

## Article

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# Determination of Peroxide Explosive TATP and Related Compounds by Dielectric Barrier Discharge Ionization-Mass Spectrometry (DBDI-MS)

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### Abstract

Dielectric barrier discharge ionization-mass spectrometry (DBDI-MS), which is based on the use of a low temperature helium plasma as ionization source, is used for the determination of trace amounts of triacetone triperoxide (TATP) and its homologue diacetone diperoxide (DADP) from surfaces. TATP is observed as  $[M+NH_4]^+$  adduct, whereas DADP is observed as  $[M+O+NH_4]^+$ . Measurement of DADP with varying deuteration degrees (DADP, DADP-d<sub>6</sub> and DADP-d<sub>12</sub>) indicates that DADP undergoes oxidation when ionized by DBDI. If acetonitrile is used as deposition solvent, TATP tends to show fragmentation and is not only detected as  $[M+NH_4]^+$  but as  $[M-CH_4+NH_4]^+$  and  $[M-C_2H_4+NH_4]^+$  as well. Quantification of TATP solutions from glass surfaces by DBDI-MS, using TATP-3,6,9-<sup>13</sup>C as internal standard, was done and validated using an LC/APCI-MS method. Achievable limits of detection (LOD) for TATP are equivalent to the deposition of 15 ng TATP and are comparable with other ambient desorption/ionization mass spectrometric techniques like desorption electrospray ionization (DESI).

## Introduction

Triacetone triperoxide (TATP) and diacetone diperoxide (DADP) are peroxide based primary explosives mainly used in improvised explosive devices (IED). Due to their straightforward synthesis based on the readily available household chemicals acetone and hydrogen peroxide, they have been the illicit explosive of choice for terrorist groups in the last decades.<sup>1,2</sup> The explosive power of TATP is comparable to that of trinitrotoluene (TNT).<sup>3</sup> Because of their high sensitivity to shock, friction and static electricity as well as their tendency to sublime rapidly, the handling and storage of large TATP or DADP quantities is dangerous and therefore they do not have any commercial or military applications.<sup>4,5</sup> TATP, first synthesized by Wolffenstein in 1895,<sup>6</sup> and DADP are both cyclic acetone peroxides. The chemical structures of TATP and DADP are depicted in figure 1. TATP is a nine-membered cyclic triperoxide whereas DADP is a six-membered cyclic diperoxide.

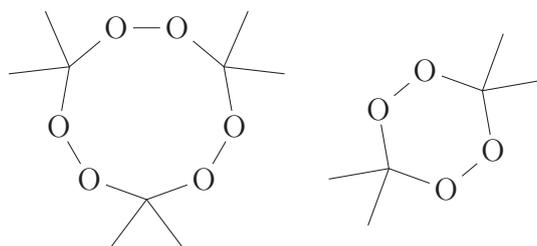


Figure 1: Structures of TATP (left) and DADP (right).

Conventional detection methods are of limited value for the determination of TATP and DADP due to their chemical structure and instability. Compared to other common explosives these peroxides lack nitro groups, metallic elements as well as aromaticity. Therefore they show no significant absorption in the ultraviolet range and exhibit no fluorescence.<sup>7</sup> Several different approaches for the determination of TATP and related compounds have been published. Applied methods include infrared spectroscopy,<sup>8</sup> raman spectroscopy,<sup>8,9</sup> enzymatic reactions,<sup>10</sup> ion mobility spectrometry (IMS),<sup>11</sup> electrogenerated chemiluminescence,<sup>12,13</sup> liquid chromatography (LC)<sup>7,14,15</sup> as well as mass spectrometry (MS). Most mass spectrometric methods rely on the hyphenation of separation techniques like gas chromatog-

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6 raphy (GC)<sup>16,17</sup> or liquid chromatography (LC)<sup>18,19</sup> to MS by utilizing various different  
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8 ionization techniques such as electron ionization (EI),<sup>9,17</sup> chemical ionization (CI),<sup>9,17</sup> elec-  
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10 tro spray ionization (ESI)<sup>18</sup> and atmospheric pressure chemical ionization (APCI).<sup>18,19</sup> These  
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12 commonly used ionization techniques mostly lead to fragment ions that are not specific to  
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14 the targeted acetone peroxide species, but only to acetone peroxides in general. Therefore  
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16 most GC/MS and LC/MS techniques solely rely on chromatographic separation.  
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19 A different mass spectrometric approach similar to the one described in this paper is the  
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21 use of desorption electrospray ionization (DESI) as a soft ionization technique for the deter-  
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23 mination of TATP from surfaces.<sup>20,21</sup> The main advantages of DESI and other techniques  
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25 for soft ionization from surfaces are minor fragmentation and thus the detection of proto-  
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27 nated molecules and adduct ions. By detecting TATP as well as DADP as molecular ions,  
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29 determination can be done without prior chromatographic separation from other peroxide  
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31 species.

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33 In this paper, a plasma-based ionization source is applied for the determination of TATP  
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35 and DADP from surfaces. As alternative to corona discharge plasma, a dielectric barrier  
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37 discharge (DBD) was used to generate a low-temperature plasma at atmospheric pressure,  
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39 that serves as an ionization source for ambient desorption mass spectrometry.<sup>22-28</sup> Deuter-  
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41 ated standards were used to confirm the allocation of mass to charge ratios ( $m/z$ ) to the  
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43 respective peroxides. To quantify TATP from surfaces TATP-3,6,9-<sup>13</sup>C was used as an in-  
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45 ternal standard. Validation of TATP quantification method was performed by use of an  
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47 LC/APCI-MS method.  
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## 50 51 Experimental

### 52 53 Safety note

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55 TATP and its homologue DADP are extremely dangerous materials, which may lead to  
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57 severe and spontaneous explosions under impact, friction and temperature changes. The  
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6 synthesis of these substances should only be carried out by qualified personnel under the  
7 use of appropriate safety measures (reinforced goggles and gloves, splinter-proof vessels,  
8 protective shield, etc.) and in small quantities. For this work, the substances were produced  
9 according to literature procedures (see below) in low quantities. Working with larger amounts  
10 of the substance strongly increases the danger associated with spontaneous explosions.  
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## 17 18 **Chemicals and reagents**

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20 Acetone (for HPLC), acetone-2-<sup>13</sup>C (99 atom% <sup>13</sup>C), acetonitrile-d<sub>3</sub> (99.8 atom% D) and chlo-  
21 roform-d (99.96 atom% D) were purchased from Sigma Aldrich Chemie GmbH (Steinheim,  
22 Germany). Hydrogen peroxide (35 wt.%) was obtained from Acros Organics (Pittsburgh,  
23 PA, USA). Acetone-d<sub>6</sub> (99.8 atom% D) was purchased from Deutero GmbH (Kastellaun,  
24 Germany). Acetonitrile (for HPLC, LC-MS grade), chloroform (for HPLC) and sulfuric  
25 acid (95 wt.%) were purchased from VWR International S.A.S (Fontenay-sous-Bois, France).  
26 Bidistilled water was obtained from a Bolarworld Scientific Aquatron A4000D system (Nemours  
27 Cedex, France).  
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## 38 **Synthesis and sample preparation**

### 39 **Synthesis of TATP, TATP-d<sub>18</sub> and TATP-3,6,9-<sup>13</sup>C**

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41 The synthesis of TATP was carried out according to Oxley *et al.*<sup>29,30</sup> Hydrogen peroxide  
42 (250 μL) was stirred in a round-bottomed flask, while sulfuric acid (10 μL) and acetone  
43 (190 μL) were added dropwise consecutively under ice cooling. The resulting white slurry  
44 was stirred for 24 h and allowed to reach room temperature over that time. After the addition  
45 of water (10 mL), the precipitate was filtered out and rinsed with copious amounts of water.  
46 To obtain isotopic labeled TATP (TATP-d<sub>18</sub> and TATP-3,6,9-<sup>13</sup>C), acetone-d<sub>6</sub> (190 μL) or  
47 acetone-2-<sup>13</sup>C (190 μL) were used instead of unlabeled acetone.  
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### Synthesis of DADP and DADP-d<sub>12</sub>

Similar to TATP synthesis, hydrogen peroxide (250  $\mu\text{L}$ ) was stirred in a round-bottomed flask, while sulfuric acid (250  $\mu\text{L}$ ) and acetone (190  $\mu\text{L}$ ) were added dropwise consecutively under ice cooling. The resulting white slurry was allowed to stir slowly for 24 h at room temperature. Isolation of the product was done equivalent to TATP. To obtain isotopic labeled DADP (DADP-d<sub>12</sub>), acetone-d<sub>6</sub> (190  $\mu\text{L}$ ) was used instead of unlabeled acetone.

### Synthesis of DADP, DADP-d<sub>6</sub> and DADP-d<sub>12</sub> mixture

Synthesis of DADP with mixed deuteration degrees (DADP, DADP-d<sub>6</sub> and DADP-d<sub>12</sub>) was done similar to DADP. An equivalent mixture of acetone (1 mg) and acetone-d<sub>6</sub> (1 mg) was used instead of unlabeled acetone.

### Sample preparation

Stock solutions of TATP, TATP-3,6,9-<sup>13</sup>C and DADP were prepared in acetonitrile-d<sub>3</sub> (10 mg mL<sup>-1</sup>). TATP-d<sub>18</sub> and DADP-d<sub>12</sub> stock solutions (10 mg mL<sup>-1</sup>) were prepared in acetonitrile. Subsequent sample solutions were diluted in both acetonitrile and chloroform. A dilution series of TATP containing TATP-3,6,9-<sup>13</sup>C (50  $\mu\text{g mL}^{-1}$ ) as internal standard was prepared from stock solutions in acetonitrile ranging from 5  $\mu\text{g mL}^{-1}$  to 1000  $\mu\text{g mL}^{-1}$ .

### Quantification of stock solutions

Due to the undefined residual moisture and purity of synthesized peroxides, prepared TATP, TATP-3,6,9-<sup>13</sup>C and DADP stock solutions were quantified using quantitative <sup>1</sup>H-NMR (<sup>1</sup>H-qNMR). Dimethylsulfoxide was added to the <sup>1</sup>H-qNMR stock solution samples serving as internal standard. TATP-d<sub>18</sub> and DADP-d<sub>12</sub> stock solutions were quantified based on <sup>1</sup>H-qNMR quantified TATP and DADP stock solutions by DBDI-MS. <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): TATP:  $\delta=1.40$  ppm (s); TATP-3,6,9-<sup>13</sup>C  $\delta=1.40$  ppm (d, J=4.6 Hz); DADP:  $\delta=1.33$  ppm (s), 1.76 ppm (s).

## Instrumentation

### DBDI setup

Ionization was carried out by a dielectric barrier discharge (DBD) microplasma probe described elsewhere as an ionization source for LC/MS.<sup>31</sup> The source setup was realized by modification of a commercial API source housing (Ion Max, Thermo Fisher Scientific, Bremen, Germany). The plasma was operated with a helium (99.996 % purity) flow of 200 mL min<sup>-1</sup>, by applying rectangular high voltage pulses of 3.5 kV and 20 kHz. The DBD probe consisted of a 3 cm long glass capillary with an inner diameter of 500  $\mu$ m and an outer diameter of 1.2 mm (ca. 5  $\mu$ l of gas volume). Soldered rings with an inner diameter of 1.2 mm are located around the capillary, forming electrodes with a separation distance of 8 mm. The distance of the electrode to the end of the capillary is 2 mm. The plasma electrodes are enclosed in a PEEK tube not only for safety precautions but also to prevent a discharge between the electrodes outside the capillary.



Figure 2: Position of the DBDI source (left) with respect to the MS inlet.

### DBDI-MS method

For DBDI-MS analysis, 5  $\mu$ L of sample solution were deposited on a glass slide. The solvent was evaporated by placing the slide orthogonally in front of the plasma cone and axially in front of the MS inlet (figure 2). After evaporation of the solvent, the analyte residue could be desorbed and ionized by means of DBDI. Mass spectrometric detection was carried out

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6 using an orbitrap Exactive (Thermo Fisher Scientific, Bremen, Germany) mass spectrometer  
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8 in full scan positive ion mode. Data was acquired in the mass range of  $m/z$  100 to 300, with  
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10 a resolution of  $R = 100\,000$  at  $m/z$  200 (full width at half maximum, FWHM). For TATP  
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12 quantification measurements data was acquired in the mass range of of  $m/z$  200 to 275. The  
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14 transfer capillary temperature was maintained at 125 °C.  
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### 17 18 **LC/APCI-MS method**

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20 Separations were performed according to Xu *et al.*<sup>19</sup> using an Ultimate 3000 HPLC system  
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22 (Thermo Fisher Scientific, Bremen, Germany) and a Nucleoshell RP-18 column (150×2 mm,  
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24 2.7 μm, Macherey-Nagel, Düren, Germany). The mobile phases A and B were water contain-  
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26 ing 5 % methanol and 5 mmol L<sup>-1</sup> NH<sub>4</sub>(HCOO) and methanol containing 5 mmol L<sup>-1</sup> NH<sub>4</sub>(HCOO),  
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28 respectively. An isocratic flow of 65 % B was used for elution. The flow rate was 400 μL min<sup>-1</sup>  
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30 and the injection volume was set to 2 μL. Column oven temperature was set to 40 °C. APCI  
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32 was performed with sheath gas set to 35 AU, auxiliary gas set to 10 AU, heater temperature  
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34 maintained at 250 °C and ion current set to 4 μA. Mass spectrometric detection was car-  
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36 ried out equivalent to the DBDI-MS method with a resolution of  $R = 50\,000$  at  $m/z$  200  
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38 (FWHM) in the mass range of  $m/z$  100 to 300.  
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## 42 43 **Results and discussion**

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45 A method for quantification of TATP directly from surfaces by DBDI-MS was developed.  
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47 Therefore, the ionization behaviors of TATP and its homologue DADP were investigated first.  
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49 Stable isotope labeled standards facilitated assignment of detected signals and were used also  
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51 for quantification. For validation the DBDI-MS method was compared to a complementary  
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53 LC/APCI-MS method.  
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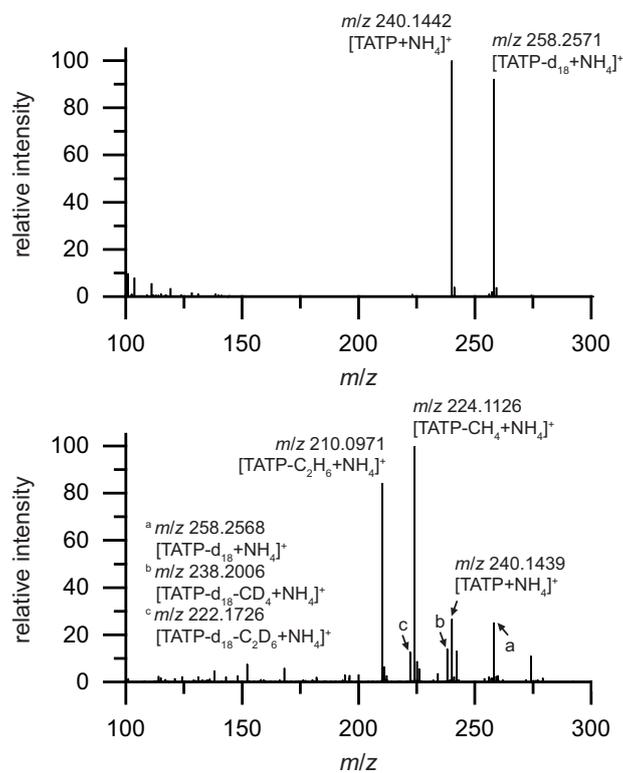


Figure 3: DBDI-MS spectra of 1  $\mu\text{g}$  TATP and 1  $\mu\text{g}$  TATP-d<sub>18</sub> deposited in chloroform (top) and acetonitrile (bottom).

## Detection of TATP by DBDI-MS

The positive ion DBDI-MS mass spectrum of TATP, deposited on a glass slide from TATP and TATP-d<sub>18</sub> in chloroform, is shown in figure 3. A dominant signal at  $m/z$  240 that can be assigned to the adduct ion  $[M+NH_4]^+$  is observed. The assignment is confirmed by simultaneous measurement of TATP-d<sub>18</sub>, which is detected as  $m/z$  258, this reflects the mass shift of 18 due to its deuteration degree. The protonated molecular ion of TATP,  $[M+H]^+$ , is detected as  $m/z$  223, however only in trace intensities of less than 1 % compared to  $m/z$  240. Note that mass errors were within 3 ppm (relative mass error). This allows unambiguous assignment of sum formulae which were further corroborated by the measurement of deuterated analogues.

In contrast to TATP deposited in chloroform, TATP deposited in acetonitrile is not only detected as  $m/z$  240 but as multiple adduct and fragment ions. Detected  $m/z$  and their corresponding calculated sum formulae are shown in figure 3. As for TATP deposited in chloroform,  $m/z$  240 corresponds to  $[M+NH_4]^+$ . The structures of TATP adduct and fragment ions  $m/z$  242, 224 and 210 are not clear and will be investigated in future work. Especially the structures of  $m/z$  224 and  $m/z$  210, which would be equivalent to  $[M-CH_4+NH_4]^+$  and  $[M-C_2H_6+NH_4]^+$ , remain of interest. Assignments of measured signals to TATP were confirmed by measurement of TATP-d<sub>18</sub>. The major effect of acetonitrile compared to chloroform as deposition solvent on the ionization of TATP remains unclear but could be explained by ion suppression caused by residual acetonitrile.<sup>32</sup> Using acetonitrile compared to methanol as mobile phase constituent in LC/APCI-MS, the TATP adduct ion  $[M+NH_4]^+$  at  $m/z$  240 can not be observed.<sup>19,32</sup>

Beside detection from glass surfaces, detection from paper, brick and cotton fabric surfaces were investigated and found to behave similarly to glass surfaces. If no deposition solvent is used, e.g. measurement of solid TATP samples, obtained spectra are in accordance with spectra using chloroform as deposition solvent.

There are two likely sources of ammonium, the helium plasma discharge and contami-

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nation of the ion source housing due to the common use of ammonium salts in buffers and as dopants in LC/MS, respectively. The stability of the measured  $[M+NH_4]^+$  signal, even after rigorous cleansing of the ion source housing, suggests the helium plasma discharge as the main source of ammonium. In case of corona discharges,  $^{63}Ni$  sources and He-H<sub>2</sub> atmospheric pressure micro plasmas, either ammonia formation<sup>33,34</sup> or NH molecular line emission (336 nm)<sup>35</sup> are described in the literature. Therefore the formation of ammonium by the atmospheric pressure-DBD is plausible.

## Detection of DADP by DBDI-MS

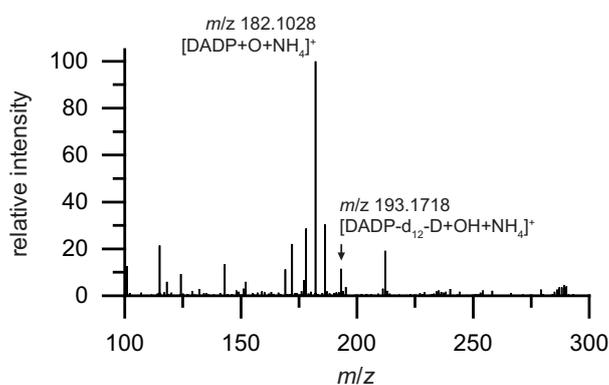


Figure 4: DBDI-MS spectrum of 1  $\mu$ g DADP and 1  $\mu$ g DADP-d<sub>12</sub> deposited in chloroform.

The DBDI-MS spectrum of DADP, deposited on a glass slide from DADP and DADP-d<sub>12</sub> in chloroform, is shown in figure 4. In contrast to TATP, DADP is not detected as  $[M+NH_4]^+$ , which would correspond to  $m/z$  166, but rather as  $m/z$  182, which corresponds to  $[M+O+NH_4]^+$ . DADP-d<sub>12</sub> is not detected as  $m/z$  194 ( $[M+O+NH_4]^+$ ) as would be expected due to the mass shift of 12 caused by its deuteration degree, but as  $m/z$  193. The detection of DADP-d<sub>12</sub> as  $m/z$  193, which corresponds to  $[M-D+OH+NH_4]^+$ , indicates that not only an  $[M+O+NH_4]^+$  adduct is formed but that DADP undergoes oxidation when ionized by DBDI. To further investigate the deuterium loss, a mixture of DADP, DADP-d<sub>6</sub> and DADP-d<sub>12</sub> was measured under the same conditions. The spectrum is shown in figure 5. In addition to  $m/z$  182 and  $m/z$  193 which are caused by DADP and DADP-d<sub>12</sub> respectively, DADP-d<sub>6</sub> is detected as

both  $m/z$  187 and  $m/z$  188 corresponding to  $[M-D+OH+NH_4]^+$  and  $[M+O+NH_4]^+$ . The measured  $m/z$  depends on the position of oxidation, either on the deuterated ( $m/z$  187) or on the undeuterated side of the molecule ( $m/z$  188). Due to the kinetic isotope effect, the intensity of measured  $m/z$  187 and 193 are by far lower than those measured for  $m/z$  188 and 182. The rate of a reaction involving a C-D bond is significantly lower than the corresponding C-H bond.<sup>36</sup> A chronogram of the four measured ions for DADP, DADP-d<sub>6</sub> and DADPD is shown in figure 5. Since the signal patterns of the four detected ions align, it is likely that they are all caused by DADP of different deuteration degrees and do not represent interfering signals, e.g. from the background. These results corroborate oxidation of DADP during ionization.

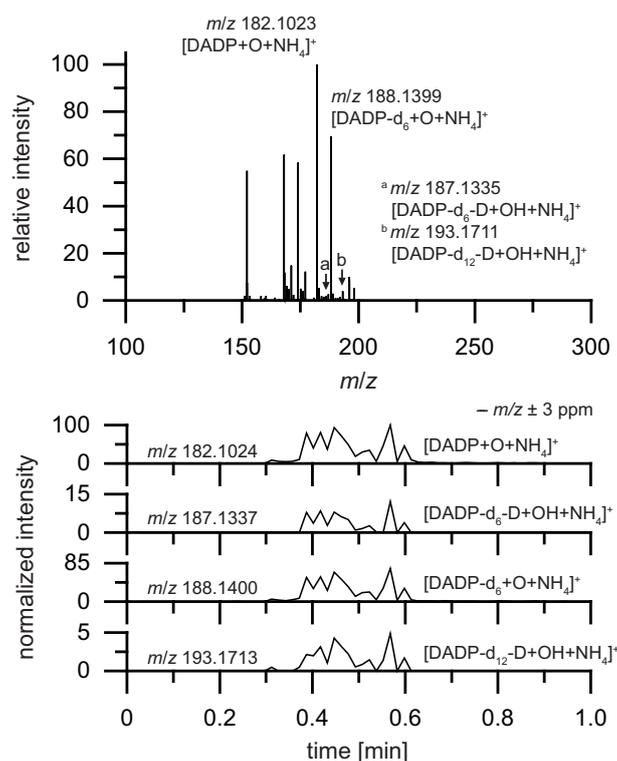


Figure 5: DBDI-MS spectra of 2  $\mu$ g of a mixture of DADP, DADP-d<sub>6</sub> and DADP-d<sub>12</sub> deposited in chloroform (top) and corresponding chronogram of measured  $m/z$  assigned to DADP, DADP-d<sub>6</sub> and DADP-d<sub>12</sub> (bottom).

## Quantification of TATP by DBDI-MS

Quantification of TATP solutions from glass surfaces was done by the addition of an internal standard to the sample solution. Two possible internal standards, TATP-d<sub>18</sub> and TATP-3,6,9-<sup>13</sup>C were investigated for this purpose. TATP-d<sub>18</sub> was discarded as a possible internal standard due to the issue of initial quantification, which can not be done by <sup>1</sup>H-qNMR, and its high deuteration degree. The high deuteration degree of TATP-d<sub>18</sub> leads to slightly different chemical properties compared to TATP, which result in a significant retention shift in LC/MS and could manifest in different ionization properties in DBDI-MS. Therefore TATP-3,6,9-<sup>13</sup>C was chosen as internal standard. Since the DBDI-MS method should be validated by LC/APCI-MS, acetonitrile was chosen as sample solvent over chloroform due to its superior compatibility to reversed phase LC/MS. The TATP fragment ion *m/z* 224, corresponding to [M-CH<sub>4</sub>+NH<sub>4</sub>]<sup>+</sup>, was chosen as quantifier because of its higher abundance compared to *m/z* 240 and due to an unknown interference leading to overestimation of internal standard TATP-3,6,9-<sup>13</sup>C if *m/z* 240 is used as quantifier. A signal threshold of 500 counts for both the TATP *m/z* 224 and corresponding internal standard signal as well as a data point threshold of 5 evaluable scans was used for the calculation of TATP sample concentrations. An exemplary chronogram of TATP *m/z* 224 and a dilution series measured in triplicate ranging from 5 μg mL<sup>-1</sup> to 1000 μg mL<sup>-1</sup> are shown in figure 6. The limit of detection (LOD) of TATP measured as *m/z* 224 or rather [M-CH<sub>4</sub>+NH<sub>4</sub>]<sup>+</sup> is equivalent to the deposition of 15 ng TATP. This is in accordance with other ambient desorption/ionization mass spectrometric techniques like desorption electrospray ionization (DESI).<sup>21</sup> In contrast to the presented DBDI method, DESI is based on directing a pneumatically assisted electrospray onto a surface. In addition to the more complex setup and operation of DESI it also requires a much higher flow rate of the carrier gas (ca. 350 m s<sup>-1</sup>).<sup>22</sup>

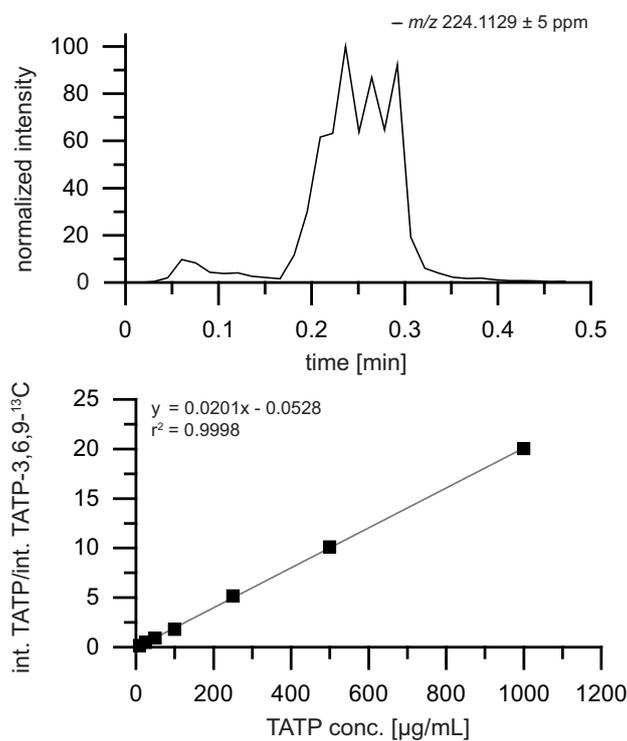


Figure 6: Chromatogramm of TATP quantifier  $m/z$  224 (top) and dilution series of TATP by use of TATP-3,6,9- $^{13}\text{C}$  as internal standard for quantification in the range of  $5 \mu\text{g mL}^{-1}$  to  $1000 \mu\text{g mL}^{-1}$  (bottom).

## Validation of DBDI-MS quantification by LC/APCI-MS

LC/APCI-MS was applied to validate DBDI-MS quantification of TATP. An exemplary chromatogram of TATP  $m/z$  240, equivalent to  $[M+NH_4]^+$ , is shown in figure 7. As described in the literature, two TATP conformers,  $D_3$  and  $C_2$ , are detected by LC-MS.<sup>18,37,38</sup> In case of the applied method, the two conformers are not baseline separated but  $C_2$  appears as a later eluting shoulder of  $D_3$ . As for DBDI-MS quantification, TATP-3,6,9- $^{13}C$  is used as internal standard. For validation of DBDI-MS quantification, the same samples solutions as for DBDI-MS quantification, ranging from  $5 \mu\text{g mL}^{-1}$  to  $1000 \mu\text{g mL}^{-1}$ , were measured in triplicate. The correlation of TATP concentrations, based on TATP-3,6,9- $^{13}C$  as internal standard, measured by DBDI-MS and LC/APCI-MS are shown in figure 7. The slope of the linear correlation between concentrations measured by DBDI-MS and LC/APCI-MS is calculated as  $m = 0.9614$ . Based on the slope and the coefficient of determination  $r^2 = 0.9994$ , quantification of TATP by DBDI-MS is validated by LC/APCI-MS.

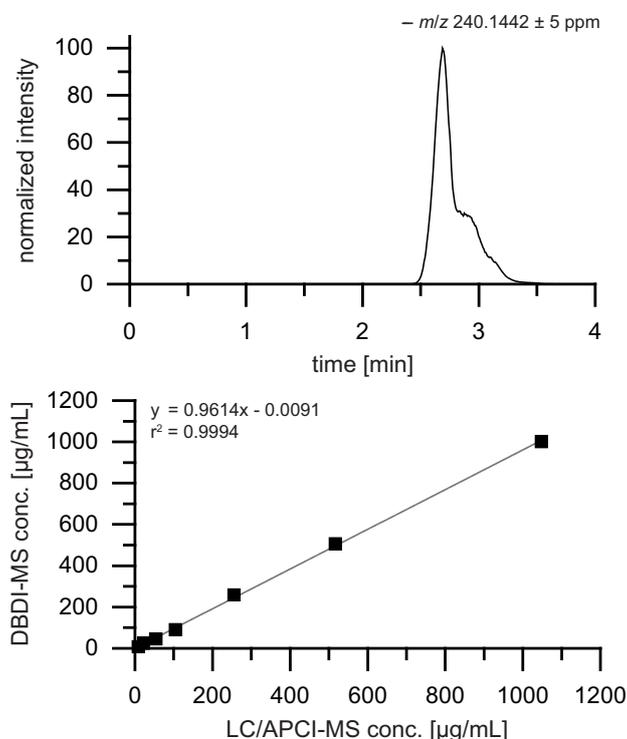


Figure 7: LC/APCI-MS chromatogram of TATP quantifier  $m/z$  240 (top) and linear correlation between TATP concentrations measured by DBDI-MS and LC/APCI-MS (bottom).

## Conclusions

A dielectric barrier discharge coupled to mass spectrometry as ionization technique allows the detection of trace amounts of TATP and DADP directly from surfaces like glass, paper or fabric without sample preparation. Depending on the deposition solvent, TATP is either detected as  $[M+NH_4]^+$  or as  $[M+NH_4]^+$  within various fragment ions. In contrast to TATP, DADP undergoes oxidation and is detected as  $[M+O+NH_4]^+$ . TATP solutions can be quantified by use of TATP-3,6,9- $^{13}C$  as internal standard from glass surfaces with an LOD in the low-nanogram range. Quantification of TATP by DBDI-MS could be validated by use of LC/APCI-MS.

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## References

- (1) Chivers, C. J. *New York Times* **2016**, *March 24*, A13.
- (2) Callimachi, R.; Rubin, A. J.; Fourquet, L. *New York Times* **2016**, *March 20*, A1.
- (3) Pachman, J.; Matyáš, R.; Künzel, M. *Shock Waves* **2014**, *24*, 439–445.
- (4) Meyer, R.; Köhler, J.; Homburg, A. *Explosives*, 6th ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007.
- (5) Dubnikova, F.; Kosloff, R.; Almog, J.; Zeiri, Y.; Boese, R.; Itzhaky, H.; Alt, A.; Keinan, E. *J. Am. Chem. Soc.* **2005**, *127*, 1146–1159.
- (6) Wolfenstein, R. *Berichte der Dtsch. Chem. Gesellschaft* **1895**, *28*, 2265–2269.

- 1  
2  
3  
4  
5  
6 (7) Schulte-Ladbeck, R.; Kolla, P.; Karst, U. *Anal. Chem.* **2003**, *75*, 731–735.  
7  
8  
9 (8) Sülzle, D.; Klæboe, P. *Acta Chem. Scand. A* **1988**, *42*, 165–170.  
10  
11 (9) Evans, H. K.; Tulleners, F. a. J.; Sanchez, B. L.; Rasmussen, C. A. *J. Forensic Sci.*  
12 **1986**, *31*, 1119–1125.  
13  
14  
15 (10) Schulte-Ladbeck, R.; Kolla, P.; Karst, U. *Analyst* **2002**, *127*, 1152–1154.  
16  
17 (11) Buttigieg, G. A.; Knight, A. K.; Denson, S.; Pommier, C.; Denton, M. B. *Forensic Sci.*  
18 *Int.* **2003**, *135*, 53–59.  
19  
20 (12) Shaw, A.; Lindhome, P.; Calhoun, R. L. *J. Electrochem. Soc.* **2013**, *160*, H782–H786.  
21  
22 (13) Parajuli, S.; Miao, W. *Anal. Chem.* **2013**, *85*, 8008–8014.  
23  
24 (14) Schulte-Ladbeck, R.; Karst, U. *Chromatographia* **2003**, *57*, S61–S65.  
25  
26 (15) Schulte-Ladbeck, R.; Edelmann, A.; Quintás, G.; Lendl, B.; Karst, U. *Anal. Chem.*  
27 **2006**, *78*, 8150–8155.  
28  
29 (16) Muller, D.; Levy, A.; Shelef, R.; Abramovich-Bar, S.; Sonenfeld, D.; Tamiri, T. *J.*  
30 *Forensic Sci.* **2004**, *49*, 1–4.  
31  
32 (17) Sigman, M. E.; Clark, C. D.; Fidler, R.; Geiger, C. L.; Clausen, C. A. *Rapid Commun.*  
33 *Mass Spectrom.* **2006**, *20*, 2851–2857.  
34  
35 (18) Widmer, L.; Watson, S.; Schlatter, K.; Crowson, A. *Analyst* **2002**, *127*, 1627–1632.  
36  
37 (19) Xu, X.; van de Craats, A. M.; Kok, E. M.; De Bruyn, P. C. A. M. *J. Forensic Sci.*  
38 **2004**, *49*, 1–7.  
39  
40 (20) Cotte-Rodríguez, I.; Chen, H.; Cooks, R. G. *Chem. Commun.* **2006**, *63*, 953.  
41  
42 (21) Cotte-Rodríguez, I.; Hernández-Soto, H.; Chen, H.; Cooks, R. G. *Anal. Chem.* **2008**,  
43 *80*, 1512–1519.  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
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- 1  
2  
3  
4  
5  
6  
7 (22) Na, N.; Zhang, C.; Zhao, M.; Zhang, S.; Yang, C.; Fang, X.; Zhang, X. *J. Mass*  
8 *Spectrom.* **2007**, *42*, 1079–1085.  
9  
10  
11 (23) Zhang, Y.; Ma, X.; Zhang, S.; Yang, C.; Ouyang, Z.; Zhang, X. *Analyst* **2009**, *134*,  
12 176–181.  
13  
14  
15 (24) Ma, X.; Zhang, S.; Lin, Z.; Liu, Y.; Xing, Z.; Yang, C.; Zhang, X. *Analyst* **2009**, *134*,  
16 1863–1867.  
17  
18  
19  
20 (25) Michels, A.; Tombrink, S.; Vautz, W.; Miclea, M.; Franzke, J. *Spectrochim. Acta - Part*  
21 *B At. Spectrosc.* **2007**, *62*, 1208–1215.  
22  
23  
24  
25 (26) Gilbert-López, B.; Schilling, M.; Ahlmann, N.; Michels, A.; Hayen, H.; Molina-Díaz, A.;  
26 García-Reyes, J. F.; Franzke, J. *Anal. Chem.* **2013**, *85*, 3174–3182.  
27  
28  
29  
30 (27) Nudnova, M. M.; Zhu, L.; Zenobi, R. *Rapid Commun. Mass Spectrom.* **2012**, *26*, 1447–  
31 1452.  
32  
33  
34  
35 (28) Wolf, J.-C.; Schaer, M.; Siegenthaler, P.; Zenobi, R. *Anal. Chem.* **2015**, *87*, 723–729.  
36  
37  
38 (29) Oxley, J. C.; Smith, J. L.; Steinkamp, L.; Zhang, G. *Propellants, Explos. Pyrotech.*  
39 **2013**, *38*, 841–851.  
40  
41  
42 (30) Oxley, J. C.; Smith, J. L.; Bowden, P. R.; Rettinger, R. C. *Propellants, Explos. Pyrotech.*  
43 **2013**, *38*, 244–254.  
44  
45  
46  
47 (31) Hayen, H.; Michels, A.; Franzke, J. *Anal. Chem.* **2009**, *81*, 10239–10245.  
48  
49  
50 (32) Colizza, K.; Mahoney, K. E.; Yevdokimov, A. V.; Smith, J. L.; Oxley, J. C. *J. Am. Soc.*  
51 *Mass Spectrom.* **2016**, *27*, 1796–1804.  
52  
53  
54 (33) Shahin, M. M. *J. Chem. Phys.* **1966**, *45*, 2600–2605.  
55  
56  
57 (34) Hartmann, N.; Klee, S.; Thinius, M.; Peters, S.; Kleffmann, J.; Benter, T. Production  
58 Of NH<sub>3</sub> In N<sub>2</sub>-Corona Discharges And <sup>63</sup>Ni Sources: Unequivocal Identification And  
59  
60

1  
2  
3  
4  
5  
6 Quantification. Present. 64th Conf. Mass Spectrom. Allied Top. San Antonio, USA,  
7  
8 2016.  
9

10  
11 (35) Rahman, A.; Yalin, A. P.; Surla, V.; Stan, O.; Hoshimiya, K.; Yu, Z.; Littlefield, E.;  
12 Collins, G. J. *Plasma Sources Sci. Technol.* **2004**, *13*, 537–547.

13  
14  
15  
16 (36) Westaway, K. C. *Adv. Phys. Org. Chem.* **2006**, *41*, 217–273.

17  
18  
19 (37) Denekamp, C.; Gottlieb, L.; Tamiri, T.; Tsoglin, A.; Shilav, R.; Kapon, M. *Org. Lett.*  
20  
21 **2005**, *7*, 2461–2464.

22  
23  
24 (38) Haroune, N.; Crowson, A.; Campbell, B. *Sci. Justice* **2011**, *51*, 50–56.  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
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## Graphical TOC Entry

