Full Paper

Phlegmatization of TATP and HMTD with Activated Charcoal as Training Aid for Explosive Detection Dogs

Isabel Wilhelm,[b] Greta Bikelytė,[c] Michael Wittek,[b] Martin Andreas Christian Härtel,*[a] Dirk Röseling,[b] and Thomas Matthias Klapötke[c]

Abstract: Both TATP and HMTD could be phlegmatized by coprecipitation with active charcoal resulting in mixtures with a nominal content of 40 wt-% (d40-TATP) and 10 wt-% (d10-HMTD), respectively. In terms of impact and friction sensitivity for both peroxides a content of 40 wt-% resulted in >30 Nm impact sensitivity and >360 N friction sensitivity. Both phlegmatized peroxides passed the Koenen Tube and Thermal Stability Test according to the UN recommendation on the transport of dangerous goods test manual. Investigations with a process mass spectrometer indicate that d40-TATP can produce a saturated TATP headspace at least in the same time as the same amount of pure TATP. Measurements with the transpiration method demonstrated that the vapor pressure p_{sat} at 298.15 K of d40-TATP (2.3 Pa) and d32.7-TATP (0.9 Pa) is lower than that of pure TATP (6.7 Pa). Headspace SPME-GC/MS measurements revealed that the active charcoal does not contribute to the vapor profile of the training aid. Both d40-TATP and d10-HMTD were tested as training aids for explosive detection dog teams (EDD). In both differentiation track and realistic environment scenarios a detection rate of 100% could be achieved by German Federal Police EDD with a false positive rate of solely 3%.

Keywords: Peroxides · Explosive Detection · Canine Training Aid · Explosive Detection Dogs · Vapor Pressure

1 Introduction

Triacetone triperoxide (TATP) is a notorious explosive that was discovered accidentally by *Wolffenstein* [1] in 1895. With respect to its high vapor pressure and extreme sensitivity towards impact and friction, the explosive neither finds military nor civil application. Dry TATP is reported to have a higher impact (0.1 J) and friction sensitivity (0.05 N) than the crude product from the aqueous synthesis (0.5 J, 0.2 N) that is stabilized by trace amounts of water [2]. Despite that, the compound is a homemade explosive that is illegally synthesized by both amateur chemists and terrorists, which is reflected by numerous incidents [3–5]. Due to the dangerous popularity of the illicit use of TATP and hexamethylene triperoxide diamine (HMTD) law enforcements units are urged to train their explosive detection dog teams (EDD) for the detection of peroxide explosives like TATP and HMTD. Regarding the sensitivity of the peroxides, training for EDD is frequently performed with training aids that contain TATP or HMTD (mostly in trace amounts) with numerous commercial, patented products available. These include microamounts of the peroxide explosives coated on porous metal [6–7] and proprietary mixtures with phlegmatization agents [8–12]. Recent research work dealing with the phlegmatization of TATP/HMTD for canine training aids includes a study using ionic liquids as an inert matrix [2] (commercially available at the Diehl Defence GmbH & Co. KG) and the microencapsulation of TATP in polymers [13–15]. The latter development has been commercialized in

form of a microsphere heater system [15]. The vapor sensing of explosive materials has been reviewed by *Lefferts* and *Castell* [16] including animal olfaction approaches like EDD. For the training of an EDD it is essential to both train the detection of confined explosives, as well as large bulk amounts of explosive material. Whilst confined explosives (e.g., well-sealed pipe bomb) release solely trace amounts of explosive vapor into the air, large open bulk amounts (e.g., a trolley filled with explosive) release a "cloud" of vapor with high concentration. If the latter scenario is not trained properly, the EDD may be overcharged by the presence of the vapor "cloud", which possibly results in inability of the EDD to locate the explosive or even non-detection. This phenomenon is called "large amount problem"[17].

Canine training aids have been reviewed in detail by *Simon et al.* [18]. Commercially available HMTD training aids

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have been characterized [19] without disclosing the brand. The results indicate headspace variation of bulk HMTD vs. commercial training aids that contain HMTD and diatomaceous earth [8–11]. Multiple research efforts [20–24] focus on the development and characterization of canine training aids, which are, to the best knowledge of the authors, not commercially available.

The majority of the commercially available canine training aids mentioned before remain to be products with proprietary ingredients, production processes (e.g., used solvents) and sparse public availability of (peer-reviewed) characterization data including the characterization of the vaporization behaviour and headspace profile.

In order to ensure the proper training of EDD for the detection of large bulk amounts of the highly sensitive peroxide explosives TATP and HMTD the German Federal Police commissioned the Fraunhofer Institute for Chemical Technology with the development of a training aid for both TATP and HMTD that is safe to handle and can be used for the training of large bulk amount scenarios of both compounds. It was our intention to publish the results without prior patenting to give the international EDD training community access to an open-source canine training aid for peroxide explosives with public availability of the synthetic procedure and extensive characterization data.

The task was realized by phlegmatization of both peroxides with activated charcoal. The resulting materials were characterized in terms of handling safety (impact and friction sensitivity), security testing (Koenen Tube Test, Thermal Stability Test), toxicity (Lumistox test) and detectability with EDD provided by German Federal Police. With respect to the difficult gas phase behaviour of HMTD [19, 25–27] solely the volatility of the TATP training aid was investigated by vapor pressure measurements with the transpiration method (performed at the University of Munich) and by real-time concentration monitoring with a process mass spectrometer. Additionally, the headspace composition of the TATP and HMTD training aids was investigated with SPME-GC/MS (solid phase microextraction gas chromatography mass spectroscopy).

2 Experimental Section

Within the framework of the development of the training aid one of the main tasks was to find a stabilizing additive that would not contribute to the odor profile of the peroxides, but would decrease the friction and impact sensitivity of the peroxides so that they could be used for safe handling in training. Activated charcoal was selected because of its odorless characteristic. A lot of other materials were tried to be used as additive materials (e.g., molecular sieve, silica gel, diatomaceous earth). Some materials (e.g., diatomaceous earth) were excluded with respect to their characteristic smell (perceived olfactorally by the experimenter), some materials have even increased the fric-

tion and impact sensitivity (e.g., sand). Within the stabilization agent screening performed in this work active charcoal provided the best results and its peroxide mixtures were further characterized.

Chemicals: Hydrogen peroxide (30%, p.a. stab.) and citric acid (without further purification) were obtained from Carl Roth GmbH + Co. KG. Activated Charcoal (SUPELCO, puriss., p.a., powder) was obtained from Sigma Aldrich. Acetone ($\geq$ 99%, technical) and hydrochloric acid (37%, Reag. Ph. Eur.) were obtained from VWR International GmbH. Urotropin (for synthesis) was obtained from Merck KGaA.

2.1 Synthesis of TATP on Activated Charcoal: d40-TATP

15.0 mL of acetone were cooled down to about -10 to $-5\,°C$, then 9.0 mL hydrogen peroxide were added within 45 minutes while cooling and stirring constantly. Afterwards 1.0 mL of hydrochloric acid (37%) was added dropwise under cooling in an ice-salt bath in the temperature range of $-10\,°C$ to $-5\,°C$ and stirring within 5 minutes. The solution was stirred for 45 minutes in the ice-salt bath and then slowly warmed up to room temperature. The TATP, which precipitated overnight, was filtered and washed with distilled water until the filtrate reached a neutral pH value. The TATP was dried at room temperature overnight. The procedure yielded ~3.0 g of pure TATP.

These 3.0 g of TATP were diluted in 15.0 mL acetone and 4.5 g of activated charcoal were slowly added while stirring. The mixture was stirred for one hour, followed by addition of 50 mL distilled water. The mixture was filtered and dried overnight at room temperature in a fume hood (Figure 1). The procedure yielded ~7.5 g TATP/activated charcoal-mixture with 40 wt.–% of TATP in the mixture (d40-TATP), as determined via GC-FID, method specified in 2.6.2.

Figure 1. Dried homogeneous TATP/activated charcoal-mixture d40-TATP on top of a filter paper (circular, folded once).

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2.3 Synthesis of HMTD on Activated Charcoal: d40-HMTD, d10-HMTD and d5-HMTD

16.0 mL of hydrogen peroxide were cooled down to −10 to −5 °C, then 8.0 g urotropin were added within 30 minutes keeping the temperature below −5 °C by the use of an ice-salt bath and stirring constantly. After an additional 20 minutes, 8.0 g of citric acid was added within the time span of 30 minutes. The solution was stirred another 20 minutes until the acid was dissolved. Then, while maintaining the cool conditions, 6.0 g of activated charcoal was added within 20 minutes. The resulting suspension was stirred for another 60 minutes in the ice-salt bath (−10 °C to −5 °C) and then slowly warmed up to room temperature. HMTD/activated charcoal precipitated overnight and was filtered and washed with distilled water until neutrality of the filtrate was reached. The HMTD/activated charcoal-mixture was dried overnight at room temperature in a fume hood (Figure 2). The procedure yielded ~9.6 g HMTD/activated charcoal-mixture with 40 wt.–% of HMTD in the mixture (d40-HMTD), as determined via HPLC, method specified in 2.4.

12.5 g of the 40 % HMTD/activated charcoal (d40-HMTD) were well mixed with 37.5 g pure activated charcoal to obtain 50.0 g of a 10 % HMTD/activated charcoal-mixture (d10-HMTD). To obtain 50.0 g of a 5 % mixture (d5-HMTD), 6.25 g of 40 % HMTD/activated charcoal were mixed with 43.75 g pure activated charcoal.

Figure 2. Dried homogeneous HMTD/activated charcoal-mixture d40-HMTD on top of a filter paper (circular, folded once).

Table 1. HPLC method eluent gradient.

Time min	B %	Flow mL/min
0	17	0.6
8	90	0.6
9	90	0.6
10	17	0.6

2.4 High Performance Liquid Chromatography (HPLC)

The content of HMTD in the mixtures was determined using a HPLC device (1290 Infinity) by Agilent.

HPLC conditions. Column: Kinetex 2.6 μm Biphenyl 100× 4.6 mm with C18 pre-column (Phenomenex); Eluent: Water (A): Acetonitrile (B), 83 : 17 (Table 1); Flow: 0.6 mL/min; Detection: 200 nm (DAD); Injection volume: 5 μL; Column temperature: 308.15 K; Analysis time: 10 min.

2.5 Impact and Friction Sensitivity

The impact sensitivity was determined by the BAM (Bundesanstalt für Materialprüfung - Federal Institute for Material Testing) Fallhammer test 3(a)(ii) and likewise the friction sensitivity was determined with BAM Friction test 3(b)(i) in accordance with the UN Recommendation on the Transport of Dangerous Goods, Manual of Tests and Criteria [28].

2.6 Gas Chromatography

2.6.1 SPME-GC/MS Analysis

The pure activated charcoal and the mixture with TATP was analyzed via SPME-GC/MS (Gas Chromatograph 7890 B and Mass Spectrometer 5977 A by Agilent; PAL autosampler by CTC Analytics). The SPME-GC/MS analysis was performed using the following parameters:

GC/MS conditions. Column: HP-5MS, 30 m×0.25 mm ID,×0.25 μm film; Liner: 2 mm, Siltek coated (Restek); Oven: 343.15 K–4 min, 10 K/min–563.15 K; Inj.-Temperature: 523.15 K, split-ratio 6; mass spectrometer: scan, 10–500 amu.

SPME conditions. Fiber: 65 μm Polydimethylsiloxane (PDMS) / DVB (Divinylbenzene) (Supelco); Incubation: 5 min at 318.15 K; Extraction: 5 min at 318.15 K; Desorption: 5 min at 523.15 K.

The activated charcoal mixture with HMTD was analyzed via SPME-GC/MS as well. (Gas Chromatograph 7890 A and Mass Spectrometer 5975 C by Agilent; PAL autosampler by CTC Analytics). This analysis was performed with the following parameters:

GC/MS conditions. Column: HP−5 MS, 30 m x 0.25 mm ID, x 0.25 μm film; Liner: 2 mm, Siltek coated (Restek) Oven: 323.15 K–3 min, 15 K/min–553.15 K; Inj.-Temperature: 533.15 K, split-ratio 10; mass spectrometer: scan, 10–500 amu.

SPME conditions. Fiber: 50/30 μm DVB / CARBOXEN-PDMS (Divinylbenzene/ Carboxen/ Polydimethylsiloxane) (Supelco); Incubation: 30 min at 323.15 K; Extraction: 15 min at 323.15 K; Desorption: 5 min at 533.15 K.

2.6.2 GC-FID TATP Content Determination[M1]

The activated charcoal mixture with TATP was analyzed via GC (Agilent 6890N) using following parameters:

Column: Supelco Equity – 5, 30m x 0.32mm ID x 1μm film; Liner: 4 mm, Siltek coated (Agilent); Oven: 333.15 K – 3 min, 10 K/min – 523.15 K; Inj.-Temperature: 423.25 K, split-ratio 20; flow: He, 2 mL/min; Detection: 523.15 K; FID: H_2/Air – 30/400 ml/min, Make-up Gas – 25 mL/min.

Sample preparation:

Approximately 10 mg of the TATP/activated charcoal samples were weighed into a 10 ml flask and filled with acetone. The flasks were then placed in an ultrasonic bath for 10 minutes and then the liquid phase was filtered off.

2.7 Security Testing: Koenen Tube Test and Thermal Stability

The Koenen Tube Test is used to determine the sensitivity of solid and liquid substances to the effect of intense heat under confinement. The requirements for the test method are listed in the UN Recommendation on the Transport of Dangerous Goods, Manual of Tests and Criteria, Koenen Tube Test 2(b) [28]. Samples of the test material are confined in a steel tube fitted with an orifice plate at the top end with varying vent hole diameters. The steel tube is heated along its entire length by four burners which are positioned around the tube (Figure 3). The vent hole diameter is decreased from 20 mm until the increased confinement causes a reaction to burst the tube. The limiting diameter is determined as the largest diameter at which an explosion is observed.

2.8 Thermal Stability

The thermal stability test type 3(c)(i) according to the UN Recommendation on the Transport of Dangerous Goods, Manual of Tests and Criteria [28] has been carried out. This test procedure is used to measure the stability of a substance when it is exposed to higher temperatures in order to determine if the substance is too dangerous for transportation. A 50 g sample is filled into a beaker, covered and placed in an oven. The oven is heated up to 348.15 K and the sample is left there for 48 hours or until an ignition or explosion occurs.

If the substance shows no signs of reaction in this test, it can be considered thermally stable. If the test result is "positive (+)", the substance should be considered as thermally unstable for transportation.
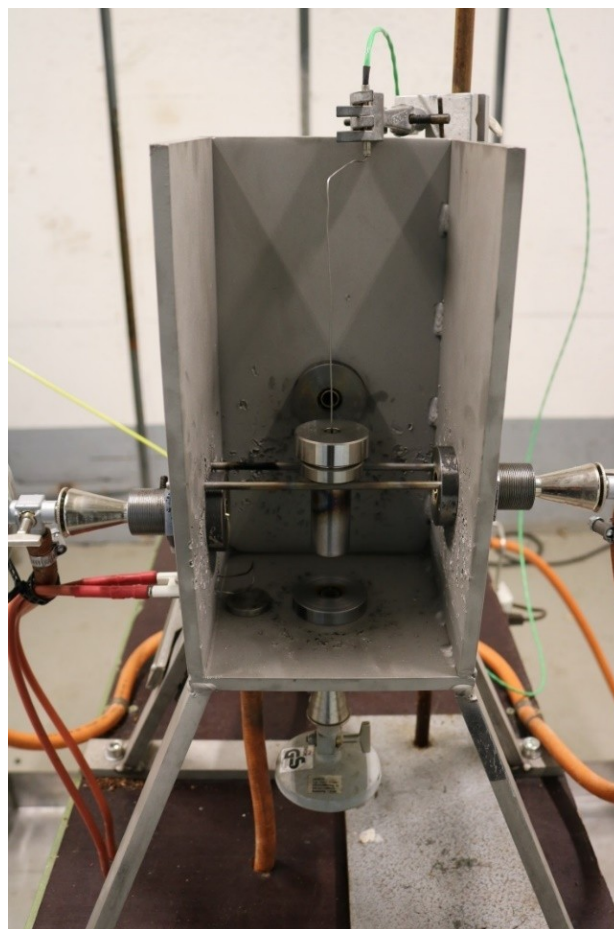

Figure 3. Koenen Tube Test Apparatus.

2.9 Accelerating Rate Calorimeter (ARC)

A dilution series for the HMTD/activated charcoal mixture was analyzed by ARC. The Accelerating Rate Calorimetry method is used for the detection of thermally induced decomposition reactions [29].

The measurements were performed in an Accelerated Rate Calorimeter (ARC ES) from Thermal Hazard Technology using the following parameters:

Weighing 300 mg, with a phi factor of approx. 7 (phi factor sample plus vessel without pressure transducer).

The sample vessel is made of titanium; Start temperature: 313.15 K; Final temperature: 513.15 K; Step size: 5 K; Sensitivity: 0.2 K/min; Waiting time: 10 min.

2.10 LUMIStox Test for Toxicity

The luminescent bacteria test was performed to estimate the acute toxicity of HMTD and TATP. This test was carried out with the LUMIStox 300 instrument from Dr. Lange. In combination with the LUMIStherm incubation block it

meets the technical requirements of DIN 38412 L34/L341 and the international standard DIN EN ISO 11348 [30, 31]. In the luminescent bacteria test, the ability of the marine bacteria *Vibrio fischeri* to glow under optimal growth conditions (bioluminescence) is used. Toxic substances cause a reduction in bioluminescence, which is proportional to the toxicity of the sample. The toxicity of the sample is expressed as G_L value [32], a dilution factor.

0.2 g of the peroxide explosives were suspended in a 2 % NaCl solution. After 3 days the suspension was filtered. The G_L value is then determined with the filtrate obtained in the luminescent bacteria test. The reported solubility of TATP in water is 177 mg L^{-1} (22 °C) [33]. According to *Matyáš* and *Pachman* [34], the solubility of HMTD in water is 100 mg L^{-1}.

2.11 Process Mass Spectrometer Measurements

In this experiment, the spread of TATP and d40-TATP in the gas phase was compared. Since d40-TATP is to be used to enable gas phase experiments under safe conditions, the time until saturation of the gas phase is reached, is valuable information. Since the saturation time depends on various external parameters such as temperature [35], humidity, gas volume, packaging, etc., the experimental setup was configured to minimize the fluctuation of these parameters. TATP and d40-TATP were laid out in a closed gas volume and the increase of concentration in the gas phase was monitored. The aim of the experiments was to verify that the mixture, which is safe to handle, shows a similar behaviour in comparison to pure TATP.

Method: The diffusion rate of any substance into the gas phase depends on the total surface area. In order to obtain the same macroscopic surface, both the TATP and d40-TATP were laid out in the same open cardboard box in DIN A4 format (297 x 210 mm). Larger agglomerates were carefully crushed so that the particle size was optically identical for d40-TATP and pure TATP. 100 g of pure TATP and 100 g of d40-TATP (40 wt.–% pure TATP) were used.

An acrylic glass cuboid (aquarium) with a volume of 150 litres was used to confine the closed gas volume (Figure 4). The cuboid has a removable cover that allows to put the TATP or the mixture into the chamber. It also has 9 inlets each closed with an Agilent long-life, non-stick inlet septum made from silicone polymers. 3 of the inlets are on the lid and 3 on each of the two smaller sides.

The concentration of TATP in the aquarium was monitored with a Pfeiffer MS OmniStar GSD 320 O mass spectrometer using the secondary electron multiplier (SEM). For monitoring the concentration in the gas phase, mass channels, that were only influenced by TATP, were selected. During the electron impact ionization of the TATP, the fragments with the following mass to charge ratios should have the highest intensity according to the literature: *m/z* 43, 58,
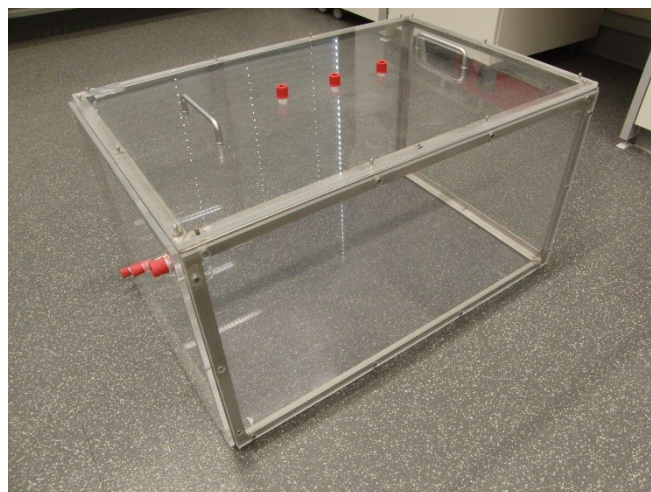

Figure 4. Glass cuboid used for the process mass spectrometer measurements.

59 and 75 [36]. For both TATP and d40-TATP a signal increase in channels 43, 58 and 59 could be observed.

Acetone is used in the synthesis of TATP and d40-TATP. Since the synthesis of TATP involves chemical precipitation with water and a subsequent additional drying process, it is very unlikely that residues of acetone will remain. However, since acetone decomposes into the same fragments with mass to charge ratios 43 and 58 during ionization [37] (Figure 5), the results of TATP and TATP/activated carbon were compared with an identical experiment carried out with 1 mL acetone. The spreading time of acetone is many times faster than that of TATP and acetone showed no signal in the m/z 59 channel. With TATP and d40-TATP, however, all channels 43, 58 and 59 showed the same concentration trends. Considering all these aspects, it is relatively safe to assume that the resulting signals in the *m/z* 43, 58, and 59 channels can be allocated to the presence of TATP.

The aquarium was filled with ambient air, and the relative humidity during the experiments averaged at about 40 %. The temperature was 24 °C.

Experimental: Before TATP or d40-TATP were laid out into the aquarium, the aquarium was cleaned thoroughly with distilled water and flushed with pure Nitrogen for a couple of hours. The lid was closed and the concentration was monitored with the mass spectrometer. No change in the background signal of the aquarium could be detected between the two measurements, ensuring an identical starting point for the experiments.

The respective substance was positioned into the aquarium and the lid was closed. The measurement was continued until saturation was achieved for several hours (Figure 6).
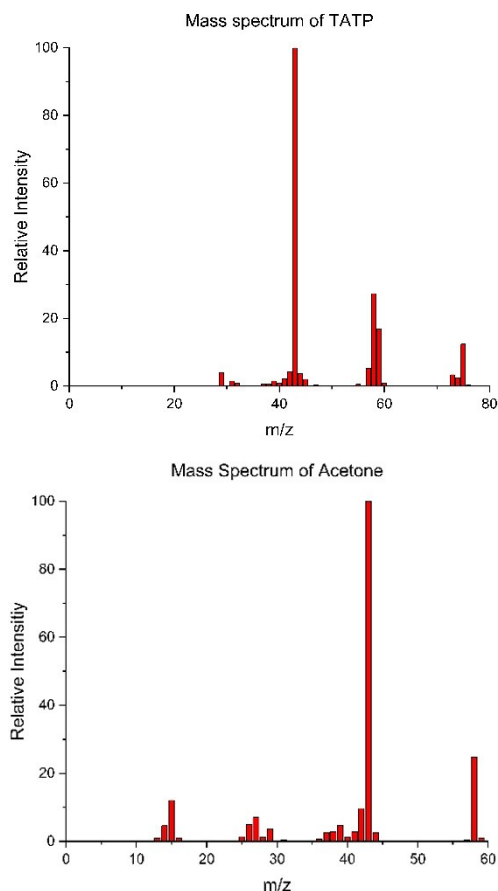
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Figure 5. Mass spectra of TATP (above) and acetone (below). Data extracted from [36] and [37].
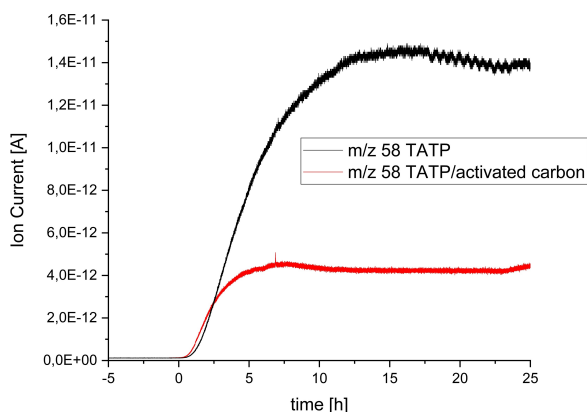

Figure 6. Comparison of the concentration increase of TATP and TATP/activated charcoal (d40-TATP). The graph with the lower final ion current corresponds to d40-TATP. The time zero represents the time at which the respective substance was placed in the aquarium and the lid was closed.

2.12 Vapor Pressure Measurements using the Transpiration Method

In order to investigate the thermochemical properties of developed phlegmatized mixtures, vapor pressures of mixtures d40-TATP and d32.7-TATP were measured using the transpiration method. This method has been successfully implemented for the measurements of vapor pressures of various energetic materials, including pure TATP [38]. The same experimental procedure that was used to determine the vapor pressures of pure TATP in the work of *Härtel et al.* [38] was also replicated in this work.

The working principle of the transpiration method has been thoroughly discussed in the literature [39]. In this work, the experimental setup was filled with TATP/activated charcoal-mixtures prepared according to the procedure, described in section 2.1. The gas saturation was confirmed by replicate measurements at different carrier gas flowrates resulting in the same derived vapor pressure. The quantification of the analytes was carried out with vacuum-outlet gas chromatography coupled with mass spectrometer (VO-GC/MS) [40] using a Shimadzu QP2010 SE device. Along with the obtained experimental *p-T* data, corresponding thermodynamic parameters and fit-functions in a form of a modified Clarke-Glew equation [41] were derived. Table 2 provides the isobaric molar heat capacities and their differences for TATP, which are necessary for the adjustment of the molar enthalpies of sublimation to the reference temperature (298.15 K) according to the procedure discussed in the work of *Chickos et al.* [42].

2.13 Explosive Detection Dog Trials

As part of the desensitization study of HMTD and TATP a test was carried out with explosive detection dog teams (EDD). For this purpose, several EDD were provided by the German Federal Police, who tested the detection of both the pure substances and the safe-to-handle mixtures at Fraunhofer ICT over a period of 3 days. The following dogs took part in the testing: two German Shepherds (both female, 4 and 5 years old), two X–Mechelaars (both male, 3 and 4 years old), one Dutch Herder (male, 7 years old) and one Malinois (female, 7 years old). All dogs participated in the tests, except for day 3: the Malinois and one German Shepherd dog (4 years old) did not participate due to a police operation. The dogs were trained before according to

Table 2. Molar heat capacities and their differences at constant pressure ($T = 298.15$ K).

Compound	$C_{p,m}^{\circ}(cr)$ J mol^{-1} K^{-1}	$-\Delta_{cr}^{g} C_{p,m}^{\circ}$ [a] J mol^{-1} K^{-1}
TATP	271.8 [43]	41.5

[a] Calculated by $-\Delta_{cr}^{g} C_{p,m}^{\circ} = 0.75 + 0.15 \times C_{p,m}^{\circ}(cr)$ [44].

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BRAS 170, which is a restricted German Federal Police internal guideline. The training of the dogs includes by routine the presence of numerous distractors (gloves, human scent, etc.) in search scenarios.

A differentiation track was used to test the detection of pure (1.0 g) and phlegmatized substances (3 g) in a time-efficient manner (Figure 7). In this test, easily accessible odor samples are placed at regular intervals on a wooden beam. The EDD have to identify the samples with the explosives in between different samples. Pure activated charcoal has been used as distractor odor sample: one of 15 samples contained an explosive (training aid) amongst samples with pure activated charcoal and blank samples. All of the tests were carried out in a single-blind fashion. This means that, besides the test assessor, neither the dog nor the handler knew where the explosive was located. The location of the target was randomly chosen and changed between every dog. The sample preparation included 5 minutes of soak time prior to testing.

Furthermore, various training aid samples were hidden in different scenarios: 40.0 g d10-HMTD in a locker of a dressing room, 40.0 g d10-HMTD in the trunk of a car and 70.0 g d40-TATP in an engine compartment of a car and

had to be found by the EDDs. The training aids were laid out 5 minutes in advance.

3 Results and Discussion

3.1 Impact and Friction Sensitivity

The materials were tested according the UN Recommendation on the Transport of Dangerous Goods, Manual of Tests and Criteria [28] (Table 3).

The test result is considered "positive (+)" if the lowest impact energy at which at least one "explosion" occurs in six trials is 2 Nm or less and the substance is considered too dangerous for transport in the form in which it was tested. Otherwise, the result is considered "negative (−)".

The test result for the friction test is considered "positive (+)" if the lowest friction load at which one "explosion" occurs in six trials is less than 80 N and the substance is considered too dangerous for transport in the form in which it was tested. Otherwise, the test result is considered "negative (−)".

Pure TATP and HMTD are extremely sensitive against friction and impact. The pure explosives are very dangerous and extreme caution is required when handling these substances.

Table 3 shows that the mixtures with the activated charcoal are significantly less sensitive than the pure peroxide explosives. Therefore, the handling of the mixtures is much safer compared to the pure peroxide explosives.

3.2 Headspace SPME-GC/MS Analysis of TATP on Activated Charcoal

A headspace SPME-GC/MS analysis of pure activated charcoal was performed. Figure 8 shows the resulting chromatogram.

The big peak at the beginning of the chromatogram is a ghost peak caused by air (maximum peak height at 3.7×10^6). The second peak at 18 minutes is caused by column bleeding, a common degradation process of the stationary phase. The resulting chromatogram of the headspace SPME-GC/MS analysis of the activated charcoal did

Figure 7. Top: Training at a differentiation track, bottom: Signal position of an EDD for detection of a compound.

Table 3. Impact and friction sensitivity of pure and desensitized substances.

	Impact Sensitivity Nm	Result +/−	Friction Sensitivity N	Result +/−
pure TATP	0.03–1.00	+	< 5.0	+
d40-TATP	> 30.0	−	> 360.0	−
pure HMTD	0.20–1.00	+	< 5.0	+
d40-HMTD	> 30.0	−	> 360.0	−
d10-HMTD	> 30.0	−	> 360.0	−
d5-HMTD	> 30.0	−	> 360.0	−

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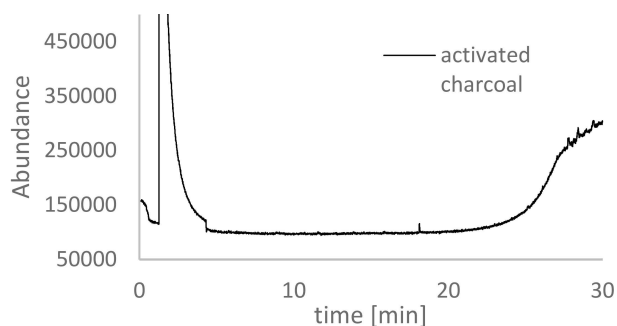
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Figure 8. GC chromatograms of pure activated charcoal.

not reveal the presence of further compounds, therefore the activated charcoal does not influence the odor signature of the peroxide explosive mixtures.

The chromatogram of the TATP/activated charcoal-mixture TATP-d40 in Figure 9 contains the ghost peak caused by air and an explicit peak for TATP at a retention time of 8 minutes. No peaks that correspond to impurities or decomposition products are present in the chromatogram.
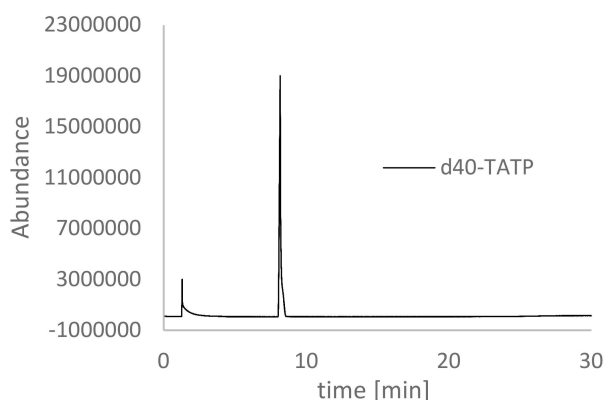

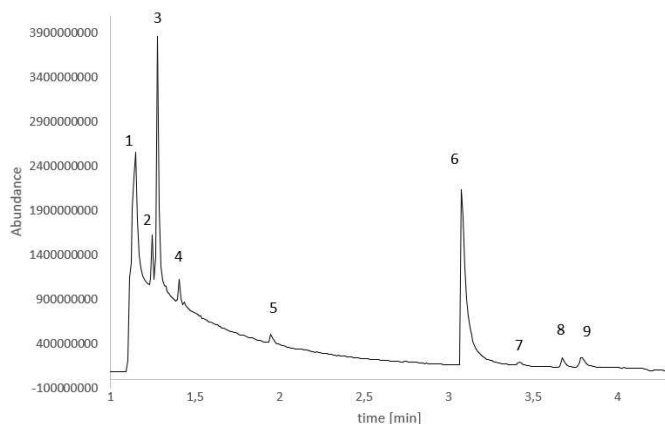**Figure 9.** GC chromatogram of d40-TATP.

Figure 10. SPME-GC/MS chromatogram of d10-HMTD.

As it is stated in the literature, the odor profile of HMTD is complex. [19, 25–27]. Using headspace SPME-GC/MS, degradation products of HMTD could be identified in the headspace of the HMTD mixture. The first peak in the chromatogram (Figure 10) is caused by air. The following degradation products of HMTD were found in the gas phase: formamide (2), formic acid (3), acetic acid (4) and dimethylformamide (6). The peaks 5, 7, 8 and 9 are siloxanes, caused by column bleeding. The qualitative headspace profile of the HMTD mixture agrees with the components found in the headspace profile of laboratory-grade and clandestine HMTD with different ages [19]. The non-detection of formaldehyde and trimethylamine, quantitative aspects of the headspace composition and ageing effects must be further investigated for the training aid presented in this work in comparison to the work by *Simon and DeGreeff* [19].

3.3 Security Testing: Koenen Tube Test, Thermal Stability

3.3.1 Koenen Tube Test

The Koenen Tube Test was performed for d40-TATP and d-40-HMTD.

For d40-TATP, explosions occurred at 2 and 3 mm vent hole diameters (Figure 11). With a nozzle diameter of 5 mm, no explosion was observed for three times. Therefore the limiting diameter of d40-TATP according to the UN test manual is 3 mm.

The results of the Koenen test for d40-HMTD indicate that the material has a limited vent hole diameter of less than 1 mm (Figure 12). However, during the tests it was observed that the mixture was blown out very fast from the steel tube after a few seconds at low thermal stress (about 370 K).

3.3.2 Thermal Stability

The test was carried out with 50.0 g of d40-TATP. Due to its density, the mixture did not fit into the 50 mL beaker proposed in the test manual. Only 14 g of the substance would fit into it. After consultation with BAM the mixture was placed in a 250 mL beaker (plane, without spout) and covered with a watch glass. The beaker was placed in an oven at 348.15 K for 48 hours. During the 48 h, no ignition or explosion took place. Weighing of the mixture indicated that a weight loss of 1.34 % had occurred. The result of the thermal stability test for d40-TATP is "negative (−)", so it is considered as thermally stable for transportation.

Likewise, the test was also performed with 50.0 g of d40-HMTD. Already after 2 hours in the oven, a deflagration of the mixture could be observed, similar to the observations made within the Koenen test. d40-HMTD must therefore be classified as "positive (+)", so the substance should be considered thermally unstable for transport.

Figure 11. Steel tubes after testing with d40-TATP. Top: 5 mm vent hole diameter (no explosion, the orifice plate and the steel tube is intact), bottom: 3 mm vent hole diameter (with explosion, the steel tube is destroyed, the orifice plate is still intact).

Figure 12. Steel tubes after testing with d40-HMTD. Top: 20 mm vent hole diameter of the orifice plate, the steel tube and the plate are still intact; bottom: 1 mm vent hole diameter; orifice plate and steel tube are both intact.

Based on this result, ARC (Accelerating Rate Calorimeter) [29] analysis of d40-HMTD was carried out. In addition, a dilution series for the HMTD/activated charcoal mixture was also analyzed by ARC. The dilution was performed as described in part 2.2.

The analysis by the adiabatic calorimeter (Figure 13) shows that the 40% HMTD/activated charcoal mixture achieves a high self-heating rate (900 K/min). In order to suppress this self-heating, active charcoal dilutions of the HMTD activated carbon mixture were examined. The 5%, 10% and 20% HMTD/activated charcoal mixtures show only low self-heating rates above 363.15 K and 353.15 K respectively (max. ~0.1 K/min).

Based on the ARC results, the thermal stability test was performed again with 50.0 g of a 5% HMTD/activated charcoal mixture. No inflammation or explosion was detected during the 48 h in the oven. Weight loss of the mixture was 1.8%. The result of d5-HMTD is "negative (−)".

The thermal stability test was also performed with the 10% HMTD/activated charcoal mixture. Again, no inflammation or explosion could be observed during the 48 h. The weight loss of the mixture was 2.1%. The result of d10-HMTD is "negative (−)". So, both d5-HMTD and d10-HMTD are considered as thermally stable for transportation.

3.4 LUMIStox Testing for Toxicity

The LUMIStox Test was performed for TATP and HMTD.

TATP has a G_L value of 1:2 and is classified as non-toxic (Table 4). The lowest achievable G_L value is 1:2 with respect to the measurement procedure. Therefore, TATP does not cause any effect on the luminescent bacteria at the lowest possible dilution level.

The first dilution level of HMTD with a light transmission of less than 20% was 1:64 and thus corresponds to the G_L value. The sample containing HMTD is classified as moder-
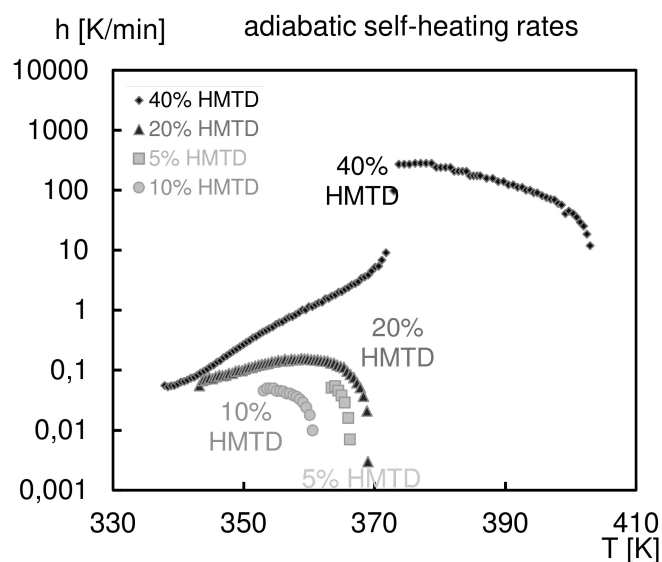
Figure 13. Adiabatic self-heating rates of HMTD/activated charcoal mixtures.

Table 4. G_L results of TATP and HMTD.

	G_L
triacetone triperoxide (TATP) + 2 % NaCl-Solution	1:2
hexamethylene triperoxide diamine (HMTD) + 2 % NaCl-Solution	1:64

ately toxic according to the classification by Wang [32], a hazard is assumed if the G_L value greater than 1:8 is exceeded.

3.5 Process Mass Spectrometer Measurements

The asymptotic nature of curves during saturation (Figure 6) combined with the signal noise makes it difficult to define the point at which saturation is reached. To compare the two experiments, the time when 10 % and 90 % of the maximum signal was reached were determined.

The data (Table 5) show that for TATP 90 % saturation was reached after about 9–10 hours, whereas for d40-TATP this took half of the time, namely 4–5 hours. The saturation point of 10 % was reached after about 2 hours for TATP, and after about 1 hour for d40-TATP. The absolute signal level for TATP was 3.5 times higher for TATP than for d40-TATP.

The observed differences between both TATP variants can be explained by several reasons. First, the absolute amount of TATP was different in both experiments, specifically 40 g vs. 100 g. It should also be mentioned that first the TATP experiment and then the experiment with TATP/ activated charcoal was performed. A possible explanation for the faster speed of saturation in the second experiment could be that the walls of the aquarium were saturated by adsorption of TATP in the first experiment. Possibly the walls could not adsorb as much TATP since they were already loaded, although cleaning was performed between the measurements. The TATP in the gas phase in the experiment with d40-TATP was possibly not adsorbed on the walls anymore, which might have led to a faster gas phase saturation.

On the other hand, the faster saturation time could be explained by a larger surface area of the d40-TATP in comparison to TATP. Due to the mixture with activated charcoal, the surface area of the TATP with activated charcoal could potentially be larger than that of pure TATP. Therefore, the time to saturation is shorter due to the larger surface area for interactions between TATP molecules and the gas phase.

Another reason could be the reproducibility of the experiment. Since the vapor pressure and the spreading time in the gas phase are very sensitive to changes in external factors, the difference in gas spreading could be due to fluctuations during both experiments. For example, it was observed that the concentration of TATP in the gas phase could be correlated with the incident solar light during the day and therefore varied by about +/−10 %.

It should be noted that the mass spectrometer could not be calibrated as there was no calibration gas generator available for calibration. Therefore, the absolute signal level cannot be correlated with a specific concentration, but the deviation in signal level is most probably not caused exclusively by the possible loss of sensitivity of the mass spectrometer during this period alone. If the concentration for

Table 5. Comparison of signal levels and corresponding times of TATP and d40-TATP.

	TATP			d40-TATP		
	m/z 43	m/z 58	m/z 59	m/z 43	m/z 58	m/z 59
Baseline [pA]	0.5	0.1	0.1	0.8	0.1	0.1
saturated signal [pA]	58.0	13.9	0.6	18.2	4.3	0.3
10 % saturated signal [pA]	6.3	1.5	0.1	2.5	0.5	0.1
90 % saturated signal [pA]	52.2	12.5	0.5	16.5	3.9	0.3
t_10 % saturated signal [h]	1.9	1.9	1.8	1.0	1.0	1.0
t_90 % saturated signal [h]	9.3	9.1	9.8	4.4	4.1	4.9

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Table 6. d40-TATP: absolute vapor pressures p_{sat} and thermodynamic properties of sublimation obtained by the transpiration method in this work.

d40-TATP: $\Delta_{cr}^{g}H_{m}^{\circ}$ (298.15 K) = 80.2 ± 0.5 kJ mol^{-1}

$\ln p_{sat}/p^{0} = \frac{317.4}{R} - \frac{92612.5}{RT} - \frac{41.5}{R}\ln\frac{T}{298.15\ K}$

T_{exp} [a] K	m [b] µg	V_{N_2} [c] dm^3	T_{amb} [d] K	Gasflow dm^3 h^{-1}	p_{sat} [e] Pa	$u(p_{sat})$ [f] Pa	$\Delta_{cr}^{g}H_{m}^{\circ}$ kJ mol^{-1}	$\Delta_{cr}^{g}S_{m}^{\circ}$ J mol^{-1} K^{-1}
274.5	30.6	2.54	297.4	2.0	0.14	0.01	81.58	184.9
274.5	21.6	1.74	298.2	2.3	0.14	0.01	80.17	180.0
274.5	19.1	1.59	297.9	1.6	0.14	0.01	80.17	179.7
279.0	21.9	0.98	298.0	2.0	0.25	0.01	79.98	179.5
279.1	21.0	0.98	296.7	2.0	0.24	0.01	79.98	179.0
283.7	19.2	0.49	297.7	2.0	0.44	0.02	79.79	178.7
288.5	32.6	0.49	298.0	2.0	0.74	0.02	79.59	177.7
293.4	58.6	0.49	297.3	2.0	1.33	0.04	79.39	177.2
293.4	56.9	0.49	298.1	2.0	1.29	0.04	79.39	177.0
293.4	58.1	0.49	298.0	2.0	1.32	0.04	79.39	177.2
298.2	97.2	0.49	297.2	2.0	2.21	0.06	79.19	176.4
303.1	162	0.49	298.0	2.0	3.70	0.10	78.98	175.8
307.9	263	0.49	296.6	2.0	5.98	0.17	80.20	179.6
307.9	274	0.49	297.4	2.0	6.23	0.18	80.20	179.9
312.7	498	0.52	297.9	2.0	10.6	0.3	80.00	179.8
312.7	454	0.49	298.0	2.0	10.3	0.3	80.00	179.5

[a] Saturation temperature ($u(T)$ = 0.1 K). [b] Mass of transferred sample condensed at 243 K. [c] Volume of nitrogen ($u(V)$ = 0.005 dm^3) used to transfer m ($u(m)/m$ = 1.5%) of the sample. [d] T_{amb} is the temperature of the soap film flowmeter used for measurement of the gas flow. [e] Vapor pressure at temperature T, calculated from the m and the residual vapor pressure at the condensation temperature, calculated by an iteration procedure; p° = 1 Pa. [f] Standard uncertainty in p was calculated with $u(p/Pa)$ = 0.005 + 0.025(p/Pa) for p < 5 Pa and $u(p/Pa)$ = 0.025 + 0.025(p/Pa) for p > 5 to 3000 Pa.

TATP was higher, this could be explained by leaks from the aquarium. The aquarium is far from being gas-tight and the lid was only loosely put on to avoid any forces during opening and closing.

The comparison of these preliminary aquarium experiments of pure TATP and d40-TATP has shown that d40-TATP needed roughly half the time for saturation of the cuboid atmosphere and produced a 3.5 times smaller signal at the mass spectrometer. Due to the sensitive characteristics of gas spreading, such as the discussed factors of wall adsorption and sunlight, further experiments need to be conducted to obtain a more conclusive picture. To get more insight into the comparison of the vaporization behaviour of bulk TATP and the phlegmatized d40-TATP under well-controlled (calibrated, gas-tight) conditions we performed vapor pressure measurements of the active charcoal mixtures d40-TATP and d32.7-TATP.

3.6 Vapor Pressure Measurements

The obtained p-T values, experimental conditions, their uncertainties and the corresponding thermodynamic properties of TATP in the mixtures d40-TATP and d32.7-TATP, obtained by vapor pressure measurements with the transpiration method are compiled in Tables 6 and 7.

The uncertainties for T, V and m are standard uncertainties. Uncertainty of the enthalpy of sublimation is the standard uncertainty, calculated including uncertainties of

vapor pressure, uncertainties from the fitting equation and the uncertainty of temperature adjustment to T = 298.15 K. Detailed information on the methods of calculations was published previously [45–46].

Comparison of experimental vapor pressures of pure TATP [38] and the phlegmatized mixtures, measured in this work are presented in the Table 8 and Figure 14.

It was observed that lowering the amount of TATP in the mixture with activated charcoal decreases the vapor pressure p_{sat} at 298.15 K (6.7 Pa for pure TATP, 2.3 Pa for d40-TATP and 0.9 Pa for d32.7-TATP) and increases the mo-
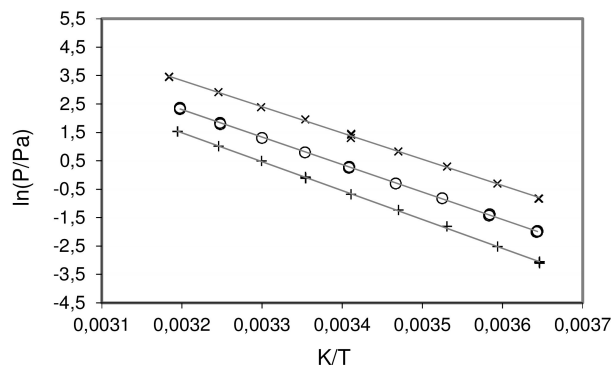

Figure 14. Experimental vapor pressures of the TATP in TATP/activated charcoal-mixtures in comparison with the literature values. Here ×–Härtel et al. [38], ○–d40-TATP from this work, + – d32.7-TATP from this work. Solid lines represent the linear fits.

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Table 7. d32.7-TATP: absolute vapor pressures p_{sat} and thermodynamic properties of sublimation obtained by the transpiration method in this work.

d32.7-TATP: $\Delta_{cr}^{g}H_{m}^{\circ}$ (298.15 K) $= 84.4 \pm 0.5$ kJ mol^{-1}
$\ln p_{sat}/p^{0} = \frac{323.8}{R} - \frac{96732.9}{RT} - \frac{41.5}{R}\ln\frac{T}{298.15\ K}$

T_{exp} [a] K	m [b] μg	V_{N_2} [c] dm^3	T_{amb} [d] K	Gasflow dm^3 h^{-1}	p_{sat} [e] Pa	$u(p_{sat})$ [f] Pa	$\Delta_{cr}^{g}H_{m}^{\circ}$ kJ mol^{-1}	$\Delta_{cr}^{g}S_{m}^{\circ}$ J mol^{-1} K^{-1}
274.3	12.3	3.05	297.1	2.0	0.05	0.01	85.35	189.7
274.3	11.8	2.78	298.0	1.4	0.05	0.01	85.35	190.1
274.3	8.5	2.06	299.7	2.2	0.05	0.01	85.35	189.9
278.3	5.1	0.70	297.9	2.0	0.08	0.01	85.18	189.5
283.3	7.4	0.50	299.0	2.0	0.16	0.01	84.98	189.3
288.2	13.2	0.50	298.4	2.0	0.29	0.01	84.77	188.2
293.2	22.9	0.50	298.2	2.0	0.51	0.02	84.57	187.2
298.1	40.4	0.50	298.9	2.0	0.90	0.02	84.36	186.4
298.1	40.2	0.50	299.3	2.0	0.90	0.03	84.36	186.3
298.1	41.4	0.50	299.4	2.0	0.93	0.03	84.36	186.6
298.2	50.2	0.60	298.8	2.0	0.94	0.03	84.36	186.7
303.1	74.4	0.51	299.2	2.0	1.6	0.1	84.15	186.1
308.1	125	0.50	299.0	2.0	2.8	0.1	83.95	185.2
313.1	210	0.51	300.1	2.0	4.6	0.1	83.74	184.5
313.1	211	0.51	299.3	2.0	4.7	0.1	83.74	184.6
313.1	209	0.50	299.7	2.0	4.6	0.1	83.74	184.5

[a] Saturation temperature ($u(T) = 0.1$ K). [b] Mass of transferred sample condensed at 243 K. [c] Volume of nitrogen ($u(V) = 0.005$ dm^3) used to transfer m ($u(m)/m = 1.5\%$) of the sample. [d] T_{amb} is the temperature of the soap film flowmeter used for measurement of the gas flow. [e] Vapor pressure at temperature T, calculated from the m and the residual vapor pressure at the condensation temperature, calculated by an iteration procedure; $p^{\circ} = 1$ Pa. [f] Standard uncertainty in p was calculated with u(p/Pa) $= 0.005 + 0.025$(p/Pa) for p < 5 Pa.

Table 8. Compilation of data on molar enthalpies of sublimation $\Delta_{cr}^{g}H_{m}^{\circ}$ of TATP and its phlegmatized mixtures.

Experiment	Method[a]	T-Range K	$\Delta_{cr}^{g}H_{m}^{\circ}$(298.15 K)[b] kJ mol^{-1}	p_{sat} [c] Pa
pure TATP [38]	T	274.3–314.1	76.7 ± 0.7	6.7
d40-TATP	T	274.5–312.7	80.1 ± 0.5	2.3
d32.7-TATP	T	274.3–313.1	84.4 ± 0.5	0.9

[a] Method: T = transpiration. [b] Enthalpies of sublimation were adjusted according to Acree and Chickos [44] with values of $\Delta_{cr}^{g}C_{p,m}^{\circ}$ and $C_{p,m}^{\circ}$(cr), stated in Table 4. Uncertainty for molar enthalpy of sublimation is expressed as standard uncertainty. [c] Vapor pressure at 298.15 K.

lar enthalpy of sublimation at 298.15 K (76.7 ± 0.7 kJ mol^{-1} for pure TATP, 80.1 ± 0.5 kJ mol^{-1} for d40-TATP and 84.4 ± 0.5 kJ mol^{-1} for d32.7-TATP) which can be attributed to absorption phenomena. This demonstrates that the volatility of the TATP in the TATP/activated charcoal-mixtures is rather sensitive to the compound concentration. For the simulation of the vaporization behavior of pure TATP with active charcoal mixtures the content should be chosen as high as feasible in terms of handling safety.

Measurements with the transpiration method demonstrated that the vapor pressure p_{sat} at 298.15 K of d40-TATP (2.3 Pa) and d32.7-TATP (0.9 Pa) is lower than that of pure TATP (6.7 Pa) but in the same order of magnitude with a strong dependency on the TATP-content in the mixture.

The results agree with the process mass spectrometer measurements (section 3.5) which indicated that d40-TATP has a lower volatility than the pure bulk material regarding the lower signal intensity (ion current) of d40-TATP in comparison to the bulk material in Figure 6.

3.7 Explosive Detection Dog Trials

Day 1:

On the first day 7 Explosive Detection Dog Teams (EDD) were available. For the start of the training at the differentiation track 1.0 g HMTD (pure substance) was used. In the afternoon, 40.0 g of the HMTD-activated charcoal mixture (d40-HMTD) were hidden in a desk container in the building for free search. The mixture was found by each team. Furthermore, in the afternoon, 1.0 g of TATP (pure substance) was hidden in a handbag placed in a room to check the detection abilities for TATP. Again, the explosive was detected and located by all teams.

Day 2:

On the second day also 7 EDD were available. The differentiation track was set up: The samples, containing one of the safe-to-handle TATP/HMTD mixtures, were placed. The quantity of d40-HMTD and d40-TATP was 3.0 g. The differ-

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entiation track experiments were continued on day 3, the results of both days are summarized in Table 9.

Day 3:

5 EDD were available on day 3. The differentiation track experiments were continued. The results are shown in Table 9. The safe mixtures of HMTD and TATP were found with a total detection rate of 100%. Afterwards 3 realistic environment tasks were prepared for exercise: 40.0 g of d40-HMTD in the trunk of a car, 70 g of d40-TATP in the engine compartment of a car and 40 g of d40-HMTD in the locker of a dressing room. All safe explosive formulations were found by all teams.

Both TATP and HMTD were detected with a rate of 100% by the EDD in their safe mixtures.

TATP/activated charcoal and HTMD/activated charcoal mixtures were found by all teams resulting in a global detection rate throughout all tests of 100%. A total of 168 blank sample vials, which were in some cases filled with activated charcoal as distractor, were used, 5 of which were indicated as explosives by the sniffer dog. Thus, a false positive alarm rate of 3% was observed. (Table 10).

4 Conclusion

Both TATP and HMTD could be phlegmatized by coprecipitation with active charcoal resulting in mixtures with a nominal content of 40 wt-% (d40-TATP) and 10 wt-% (d10-HMTD), respectively. In terms of impact and friction sensitivity for both peroxides a content of 40 wt-% resulted in >30 Nm impact sensitivity and >360 N friction sensitivity. Both phlegmatized peroxides were tested according to the UN recommendation on the transport of dangerous goods test manual. (Koenen Tube Test and Thermal Stability). For the Koenen Tube Test a limiting diameter of 3 mm was determined for d40-TATP and 1 mm was determined for d40-HMTD. The thermal stability test for d40-TATP resulted in a weight loss of 1.34% (pass ("-")). For d40-HMTD the thermal stability test resulted in a deflagration (fail ("+")), whilst for d10-HMTD the test was passed with a weight loss of 2.1%. In terms of toxicity TATP was classified as non-toxic and HMTD as moderately toxic for aquatic organisms by the LUMIstox test. The volatility of the phlegmatized TATP was further investigated. Investigations with a process mass spectrometer indicate that d40-TATP is likely to produce a saturated atmosphere at least in the same time as the same amount of pure TATP. Despite that it should be noted that the process mass spectrometer experiment was only performed once and remeasurements should be carried out to check for reproducibility of the results. Measurements with the transpiration method demonstrated that the vapor pressure p_{sat} at 298.15 K of d40-TATP (2.3 Pa) and d32.7-TATP (0.9 Pa) is lower than that of pure TATP (6.7 Pa) but in the same order of magnitude with a strong dependency on the TATP-content in the mixture. Headspace SPME-GC/MS measurements revealed that the active charcoal does not contribute to the vapor profile of the training aid. Finally, both d40-TATP and d10-HMTD were tested as training aids for EDD. In both differentiation track and realistic environment scenarios a detection rate of 100% could be achieved by EDD of German Federal Police with a false positive rate of solely 3%. It should be noted that the published results did not verify whether dogs that have never been conditioned for the detection of HMTD and TATP will detect the bulk materials after exclusive conditioning with the developed training aids. The authors encourage appropriate authorities for bilateral exchange. Consequently, a promising canine training aid for both TATP and HMTD was developed. It has the potential for enabling both trace and bulk amount detection scenarios and was reported without prior patenting of the technology. First tests towards a UN transport classification for dangerous goods were performed and will be continued. For a deeper understanding of the gas phase release of bulk and phlegmatized TATP quantitative vapor analysis will be performed in the near future.

Table 9. Detection rate for the safe mixtures.

	d40-TATP	d40-HMTD
Counts	12	15
Notification/Signal	12	15
Detection rate	100%	100%

Table 10. Summarized results for all scenarios of the explosive dog detection trials.

	Blank sample	Safe mixtures
Counts	168	27
Notification/Signal	5	27
Failure rate	3%	–
Detection rate	–	100%

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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