Full Paper

Direct Detection of Triacetone Triperoxide (TATP) in Real Banknotes from ATM Explosion by EASI-MS

Deleon Nascimento Correa,*[a, d] Jose J. Melendez-Perez,[a] Jorge Jardim Zacca,[b] Rodrigo Borges,[c] Eduardo Morgado Schmidt,[a] Marcos Nogueira Eberlin,[a] and Eduardo César Meurer[e]

Abstract: In Brazil, automated teller machine (ATM) has become a major target of theft incursions toward explosion. Efficient analysis of explosives residues on suspect banknotes is a serious issue in forensic labs, and guide to the crime solution. Easy ambient sonic-spray ionization mass spectrometry (EASI-MS) is shown to be a simple and selective screening tool to identify peroxide explosives on real banknotes collected from ATM explosion. Analyses were carried out directly on the banknotes surfaces without any sample preparation, identifying triacetone triperoxide (TATP) and diacetone diperoxide (DADP). Homemade EASI source was coupled to ultrahigh-resolution and ultrahigh accuracy FT-ICR MS and revealed the ion of m/z 245 correspondent to sodiated TATP $[C_9H_{18}O_6Na]^+$ and the ion of m/z 171 related to sodiated DADP $[C_6H_{12}O_4Na]^+$, ions that is the sodiated DADP and the ions of m/z 173 and 189 related to $[C_6H_{14}O_4Na]^+$ and $[C_6H_{14}O_4K]^+$, respectively, which are associated to chemical markers of TATP domestic route synthesis. EASI source coupled to a single quadrupole mass spectrometer provides an intelligent and simple way to identify the explosives TATP, DADP and its domestic synthesis markers.

1 Introduction

Explosives might be exalted as one class of compounds with high interest for humanity, used to open transport channels, and to help to extract commodities allowing human kind to achieve high technological level. Open access to information for everybody may lead us to experience even higher levels of development. Otherwise the open access to explosive synthesis may expose the society to a variety of dangerous artifacts facilitating criminals to commit offenses to civil people, and their goods.

Commercialization of pure reagents is regulated by the army, but criminals may obtain in internet their recipes and bulletin boards on how to prepare peroxides explosives using diluted reagents making the control task difficult to achieve properly. Although triacetone triperoxide (TATP) and diacetone diperoxide (DADP) present poorer performance as compared to other explosives [e.g. trinitrotoluene (TNT), for example], these peroxides easily fulfil the requisites that criminals are looking for and become illicit explosives of choice (Figure 1) in Brazil [1].

TATP is a sensitive and easily-produced explosive, used traditionally by terrorist organizations, but also have been produced by "garage chemists" and clandestine drug manufacturers. The popular appeal of TATP in terrorist bombings might be related to their straightforward synthesis using readily available precursor chemicals, such as acetone and hydrogen peroxide [2], and recently have been using in improvised explosive artifacts with chemicals easily obtained from local pharmacies [3]. TATP was first discovered by Richard Wolffenstein [4] in 1895. There are many protocols to synthesize TATP and DADP, but basically its synthesis route starts reacting ketone with hydrogen peroxide in a acid solution [5, 6] or in a neutral solution [7, 8] forming 1,1′-dihydroxypropyl peroxide [9] an important intermediary that forms DADP by ring closing, and subsequently react again

[a] D. Nascimento Correa, J. Melendez-Perez, E. Morgado Schmidt, M. Eberlin
ThoMSon Mass Spectrometry Laboratory
Department of Analytical Chemistry, Institute of Chemistry
University of Campinas – UNICAMP
13083–970 Campinas, SP, Brazil
*e-mail: deleon17@gmail.com

[b] J. Jardim Zacca
Brazilian Federal Police
Scientific and Technical Dept.
70037–900, Brasília, DF, Brazil

[c] R. Borges
National Institute of Metrology
Quality and Technology – INMETRO
25250–020, Duque de Caxias, RJ, Brazil

[d] D. Nascimento Correa
Technical-Scientific Police Superintendency from São Paulo State
Criminalistic Institute
05507–060, São Paulo, SP, Brazil

[e] E. Meurer
Fenn Laboratory of Mass Spectrometry
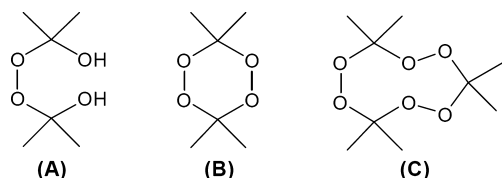Federal University of Paraná
Paraná, Brazil

D. Nascimento Correa et al.

Figure 1. (A) 1,1′-Dihydroxypropyl peroxide (DHPP) observed as sodiated adduct at *m/z* 173, (B) diacetone diperoxide (DADP) observed as sodiated adduct at *m/z* 171, and (C) triacetone triperoxide (TATP) observed as sodiated adduct at *m/z* 245.

with ketone forming an eight membered ring TATP (Figure 1).

Recently, explosives have been used in Brazil applied to explode Automated Teller Machines (ATMs) [10, 11] that are somehow exposed to this kind of robbery [12]. About to TATP and related peroxides explosives, there are four main reasons why these explosives are so alluring to thefts: (1) they are cheap and easy to make in large quantities from non-controlled materials; (2) they present a high explosive yield, possessing about 83 % of TNT's power; (3) in contrast to other commercial explosives such as TNT or RDX, they can be detonated without a blasting or similar detonator; and (4) they are difficult to detect by traditional security methods.

In forensic science and in the specific field of explosive analysis, TATP has been detected using numerous techniques and a variety of analytical methodologies. Both infrared and Raman spectroscopy [13, 14] have been used in the non-destructive forensic analysis of explosives, however, they present some drawbacks such as high demands on data processing, very similar spectra, and the occurrence of matrix effects. Gas chromatography/mass spectrometry (GC/MS) [2, 15–17], liquid chromatography/mass spectrometry (LC/MS) [18] and ion mobility spectrometry (IMS) [19–21] have all been reported in the analysis of TATP, although sample preparation procedures are usually time-consuming and may result in irreparable harm to the sample, which is not convenient in forensic applications.

Recently, a new class of ionization sources named as ambient mass spectrometry [22–25] has been developed. These techniques allow desorption, ionization, and mass spectrometry characterization of volatile and nonvolatile analytes directly from their natural surfaces and matrixes in an open atmosphere with little or no prior sample work up, becoming an attractive tool for direct characterization of forensic analytes in suspect objects surfaces allowing for sample preservation [26]. A set of these ambient ionization techniques, desorption electrospray ionization (DESI) [27], direct analysis in real time (DART) [28] and extractive electrospray ionization EESI [29] have been used to study TATP and DADP explosives on different surfaces. The application of DESI [30, 31], DART [32, 33], and EESI [34, 35] sources for explosive detection showed direct in-situ identification of trace amounts of TATP on a wide variety of surfaces and

various complex matrices. They provide nanogram level detection limits, allowing rapid and accurate determination of peroxide explosives in contrast with other chromatography based methods coupled to mass spectrometric detection.

In this work, easy ambient sonic-spray ionization (EASI) [36] – a fast ambient ionization source – is used to identify TATP products directly on real seized banknotes from ATM explosions.

2 Experimental

2.1 Methods and Materials

HPLC-grade methanol and formic acid were purchased from Burdick & Jackson (Muskegon, MI). Six seized banknotes suspected of ATM theft with the use of explosives, both with the nominal value of R$50, were provided by the Criminalistics Institute Dr. Octávio Eduardo de Brito Alvarenga of the São Paulo Technical-Scientific Police Superintendency (IC-SPTC-SP), Brazil. The banknote set, which has been seized in the possession of suspect individuals, showed signs of charring and partial destruction (Figure 2C). From the court of Justice standpoint the main question was to establish if the banknotes were products of ATM explosion or not, since this type of attack would have occurred recently in that region. A triplicate set of banknotes with the same nominal value, R$50, obtained at a local bank, were analyzed to produce the free contamination banknote control MS chemical profile. Preparation of TATP followed the acid solution [5, 6] method as follows: a 500 mL round-bottomed flask was immersed in a dry ice bath and hydrogen peroxide (80 mL) 40 vol % and acetone (80 mL) 50 % solution, purchased at local pharmacies, was mixed followed by the addition of muriatic acid (HCl) purchased in a local store building supplies. After 24 h in the freezer the mixture was filtered yielding a white precipitate. TATP is highly explosive, shock and friction sensitive, and should only be prepared in very small quantities by qualified personnel taking appropriate safety precautions.

2.2 Instrumentation: EASI-MS

Experiments were performed with a single quadrupole mass spectrometer (LCMS-2010EV; Shimadzu Corp., Kyoto, Japan) equipped with a home-made easy ambient sonic-spray ionization (EASI) source (Figure 2A) [36]. Acidified methanol (with 0.1 % in volume of formic acid) at a flow rate of 20 μL min^{-1} and N$_2$ at 100 psi were used to form the sonic spray used in the positive ion mode, EASI(+)-MS. The entrance angle of the capillary relative to the sample surface was ca. 45°. Each banknote sample (genuine set and seized set) was directly analyzed by EASI(+)-MS, without any sample treatment in the same three different points on samples surfaces. To confirm the molecular formula of the com-
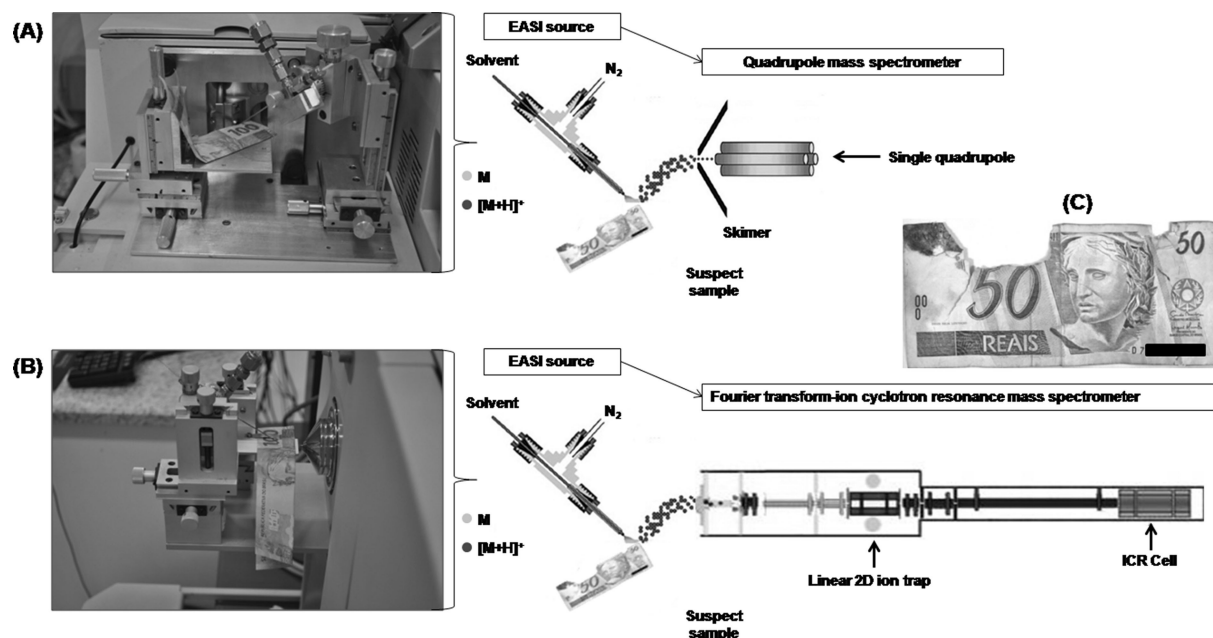
Figure 2. Schematics of easy ambient sonic-spray ionization (EASI) source for voltage-free ambient mass spectrometry as applied to banknotes samples suspected of being originated from an ATM blown up: (A) EASI source coupled to a single quadrupole mass spectrometer in positive ion mode, EASI(+)-MS, (B) EASI source coupled to Fourier transform-ion cyclotron resonance mass spectrometer, in positive ion mode, EASI(+) FT MS, and (C) suspect seized banknote. Adapted from references [24, 37].

pounds detected in the surface of the seized suspect counterfeited banknotes and verify the versatility of the ambient ionization source, an EASI source operated in the positive ion mode was coupled to ultrahigh-resolution and ultrahigh accuracy Fourier transform-ion cyclotron resonance mass spectrometer (FT-ICR MS, ThermoScientific, Bremen, Germany, Figure 2B) [37]. Mass spectra were accumulated over 100 microscans, centered and aligned using the Xcalibur 2.0 software (ThermoScientific). The elemental compositions of the compounds were attributed by the measurement of m/z values. The EASI-FT-ICR MS system followed the same specifications applied in the single quadrupole case, i.e., methanol (with 0.1% in volume of formic acid) at a flow rate of 20 μL min^{-1} and N$_2$ at 100 psi were used to form the sonic spray, with the entrance angle of the capillary relative to the sample surface was ca. 45°. The mass spectrometers have the m/z calibrated on different ways. EASI-MS is a unit resolution mass spectrometer then the calibration is verified using PPG. EASI(+) FT-ICR-MS is an high resolution mass spectrometer calibrated with a mixture of caffein, MRFA, and ultramark 1621. More details of the EASI source and its operation also are provided elsewhere.

3 Results and Discussion

3.1 EASI(+) FT-ICR MS

Standard as well as suspect banknotes were analyzed by applying the EASI source coupled to the high-resolution/high-accuracy ICR cell of a linear ion trap Fourier transform mass spectrometry instrument (Figure 2B). Figure 3A shows the characteristic spectra and the ions observed for the con-
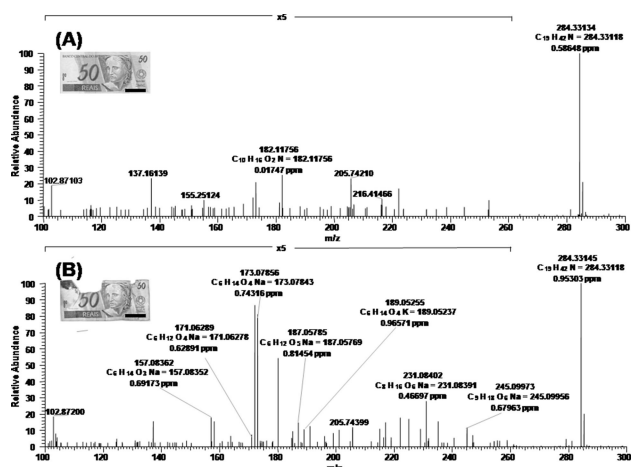

Figure 3. EASI(+)-FT-ICR MS spectra for a (A) free contamination banknote control, and (B) suspect banknote from ATM explosion.

trol banknotes free of explosives or surface contamination [38–40]. Considering the mass range of 100–300 *m/z* showed at the Figure 3A, the free contamination banknote control EASI(+)-FT-ICR MS spectra presents unique and most intense quaternary ammonium compound ion $[C_{19}H_{42}N]^+$ with the monoisotopic mass of 284,33118 and error of 0.58648 ppm, and when the mass region of 100–260 *m/z* was amplified for a five factor (5 ×), about the standard banknote, just noise and background signals was assigned. Figure 3B, besides the usual normal banknote mass spectrum profile presents the characteristic *m/z* 284, the suspect banknotes presented ions identified with an exact monoisotopic mass of *m/z* 245.09985 and *m/z* 171.06278 which are related to the cyclic adduct trimer sodiated TATP $[C_9H_{18}O_6Na]^+$ and to the cyclic adduct dimer sodiated DADP $[C_6H_{12}O_4Na]^+$.

These diagnostic explosive adducts are reported herein by high resolution and sensibility mass spectrometry with an error of 0.67963 and 0.62891 ppm, respectively. The exact mass monoisotopic ion of *m/z* 173.07856 and *m/z* 189.05237 were attributed to the molecular formulae $[C_6H_{14}O_4Na]^+$ and $[C_6H_{14}O_4K]^+$ with an error less than 1.0 ppm, consisting in a observation of sodiated and potassiated adduct DHPP (Figure 1). This compound has been reported by Antonovskii et al [7, 8], who synthesized it by reacting ketone with hydrogen peroxide in a neutral solution. The ob-

servation of DHPP, thus confirms the domestic TATP synthesis route probably in clandestine laboratories.

The use of a high resolution mass spectrometer for screening analysis is not feasible in a conventional forensic laboratory due to its high cost and complex operation, but it may be used for confirmatory analysis as did before. The chemical profiles of normal banknotes and suspect banknotes were obtained in positive ion mode by EASI(+) in a quadrupole mass spectrometry system (Figure 2A, Figure 4A and B). The carbonized position on the surface of suspect banknotes were analyzed and are illustrated in the insert of Figure 4B. Different chemical profiles are obtained when comparing normal and suspect banknotes. The best MS scan range for analysis ranged from *m/z* 100 to *m/z* 300 showing a variety of diagnostic ions (Figure 4A and B, Table 1).

Figure 4B exhibits the same profile obtained by EASI(+) FT-ICR MS for a suspect banknote, showing the ion of *m/z* 173 DHPP and the low intensity ion of *m/z* 171 (DADP) related to TATP domestic production. TATP samples were synthesized in the Thomson Laboratory as quoted elsewhere in material and methods section. Figure 5 shows the EASI (+)-MS profiles comparing TATP contamination possibilities on banknote surface, confirming that the ions of *m/z* 173 and *m/z* 171 are diagnostic markers for domestic production of this explosive after the explosion.

4 Conclusions

In this work the analysis of suspect banknotes revealed that TATP has been used by criminals in ATM explosions in Brazil. Herein we showed that applying the MS source EASI it is possible to obtain a chemical profile relating the ions of *m/z* 171, 173 and 245 to the presence of TATP explosives in a suspect samples surface. EASI technique is a versatile ionization source for suspect surfaces analysis without sample treatment or damage and might be used in a simple quadrupole mass spectrometer for screening applied to identification of TATP explosive. The source EASI is very simple and most easily implemented since it uses no heating, no high voltages, no laser beams, no UV lights, no corona discharges, and no auxiliary gases, may be coupled in simple or sophisticated mass spectrometers how showed herein,
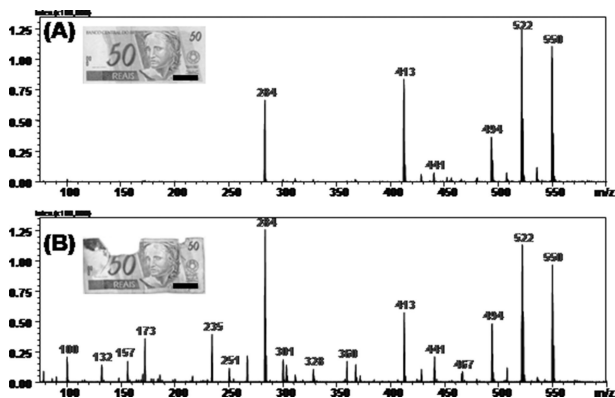

Figure 4. Chemical profiles obtained by EASI(+)-MS in a range of 75–600 *m/z* for a (A) free contamination banknote control, and (B) suspect banknotes from an ATM explosion.

Table 1. Diagnostic ions attributed formulae and error predicted supplied by EASI(+)-FT-ICR MS for suspect seized banknote in Figure 3 B.

m/z	Relative [%]	Mass (calcd.)	Error [ppm]	Composition	Identification[a]
171.06289	1.47	171.06278	0.62891	$[C_6H_{12}O_4Na]^+$	DADP
173.07856	16.58	173.07843	0.74316	$[C_6H_{14}O_4Na]^+$	Sodiated DHPP
189.05255	2.14	189.05237	0.96571	$[C_6H_{14}O_4K]^+$	Potassiated DHPP
222.10869	3.55	222.10979	4.93242	$[C_9H_{18}O_6]^+$	TATP
245.09973	2.41	245.09956	0.67963	$[C_9H_{18}O_6Na]^+$	Sodiated TATP
284.33145	100	284.33118	0.95303	$[C_{19}H_{42}N]^+$	Banknote signal

a) DADP = diacetone diperoxide; DHPP = 1,1′-dihydroxypropyl peroxide; TATP = triacetone triperoxide.
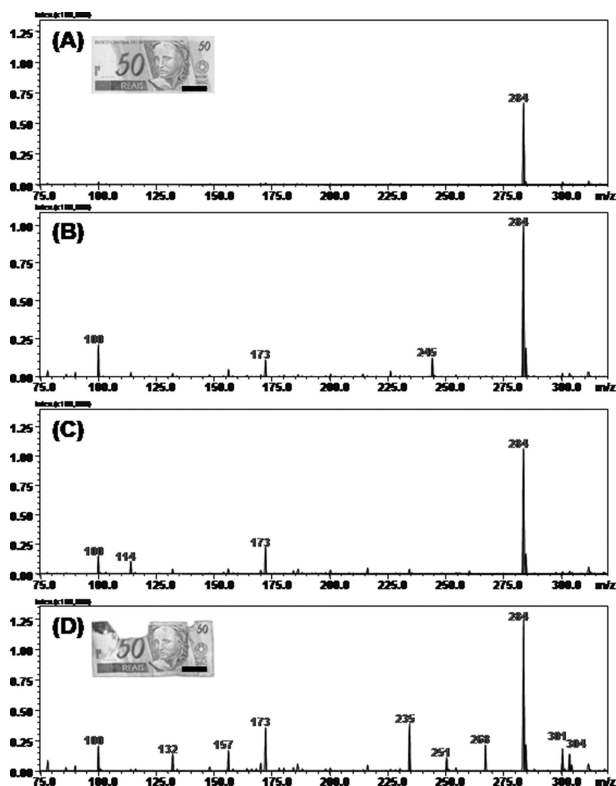
Figure 5. EASI(+)-MS in a range of 75–320 *m/z* for (A) free contamination banknote control, (B) synthesized TATP placed on banknote, (C) synthesized TATP exploded on banknote, and (D) seized suspect banknotes from ATM blown up.

allowing the implementation in forensic laboratories, and routine analysis.

Acknowledgments

References

[1] H. K. Evans, F. A. J. Tulleners, B. L. Sanchez, C. A. Rasmussen, An Unusual Explosive, Triacetonetriperoxide (TATP), *J. Forensic Sci.* **1986**, *31*, 1119–1125.

[2] G. M. White, An Explosive Drug Case, *J. Forensic Sci.* **1992**, *37*, 652–656.

[3] J. C. Oxley, J. L. Smith, J. Huang, W. Luo, Destruction of Peroxide Explosives, *J. Forensic Sci.* **2009**, *54*, 1029–1033.

[4] R. Wolffenstein, Ueber die Einwirkung von Wasserstoffsuperoxyd auf Aceton und Mesityloxyd, *Ber. Dtsch. Chem. Gesellsch.* **1895**, *28*, 2265–2269.

[5] A. Baeyer, V. Villiger, Ueber die Nomenclatur der Superoxyde und die Superoxyde der Aldehyde, *Ber. Dtsch. Chem. Gesellsch.* **1900**, *33*, 2479–2487.

[6] N. A. Milas, A. Golubović, Studies in Organic Peroxides. XXIV. Preparation, Separation and Identification of Peroxides Derived from Diethyl Ketone and Hydrogen Peroxide, *J. Am. Chem. Soc.* **1959**, *81*, 3361–3364.

[7] V. Antonovs, V. A. Terentev, Behavior of Ketone Peroxides in Solution. 3. Effect of Hydrogen Bond on Kinetics of Dissociation of 1-Hydroxy-1′-Hydroperoxydicyclohexyl Peroxide, *Russ. J. Phys. Chem.* **1966**, *40*, 9.

[8] V. A. Terentev, A. F. Nesterov, V. Antonovs, IR Spectra and Hydrogen Bonding of Methylcyclohexanone Peroxides, *J. Gen. Chem. USSR* **1967**, *37*, 1479–1483.

[9] P. R. Story, B. Lee, C. E. Bishop, D. D. Denson, P. Busch, Macrocyclic Synthesis. II. Cyclohexanone Peroxides, *J. Org. Chem.* **1970**, *35*, 3059–3062.

[10] E. M. Schmidt, M. F. Franco, C. J. Cuelbas, J. J. Zacca, W. F. de Carvalho Rocha, R. Borges, W. de Souza, A. C. H. F. Sawaya, M. N. Eberlin, D. N. Correa, Characterization of *anti*-theft Devices Directly from the Surface of Banknotes via Easy Ambient Sonic Spray Ionization Mass Spectrometry, *Sci. Justice* **2015**, *55*, 285–290.

[11] D. N. Correa, J. J. Zacca, W. F. C. Rocha, R. Borges, W. de Souza, R. Augusti, M. N. Eberlin, P. H. Vendramini, Anti-theft Device Staining on Banknotes Detected by Mass Spectrometry Imaging, *Forensic Sci. Int.* **2016**, *260*, 22–26.

[12] V. V. Hernandes, M. F. Franco, J. M. Santos, J. J. Melendez-Perez, D. R. Morais, W. F. D. C. Rocha, R. Borges, W. de Souza, J. J. Zacca, L. P. L. Logrado, Characterization of ANFO Explosive by High Accuracy ESI(±)-FTMS with Forensic Identification on Real Samples by EASI(−)-MS, *Forensic Sci. Int.* **2015**, *249*, 156–164.

[13] H. Wackerbarth, C. Salb, L. Gundrum, M. Niederkrüger, K. Christou, V. Beushausen, W. W. Viöl, Detection of Explosives based on Surface-enhanced Raman Spectroscopy, *Appl. Optics* **2010**, *49*, 4362–4366.

[14] G. A. Buttigieg, A. K. Knight, S. Denson, C. Pommier, M. Bonner Denton, Characterization of the Explosive Triacetone Triperoxide and Detection by Ion Mobility Spectrometry, *Forensic Sci. Int.* **2003**, *135*, 53–59.

[15] A. Stambouli, A. El Bouri, T. Bouayoun, M. A. Bellimam, Headspace-GC/MS Detection of TATP Traces in Post-explosion Debris, *Forensic Sci. Int.* **2004**, *146*, S191-S194.

[16] G. W. Cook, P. T. LaPuma, G. L. Hook, B. A. Eckenrode, Using Gas Chromatography with Ion Mobility Spectrometry to Resolve Explosive Compounds in the Presence of Interferents, *J. Forensic Sci.* **2010**, *55*, 1582–1591.

[17] M. Fitzgerald, D. Bilusich, Sulfuric, Hydrochloric, and Nitric Acid-Catalyzed Triacetone Triperoxide (TATP) Reaction Mixtures, An Aging Study, *J. Forensic Sci.* **2011**, *56*, 1143–1149.

[18] 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*, 1627–1632.

[19] J. C. Oxley, J. L. Smith, L. J. Kirschenbaum, S. Marimganti, S. Vadlamannati, Detection of Explosives in Hair Using Ion Mobility Spectrometry, *J. Forensic Sci.* **2008**, *53*, 690–693.

[20] R.-M. Räsänen, M. Nousiainen, K. Peräkorpi, M. Sillanpää, L. Polari, O. Anttalainen, M. Utriainen, Determination of Gas Phase Triacetone Triperoxide with Aspiration Ion Mobility Spectrometry and Gas Chromatography – Mass Dpectrometry, *Anal. Chim. Acta* **2008**, *623*, 59–65.

[21] C. K. Hilton, C. A. Krueger, A. J. Midey, M. Osgood, J. Wu, C. Wu, Improved Analysis of Explosives Samples with Electrospray Ionization-high Resolution Ion Mobility Spectrometry (ESI-HRIMS), *Int. J. Mass Spectrom.* **2010**, *298*, 64–71.

[22] D. J. Weston, Ambient Ionization Mass Spectrometry: Current Understanding of Mechanistic Theory, Analytical Performance and Application Areas, *Analyst* **2010**, *135*, 661–668.

[23] G. A. Harris, L. Nyadong, F. M. Fernandez, Recent Developments in Ambient Ionization Techniques for Analytical Mass Spectrometry, *Analyst* **2008**, *133*, 1297–1301.

[24] R. M. Alberici, R. C. Simas, G. B. Sanvido, W. Romão, P. M. Lalli, M. Benassi, I. B. S. Cunha, M. N. Eberlin, Ambient Mass Spectrometry: Bringing MS into the "Real World", *Anal. Bioanal. Chem.* **2010**, *398*, 265–294.

[25] D. R. Ifa, C. Wu, Z. Ouyang, R. G. Cooks, Desorption Electrospray Ionization and Other Ambient Ionization Methods: Current Progress and Preview, *Analyst* **2010**, *135*, 669–681.

[26] D. N. Correa, J. M. Santos, S. F. Teunissen, L. S. Eberlin, M. N. Eberlin, Forensic Chemistry and Ambient Mass Spectrometry: A Perfect Couple Destined for a Happy Marriage?, *Anal. Chem.* **2016**, *88*, 2515–2526.

[27] Z. Takáts, J. M. Wiseman, R. G. Cooks, Ambient Mass Spectrometry using Desorption Eectrospray Ionization (DESI), Instrumentation, Mechanisms and Applications in Forensics, Chemistry, and Biology, *J. Mass Spectrom.* **2005**, *40*, 1261–1275.

[28] 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*, 2297–2302.

[29] H. Chen, S. Yang, A. Wortmann, R. Zenobi, Neutral Desorption Sampling of Living Objects for Rapid Analysis by Extractive Electrospray Ionization Mass Spectrometry, *Angew. Chem. Int. Ed.* **2007**, *46*, 7591–7594.

[30] I. Cotte-Rodríguez, H. Chen, R. G. Cooks, Rapid Trace Detection of Triacetone Triperoxide (TATP) by Complexation Reactions during Desorption Electrospray Ionization, *Chem. Commun.* **2006**, 953–955.

[31] I. Cotte-Rodríguez, H. Hernández-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*, 1512–1519.

[32] A. J. Peña-Quevedo, J. A. Laramee, H. D. Durst, S. P. Hernández-Rivera, Cyclic organic Peroxides Characterization by Mass Spectrometry and Raman Microscopy, *IEEE Sensors J.* **2011**, *11*, 1053–1060.

[33] E. A. Espinosa-Fuentes, L. C. Pacheco-Londoño, M. A. Barreto-Cabán, S. P. Hernández-Rivera, Novel Uncatalyzed Synthesis and Characterization of Diacetone Diperoxide, *Propellants Explos. Pyrotech.* **2012**, *37*, 413–421.

[34] H. Gu, S. Yang, J. Li, B. Hu, H. Chen, L. Zhang, Q. Fei, Geometry-Independent Neutral Desorption Device for the Sensitive EESI-MS Detection of Explosives on various surfaces, *Analyst* **2010**, *135*, 779–788.

[35] H. Chen, B. Hu, Y. Hu, Y. Huan, Z. Zhou, X. Qiao, Neutral Desorption Using a Sealed Enclosure to Sample Explosives on Human Skin for Rapid Detection by EESI-MS, *J. Am. Soc. Mass Spectrom.* **2009**, *20*, 719–722.

[36] R. Haddad, R. Sparrapan, M. N. Eberlin, Desorption Sonic Spray Ionization for (High)voltage-free Ambient Mass Spectrometry, *Rapid Commun. Mass Spectrom.* **2006**, *20*, 2901–2905.

[37] Y. E. Corilo, B. G. Vaz, R. C. Simas, H. D. Lopes Nascimento, C. F. Klitzke, R. C. L. Pereira, W. L. Bastos, E. V. Santos Neto, R. P. Rodgers, M. N. Eberlin, Petroleomics by EASI(±) FT-ICR MS, *Anal. Chem.* **2010**, *82*, 3990–3996.

[38] L. S. Eberlin, R. Haddad, R. C. Sarabia Neto, R. G. Cosso, D. R. J. Maia, A. O. Maldaner, J. J. Zacca, G. B. Sanvido, W. Romão, B. G. Vaz, et al. Instantaneous Chemical Profiles of Banknotes by Ambient Mass Spectrometry, *Analyst* **2010**, *135*, 2533–2539.

[39] E. M. Schmidt, M. F. Franco, K. G. Regino, E. L. Lehmann, M. A. Z. Arruda, W. F. de Carvalho Rocha, R. Borges, W. de Souza, M. N. Eberlin, D. N. Correa, Direct and Non-Destructive Proof of Authenticity for the 2nd Generation of Brazilian Real Banknotes via Easy Ambient Sonic Spray Ionization Mass Spectrometry, *Sci. Justice* **2015**, *54*, 459–464..

[40] W. Romao, B. G. Vaz, P. M. Lalli, M. I. M. S. Bueno, D. N. Correa, V. L. C. N. Telles, E. V. R de Castro, M. N. Eberlin, Analyzing Brazilian Vehicle Documents for Authenticity by Easy Ambient Sonic-Spray Ionization Mass Spectrometry, *J. Forensic Sci.* **2012**, *57*, 539–543.