MS with electron ionization (EI) and chemical ionization (CI) [29]. Positive ion CI was induced using ammonium ion to generate a molecular adduct at m/z 240. This method enabled the detection of picograms levels of TATP. Finally, the computational method proposed earlier was proven by electrochemical detection of HMTD and TATP using a Prussian-blue electrode [30]. In 2007, open-air chemical ionization (OACI)-TOF–MS was used to detect TATP, HMTD, and other peroxides, and the results were compared with EI [2], [31], [32]. The instrument used is commercially termed DART™ which is the contraction for “Direct Analysis in Real Time” used by JEOL-USA for OACI-MS. The heart of this technique is an ionizing jet of “metastable” helium that impinges on the sample to be analyzed. The ionization occurs at atmospheric pressure and ions of the material under analysis pass through an orifice and into a high resolution time of flight (TOF) mass spectrometer (MS). Recently, DESI was compared with desorption atmospheric pressure chemical ionization. The results showed that DESI formed adduct ions with Na⁺, K⁺ and NH₄⁺ [33]. These multiple representations of the analyte complicate the interpretation of the spectrum. In addition, a simple method for TATP analysis using electrospray ionization (ESI) direct injection was presented to demonstrate fragmentation of TATP under these conditions [34]. Recent work focused on the analysis of TATP and its decomposition products by GC–MS using diluted sample insertion and solid phase micro extraction (SPME) [35].

This paper presents syntheses of cyclic organic peroxides, some of which are new and others were prepared for the study. Vibrational spectroscopy was used for characterization of known organic peroxides TATP, HMTD, benzoyl peroxide (BP), cyclopentanone triperoxide, and cyclic amide peroxide: tetramethylene diperoxide dicarbamide (TMDD). Raman spectroscopy was also used for purity check and in some cases as the only means for determining the success of the synthetic methods utilized. High resolution TOF measurements allowed peroxides to be identified even in complex mixtures. EI–MS and OACI–MS were compared and contrasted in organic peroxides characterization. Isotopic labeling experiments were used to help elucidate MS fragmentation mechanisms and assist in peak assignments for both MS and Raman spectroscopy spectra. One of the main contributions of this work is the validation of a fast, chemical preparation free, solventless methodology for home made explosives detection, including cyclic organic peroxides: OACI-TOF–MS was used as mass spectroscopic characterization tool and as a means of detecting these important chemical threats in ambient pressure in situ analysis mode.

II. PROCEDURES

A. Instrumentation

Vibrational characterization of cyclic organic peroxides was carried out using a Renishaw Raman Microspectrometer model RM2000 Renishaw, Inc. (Chicago, IL) equipped with CCD detector and Leica LM/LS microscope using an ultra long working distance 50X objective. HMTD, TATP, TATP-d₁₈, TMDD and cyclopentanone triperoxide spontaneous Raman analysis was accomplished at excitation lines: 488, 514, 532, and 785 nm using laser power at sample of < 10 mW. The excitation sources were INNOVA 308 Ar⁺ laser system wavelength selected for 488 nm blue line and 514.5 nm green line; VERDI-6 diode-pumped 532 nm laser with a variable output power of up to 6 W; and 899-01 Titanium/Sapphire ring laser operating at 785 nm pumped by the 532 nm laser (all laser systems from Coherent Laser Group, Santa Clara, CA.). Raman spectra were collected in the Raman Shift range of 100–4000 cm⁻¹, with three acquisitions and integration time of 10 s per scan. Dispersive Raman equipment was operated in confocal mode. Fourier transform infrared (FTIR) spectrometer used was a Thermo-Nicolet FT-IR spectrometer Nexus E.S.P with attenuated total reflectance (ATR) accessory and Bruker Optics model IFS 66 v/S FT-IR microscope.

An Agilent Technologies gas chromatograph model GC–MS 5890 GC system coupled to a 5790 mass selective detector was used in electron ionization (EI) mode-mass spectroscopy experiments. A JEOL GC-MateII direct probe system was also used to analyze by EI at 70 eV. A DART-TOF–MS (JEOL, USA, Inc., Peabody, MA) was used for the atmospheric pressure-CI–MS experiments.

B. Reagents

Chemical reagents used in this research included d₅-acetone (99% isotope), acetone, cyclopentanone, hexamethylene tetramine, benzoyl peroxide (98% w/w), and formaldehyde (CH₂O, 37% wt), all obtained from Acros-Organics, Fairlawn, NJ. Hydrogen peroxide (H₂O₂, 50%) and urea (98% w/w) were obtained from Fisher Scientific International, Fairlawn, NJ. Hydrochloric acid (HCl, 12 M, VWR International, Inc., West Chester, PA) was used as catalytic agent. High purity acetonitrile Omnisolv (GC/HPLC/gradient analysis grade) was obtained from EMD Chemicals Inc., Gibbstown, NJ.

C. Preparation of Cyclic Organic Peroxides

HMTD and TATP, although commercially available as GC–MS standards (1 mg/mL), were synthesized to have a relatively large supply for the study. Recrystallized samples had lower impurities than commercial samples. Other cyclic organic peroxides were not commercially available and had to be synthesized and purified. White light images of TATP, cyclopentanone, HMTD and TMDD show well ordered crystals [Fig. 1(a)–(d)].
D. TATP, d18-TATP and Cyclopentanone Triperoxide

TATP, d18-TATP and cyclopentanone were synthesized following Wolffstein’s original procedure [36]. The reaction mixture as crystallized by ether evaporation and then purified by sublimation at a constant temperature of 80°C.

E. Hexamethylene Triperoxide Diamine, HMTD

HMTD was synthesized following the method used by Von Girsewald [37]. The crystals were filtered out and washed with water. Due to the low yield of preparation, no purification was performed.

F. Tetramethylene Diperoxide Dicarbamide, TMDD

TMDD was prepared using Von Girsewald and Siegen method [38]. After three days of standing at 0°C in a refrigerator, a white powder-like substance was obtained. This precipitate was filtered with a Büchner funnel and washed with distilled water. The crude product was allowed to dry and recovered.

G. Ambient Pressure Chemical Ionization MS Analysis

Stock solutions of 1.0 mg/mL of TATP, d18-TATP, BP, HMTD, and TMDD were prepared in acetonitrile. The sealed end of a capillary tube was dipped into the solutions and placed in the ambient pressure ionization zone (Fig. 2). Quantitative measurements were made using a 2 μL micropipette to aliquot an accurate amount of sample onto the capillary. Ammonium hydroxide can be used as an adduct forming agent in some types of compounds [31]. The use of NH4+ as an adduct formation promoter is routinely used for CI-MS analysis of ketones, acids, alcohols, and other oxygen-rich compounds such as peroxides and ethers [29], [39]. The effect of addition of a source of ammonium ions was investigated for organic peroxides studied.

III. RESULTS AND DISCUSSION

A. Raman Spectroscopy

Raman spectroscopy is an ideal technique for characterizing peroxides. The oxygen-oxygen bond vibration is unique to the peroxide moiety since it defines its chemical structure. These vibrations occur at 1000 cm⁻¹, 880 cm⁻¹, and 870 cm⁻¹. These same bands were also observed for cyclopentanone triperoxide. The large vibrational shift of the methyl group upon substitution of CH3 for the CD3 moiety was used to differentiate TATP from d18-TATP. The higher mass of the deuterium atoms causes the methyl stretching to shift from 3000–2700 cm⁻¹ for TATP to 2300–2000 cm⁻¹ for d18-TATP (Fig. 3). Using these data, the degree of deuterium isotope incorporation was estimated at 99 atom %.

HMTD and TMDD exhibited similar methylene vibrational bands ca. 2990–2830 cm⁻¹. Characteristic peroxide bands were observed in the range of 980–900 cm⁻¹ and near 770 cm⁻¹. Our HMTD results compare well with previous results [7]. No reference data for TMDD was found. The principal evidence of the synthesis of a carbamide compound is the strong absorption of the N-H stretching at 3336 cm⁻¹ in FTIR absorption and 3346 cm⁻¹ in Raman scattering [40], [41]. Urea has a strong carbonyl absorption in the range of 1700–1600 cm⁻¹; TMDD also showed the presence of this vibrational signature.

In the IR spectra, strong absorptions in the range of 1500–1660 cm⁻¹ demonstrate the presence of a carbonyl group. The corresponding Raman signal was observed about 1650–1770 cm⁻¹. Characterization of the nitrogen-carbon bond present in amides can be observed at 1253, 1296, and 1127 cm⁻¹ \(\nu(N\cdotsO)\). These results not only verify that TMDD was prepared but predicts a possible structure for it.

B. GC–MS

GC–MS using electron impact ionization is a common analytical technique. A weak molecular ion is produced for the fragile TATP molecule. (Fig. 4), and abundant fragment ions at \(m/z\) 117 \([C_5H_9O_3]^+\), 101 \([C_5H_9O_2]^+\), 75 \([C_3H_6O_2]^+\), 59 \([C_3H_7O]^+\), 58 \([C_3H_6O]^+\) and a base peak at \(m/z\) 43 \([C_2H_3O]^+\) were observed.

The identity of the fragment ions is supported by predicted mass shifts for the d18-TATP analog, these are \(m/z\) 126 \([C_5D_9O_3]^+\), 110 \([C_5D_9O_2]^+\), 82 \([C_3D_7O_2]^+\), 66 \([C_3D_7O]^+\),...
64 [C$_3$D$_6$O]$^+$ and the base peak at m/z 46 [C$_2$D$_3$O]$^+$ (Fig. 5). The presence of these fragments together with the Raman results was used to characterize and verify the synthesis of TATP and of d$_{18}$TATP. GC/MS also showed a single peak in the chromatograms which confirms its purity.

On the other hand the low vapor pressure of HMTD impedes a determination of its purity by GC methods, which are overcome using a direct insertion probe. HMTD showed a strong molecular ion at m/z 208 and compares well with literature results [8], [15]. Fragment ions were seen at m/z 176 (loss of oxygen molecule) and m/z 88. Other typical fragments were observed at m/z: 149, 117, 112, 104, 73, 59, 58, 45 [CH$_2$NO]$^+$, 42 [CH$_2$NCH$_2$]$^+$, 32, 31, and 30 [CH$_4$N]$^+$.

C. Cyclic Ketone Peroxides and Benzoyl Peroxide

Some of the organic peroxides studied did not produce molecular peaks of significantly intensity when ionized with the APCI source. Instead, the formation of an adduct peak with ammonium was observed. To increase the molecular adduct peak signal in these peroxides, aqueous ammonium hydroxide was placed in the ionization region. This simple improvement enhanced the production of peroxide molecular adduct ions, even at relatively high temperatures (200 °C).

Benzoyl peroxide (BP) was analyzed by ambient pressure ionization–MS because it is commercially available and it is extensively used in medical treatments. BP has a molecular mass of 242.06 g/mol. API–MS produced a strong peak at m/z 260.09 [BP + NH$_4$]$^+$ (Fig. 6). The next peak of significant intensity was located at m/z 216.106 could be observed under certain conditions. This signal can be assigned to [M + NH$_4$-CO$_2$]$^+$. By changing the temperature of the ionization chamber additional fragmentation was observed.

TATP was analyzed at different temperatures and in contrast with GC/EI–MS that requires low detector temperatures, API–MS analysis with NH$_4$OH vapor produced the molecular adduct at 200 °C, above TATP flash point at 150 °C. Fig. 7 shows the mass spectrum of TATP which presents a molecular adduct at m/z 240.146 [TATP + NH$_4$]$^+$. No molecular peaks were observed at m/z 222.110 [TATP]$^+$ or at m/z 223.118 [TATP + H]$^+$. These results indicate that ammonium hydroxide stabilized the ionization of TATP and increased its detection. This property was also observed when d$_{18}$-TATP was analyzed by API–MS. A strong peak was observed at m/z 258.258 [d$_{18}$-TATP + NH$_4$]$^+$ with complete absence of signals at m/z 240.223 [d$_{18}$-TATP]$^+$ and at m/z 241.231 [d$_{18}$-TATP + H]$^+$ (Fig. 8).

Cyclopentanone triperoxide showed also a similar behavior as TATP, at m/z 318.190 [M + NH$_4$]$^+$ (Fig. 9). m/z 0.059 belongs to an ion that is ascribed to an oxidized form of cyclopentanone, [C$_5$H$_9$O$_2$]$^+$. This peak can be attributed to a contaminant or a decomposition product of the peroxide studied.

D. Amine and Amide Peroxide: HMTD and TMDD

HMTD has low solubility in most common solvents used and very low vapor pressure, which limits analysis by GC. It
is slightly soluble in chloroform, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). TMDD is insoluble in most organic solvents. This hampers most chromatographic analysis, including GC and HPLC. API-TOF–MS provided an excellent method for detection with considerably low detection limits. Other MS analysis methods were tried including GC/EI–MS and HPLC/EI–MS and direct insertion probe EI–MS, but results were limited by the low solubility of TMDD in the solvents tested and its extremely low vapor pressure.

E. TATP and HMTD Mixture Analysis

The soft chemical ionization that promotes the formation of the molecular ion or its adducts accompanied with minimum fragmentation, in most cases, combined with high mass resolution of the reflector TOF allowed identification of mixtures of peroxides and differentiation of fragments with possible interferences. When a sample of TATP was placed in the APCI stream it was common to observe a peak at m/z 226.114 [M + NH₄]⁺, showing an ammonium ion adduct peak [M + NH₄]⁺ at m/z 252.111. When NH₄⁺ vapor was added, TMDD behaved similar to TATP, showing a strong molecular adduct ion [1]. Fig. 11 shows TMDD mass spectrum with API-TOF–MS at low inlet temperature (150 °C). Even at this low temperature considerable fragmentation was observed with peaks at m/z 189.062, 175.083, 161.068, 146.058, 130.062, 118.061, and 102.069. To our knowledge, these results represent the only reported method of analysis for TMDD characterization and detection. Other MS analysis methods were tried including GC/EI–MS and HPLC/EI–MS and direct insertion probe EI–MS, but results were limited by the low solubility of TMDD in the solvents tested and its extremely low vapor pressure.

Initially, TMDD required a higher ionization port temperature to detect the MS spectrum. Mass spectrum was optimally collected at inlet port temperature of 180 °C, close to its melting point. At this temperature TMDD showed the molecular peak at m/z 237.085 [TMDD + H]⁺, similar to HMTD, but considerable fragmentation was also observed. After the first mass spectrum was obtained and confirmed using different ionization port conditions including using NH₄OH to generate NH₄⁺ dopant, it was possible to lower the inlet port temperature to 150 °C showing an ammonium ion adduct peak [M + NH₄]⁺ at m/z 252.111. When NH₄⁺ vapor was added, TMDD behaved similar to TATP, showing a strong molecular adduct ion [1]. Fig. 11 shows TMDD mass spectrum with API-TOF–MS at low inlet temperature (150 °C). Even at this low temperature considerable fragmentation was observed with peaks at m/z 189.062, 175.083, 161.068, 146.058, 130.062, 118.061, and 102.069. To our knowledge, these results represent the only reported method of analysis for TMDD characterization and detection. Other MS analysis methods were tried including GC/EI–MS and HPLC/EI–MS and direct insertion probe EI–MS, but results were limited by the low solubility of TMDD in the solvents tested and its extremely low vapor pressure.
ion source coupled with the high mass accuracy of the AccuTOF mass spectrometer allowed rapid and accurate determination of the peroxide explosives. In contrast, other chromatographic based methods coupled to mass spectrometric detection require a factor of 100× longer analysis time.

TATP and HMTD ionize by different CI mechanisms to produce different types of molecular ion adducts, even when both chemicals are ionized simultaneously in situ. In the case of TMDD, the formation of both types of molecular ion adducts was observed, although the adduct form with NH₄⁺ was more intense. In contrast to other organic peroxides analyzed by OS–MS, TMDD produced profuse fragmentation. Some TMDD fragments were identified. The possibility of achieving parts-per-billion to parts-per-trillion detection levels without sample preparation in open air sampling makes OA–MS an attractive technique for defense and security applications.

IV. CONCLUSION

A method for detecting organic peroxide explosives using ambient pressure chemical ionization–mass spectrometry (API–MS) was presented. The high speed analysis of DART ionized by different mechanisms. This is useful because the analyte is detected without regard to ionizing preparation conditions. This is not the case with other ionization techniques, such as DESI. There both compounds share a similar behavior regarding the type of adducts generated, and it depends upon the preparation conditions rather than on the analyte. Although quantitative assessment of detection limits for TATP and HMTD was not done, an estimate of the detection capability for both compounds was obtained by diluting a 350 ppm stock solution mixture of the explosives by a factor of 10 and transferring two microliters to the sampling capillary tube. This corresponded to 70 pg of TATP and HMTD and resulted in a signal to noise ratio (S/N) of 70 pg of TATP and HMTD and resulted in a signal to noise ratio (S/N) of 150 °C. experiments for lower detection limits are in progress but somewhat hindered by the fast decomposition of HMTD and the increase in the relative abundance of the fragments ions at m/z 179 and 145.

ACKNOWLEDGMENT

The authors would like to thank Dr. R. B. Cody of JEOL USA, Inc., Peabody MA, and Miss. M. R. Ramos-Torres for their help and collaborations. Collaboration with the Chemical Imaging Center of the Department of Chemistry of the University of Puerto Rico-Mayagüez is also acknowledged.

REFERENCES


Álvaro J. Peña-Quevedo was born in Hato Rey, Puerto Rico. He received the B.S. degree in chemistry and mathematics from the Interamerican University of Puerto Rico, San German, the M.S. degree in chemistry from the University of Puerto Rico-Mayagüez (UPRM), and is currently pursuing the Ph.D. degree in applied chemistry (material sciences) at UPRM.

He works as a Research Chemist for the Center for Chemical Sensor Development at UPRM-Mayagüez. His research interests are related to method development for organic peroxide detection and the characterization of uncommon organic peroxides by novel techniques.

Mr. Peña-Quevedo is a member of the American Chemical Society and Puerto Rico Chemist Association.

James A. Laramée has been the Principal Scientist at EAI Corporation (SAIC subsidiary), Abingdon, MD, since 2002. He is a SERC Research Fellow Warwick University, Warwick. He was a faculty member at Oregon State University of Agricultural Chemistry, and Associate at the National Institutes of Health Environmental Health Sciences Center. His areas of expertise are analytical chemistry of chemical warfare agents, environmental toxins, explosives, design and construction of analytical instrumentation, originator and inventor of the direct analysis in real time (DART), and algorithm development in discrete mathematics.

H. DuPont Durst has been a Research Chemist at Edgewood Chemical Biological Center, Aberdeen, MD, since 1984. He was a member of the chemistry faculty at State University of New York at Buffalo and University of Puerto Rico at Rio Piedras. His areas of interest are chemical reactivity of organic phosphorus and other military unique compounds; mechanisms and utilization of organophosphorus media; trace analysis, both qualitative and quantitative, of organic materials in the environment; sensors for “real-time” detection of toxic vapors; defense-related experience: decontamination protection and detection of chemical warfare agents.

Álvaro J. Peña-Quevedo

James A. Laramée

H. DuPont Durst
Samuel P. Hernández-Rivera received the B.S. and M.S. degrees from the University of Puerto Rico, Mayagüez (UPRM) and the Ph.D. degree from the Johns Hopkins University, Baltimore, MD.

He is currently a Professor of physical chemistry in the Department of Chemistry, UPRM. He is the Director of the DoD-MURI sponsored Center for Sensors Development and the UPRM based Chemical Imaging Center. His research interests are in IR/Raman microspectroscopies in applied and fundamental studies and standoff and point detection of explosives, chemical, and biological agents using vibrational spectroscopy. Other interests are in SERS and in chemometrics enhancement of spectroscopic data and discriminant and cluster analysis of populations.

Dr. Hernández-Rivera is a member of the American Chemical Society, American Physical Society, Sigma Xi, Phi Kappa Phi, Society for Photo-Optical Instrumentation Engineers (SPIE) and Puerto Rico Chemists Association. He is also member of the editorial board of Sensing and Imaging: An International Journal.