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July 29, 2021

Propellants, Explosives, Pyrotechnics

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Research Article

Propellants, Explosives, Pyrotechnics

doi.org/10.1002/prep.202100224

pep.wiley-vch.de

Trace Compound Analysis in TATB by Liquid Chromatography coupled with Spectroscopic and Spectrometric Detection

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Abstract: Accurate quantitation of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is important because of its strategic use as an energetic material. A purity determination is also needed for the proper assessment of performance. A fast and sensitive method has been developed to measure the purity of TATB in polymer-bonded materials. The target material is extracted with DMSO, and the extract is separated on a reversed-phase chromatography column. The column effluent is monitored by diode array detection (DAD) at 354 nm. The characteristic UV-Vis response and retention time identify the individual components when compared to pure compound standards. The chemical structures of compounds with no pure standards available have been determined by high-resolution mass spectrometry (MS) and MS/MS. The major component, TATB, along with 1-chloro-3,5-dinitro-2,4,6-triaminobenzene (T4A) and mono-benzofuroxan (FX1) were quantitated directly from pure compound standards. Several trace concentration components, mono-benzofurazan (F1), 1-bromo-3,5-dinitro-2,4,6-triaminobenzene (Br-T4A), 2,4,6-triamino-1-nitroso-3,5-dinitrobenzene (MN-TATB), 2,4,6-triamino-1-hydroxyl-3,5-dinitrobenzene (HO-TATB), and 2,4,6-triamino-1-nitrile-3,5-dinitrobenzene (Nitrile-TATB) were also detected and structures verified via MS/MS. Approximate concentrations were determined using calibrations from standards of similar structures. Additional trace components were also detected by MS. Contained herein are the results of analyses of TATB-based materials characterized for polymer-bonded formulations compared to different preparations of TATB. The accuracy, details, and process of developing this method are reported here.

Keywords: TATB impurities · HPLC analysis · Explosive impurities · mass spectrometry detection

1 Introduction

TATB, shown in Figure 1, is classified as an insensitive high explosive. The structure has been determined [1] as a fully substituted aromatic molecule with alternating amino and nitro groups around the ring. The combination of the full substitution, the alternating donating and withdrawing groups on the ring, and the secondary interactions when the molecule crystallizes makes TATB a very stable and highly desirable molecule for munition applications [2]. It is generally formulated into a polymer-bound material such as LX-17 (92.5 wt.% TATB, 7.5 wt.% Kel-F 800) or PBX 9502 (95 wt.% TATB, 5 wt.% Kel-F 800) before use because formulated explosives have superior molding properties.

Because of the extensive use of TATB-based materials, analytical methods have been developed to assay the amount or purity of the TATB component in samples. Many methods first utilized the reaction of TATB in strong basic aqueous/organic solutions. Faubion (1974) [3] used a basic hydrolysis method converting the amino groups into hydroxyl groups followed by potentiometric titration. Rigdon et al. (1983) [4] used basic hydrolysis, titrated the amino and nitro groups by electrolytic reduction followed by controlled-potential coulometry. HEMRL (2004–2005) [5] developed a basic hydrolysis method, using a Kjeldahl digestion, releasing the amino group as NH_3, followed by aqueous acid-base titration to quantify the TATB based on amine-nitrogen content. Nandi et al. (2014) [6] used basic hydrolysis then back titrated the residue with aqueous acid. Several HPLC methods coupled with detection have been developed over the years-MacDougall (1977) [7], Schaffer (1978 & 1992) [8,9], Kayser (1982) [10], Bellamy et al. (2002) [11], and Bhattacharyya et al. (2016) [5]-all using various permutations of the highly effective technique. Kinghorn et al. 2007

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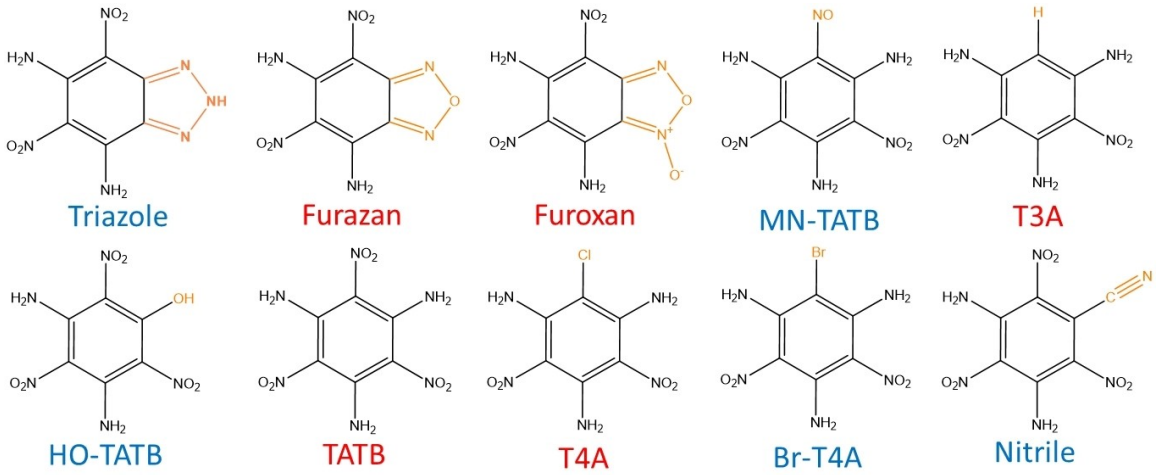

Figure 1. Structure of compounds detected by HPLC-DAD and verified by MS; red text indicates structures verified using reference materials.

[12], DeTata et al. (2013) [13], and Schramm et al. 2015 [14] have coupled HPLC with MS for fast forensic and environmental analyses of TATB and its decomposition products.

The body of work found in peer-reviewed journals and reports centers on the detection of various explosives in mixed samples. This includes the detection of TATB, but few of the published methods are tailored to the separation and detection of the minor compounds found in TATB samples. Yasuda (1972) [15] developed a convenient two-dimensional thin-layer chromatography (TLC) method to detect various reaction by-products, unreacted synthesis reagents, and component impurities focusing on bulk recrystallization methods and found 11 impurities along with TATB. Schaffer (1978) [8] extended the work utilizing a densitometer for quantitation and Schaffer (1983) [16] adapted an HPLC method and assigned several of these impurities along with TATB. Haddiz (2013) [17] identified several additional impurities. Others have developed techniques for specific applications, narrowing the analysis to specific materials. Nandi et al. (2012) [18] characterized T4A because it was a persistent impurity in the larger-scale production of TATB. Tan et al. (1991) [19] developed a supercritical extraction method to remove tri-chloro-trinitrobenzene (TCTNB), which avoided heating solvent solutions, perhaps for safety reasons. Kelly & Brown (2021) [20] thoroughly investigated TCTNB in DMSO as an analytical standard for TATB research efforts. However, none of these techniques were optimized for the detection of a broad range of TATB related compounds.

A technique for the detection, identification, and quantification of the minor components found in TATB has been needed to: 1) compare TATB produced from different synthesis routes, 2) compare TATB batches of the same route as well as, 3) study the effects of formulating TATB with polymers. The chromatographic and analysis methods described here were developed for these reasons and to study the aging of TATB by various means. These methods have been used to characterize samples exposed to abnormal thermal conditions to the point of decomposition. Interest in reaction products found in these samples was driven by concern for the safe handling of damaged energetic materials. Kahl et al. (2018) [21] and Kahl et al. (2020) [22] reported the effects of several types of thermal exposure of LX-17 on safety parameters, utilizing the TATB and minor component analyses developed here. Reynolds et al. (2021) [23] characterized product solids from LX-17 heated to the explosion in a confined reactor. To address the need of monitoring how TATB changes through its life cycle from synthesis, purification, formulation, use, through degradation, this technique was developed.

This present research effort utilizes HPLC methods coupled with diode array detection (DAD) and mass spectrometry (MS) to detect and identify minor components in TATB. The methods utilize a dimethyl-sulfoxide (DMSO) extraction sample preparation in the first step followed by HPLC-DAD-MS analysis of the soluble fraction. These methods are also applicable to TATB-based formulations, such as LX-17 and PBX 9502. As well, these techniques are suitable to analyze solids of any type thought to contain TATB and have been used successfully to analyze black char produced from TATB exposed to extreme temperatures without detonation. This report focuses on a small number of TATB, PBX 9502, and LX-17 samples.

2 Experimental

Materials. The standard materials for TATB [24], T4A [18], and FX1 [25–27] were synthesized and have been used as calibrants for many years. The standard materials, while very pure, are not 100%. For example, the TATB standard used is approximately 98% pure, thus samples containing up to 102% TATB are possible. The PBX 9502 used here contains TATB synthesized in the mid-1980s by an outside

contractor located in Texas. The LX-17 sample was from an accumulation of several lots since the 1980s. All solvents (DMSO, acetonitrile, and acetone) and reagents (formic acid) were purchased from Sigma-Aldrich. The water used was produced locally using reverse osmosis and milli-q water purification system.

Sample Preparation in DMSO. These preparations were primarily intended for the quantitation of TATB and other minor components for which standards exist [28, 29]. An approximately 10-mg aliquot of sample material was placed into a 250-mL volumetric flask. If binder was present, 25 mL of acetone was added to dissolve the binder and expose the TATB. The flask was filled just below the neck with DMSO to dissolve the TATB and related compounds. To assist dissolution, the flask was heated to 50 °C in a water bath and frequently agitated by spinning by hand. Sonication of the flask caused the particulates to congregate at the bottom of the flask and was used to test if the sample was fully dissolved. Sonication was not used during dissolution because TATB was found to take longer to dissolve with the material agglomerated as opposed to evenly dispersed in the flask. Once the material was fully dissolved (no noticeable agglomeration after sonication) or stopped dissolving due to the presence of insoluble detritus or degradation products, the flask was cooled to 20.0 °C and filled to the mark with additional DMSO. Undissolved material, if present, was removed and dried for further analysis. Six replicate preparations were made for each lot of materials investigated. Samples were kept in the dark as much as practical during dissolution, sampling, and storage to prevent photo-degradation of the solvated TATB.

Analysis by LC-DAD. This assay was primarily used for the quantitation of TATB and T4A, for which standards are available [28, 29]; however, it was sufficient to separate a wide variety of minor compounds eluting before and after TATB. Both Agilent and Thermo Fisher liquid chromatography and DAD systems were used. Five injections of each prepared sample were analyzed as follows. A 5-μL aliquot was injected onto a C18 column (Atlantis T3, 5 μm; 4.6×250 mm) to perform reverse-phase chromatography. An 11-min isocratic run was performed with 25 % CH_3CN and 75 % H_2O (0.1 % formic acid) solution at 1.3 mL/min flow rate at 70 °C. Detection was done by DAD with a 60-mm flow cell monitoring between 190 to 640 nm. Absorbance at 354 nm (bandwidth 4 nm; no reference) was determined empirically to be optimal for TATB and its related compounds. At the end of each run, the column was flushed with 90 % CH_3CN for 2 min then returned to the 25 % mixture for 5 min to condition for the next injection. The flush was intended to keep binder materials from building up on the column. Total run time was 17.5 min.

An ultra-high-performance LC (μHPLC) method has been developed with similar performance for TATB and T4A determinations but exhibited degraded performance for the minor compounds [29]. The faster method is isocratic at 20 % organic and has a total run time of 6 instead of the 17.5 min in the Standard Operating Method (SOP). The results shown in this paper are for the 17.5 min run time.

Calibration was performed using standards synthesized at LLNL. Calibrations consisted of five injections of each calibrant before injection of the samples and a sixth injection (spot check) was performed after the injection of the samples. The calibration curves consist of a minimum of 6 points across the range of concentrations at which the samples were prepared. Typically, the calibration ranges were from 20 to 50 ppm for TATB and 1 ppb to 5 ppm for T4A and FX1. Continuing Calibration Verification (CCV) injections and a process blank were run between each set of replicate samples. Data at all wavelengths between 190 and 640 nm were collected, however, a UV absorbance value at 354 nm (bandwidth 4 nm, no reference) was optimal for TATB and related compounds.

The standard deviation on each value for a given sample was from 5 replicate injections of one sample. The average standard deviation for a given sample type is an average of all injections from all replicate samples, typically 6 DMSO replicate samples for a total of 30 measurements for each lot.

Analysis by LC-DAD-MS. This assay is like the SOP and μHPLC methods used for quantification but differs in two ways: the H_2O portion of the mobile phase was not acidified, and the flow rate was reduced to 0.5 mL/min to accommodate the spray conditions required for atmospheric pressure chemical ionization (APCI) and heated electrospray ionization (HESI) ion sources. A Themo Fisher Vanquish LC and QE mass spectrometer were used.

Two ionization techniques were applied, APCI and HESI, and both positive and negative ions were monitored for the HPLC-MS column effluent. The type of ionization technique used can directly affect whether a compound is detected or not. HESI requires that the compound be an ion in solution while APCI does not and should assist in the detection of compounds remaining neutral in solution. These differences will be discussed further in the Results section.

3 Results

3.1 LC-DAD Analyses of Dissolved Samples in DMSO

Calibration. Solutions of TATB, T4A, and FX1 were used for the calibration of the DMSO solutions. Concentration ranges were chosen to match the expected concentrations of the samples. TATB was calibrated over the concentration range of 10 to 55 ppm, T4A over 1 ppb to 5 ppm, and FX1 over 0.1 ppb to 30 ppm. See Figure S-1 in the supplemental material for the curves. Both T4A and FX1 are detected at very low concentrations compared to TATB and are subject to variability near the detection limits of the system.

Quantitative Determinations of Concentrations in TATB samples. Table 1 shows the concentration of TATB and T4A as detected by HPLC-DAD for replicate samples of the same

Table 1. Weight percent TATB and T4A in six replicates of PBX 9502 from HPLC-DAD analysis of DMSO extracts (values are quantitative); detection by absorbance at 354 nm.

Sample	TATB Weight, %	STDEV[a]	% RSV[b]	T4A Weight, %	STDEV[a]	% RSV[b]	Σ TATB + T4A[c] Weight, %
9502-A	96.17	0.08	0.08	0.188	0.009	4.67	96.36
9502-B	92.96	0.11	0.11	0.219	0.012	5.24	93.18
9502-C	95.99	0.16	0.16	0.181	0.020	10.91	96.17
9502-D	93.98	0.11	0.12	0.200	0.015	7.43	94.18
9502-E	93.81	0.12	0.13	0.176	0.031	17.74	93.99
9502-F	95.57	0.18	0.18	0.207	0.010	4.85	95.78
Average	**94.75**	**1.24**	**1.31**	**0.195**	**0.022**	**11.41**	**94.94**

[a] STDEV (standard deviation). [b] % RSV (% relative standard variation) defined in experimental section. [c] Sum of weight % of TATB & T4A determined by this method.

lot of PBX 9502. Note, the binder is not assayed and is assumed to be around 5 wt.%, thus theoretically, the summation of TATB + T4A should be 95 wt.% of the total. The minor variation observed in the composition is due to the relatively small (10-mg or less) sample sizes and the inhomogeneity of the material after the process of formulation, which is discussed below. The precision of the method is demonstrated by small relative standard variation (RSV) for each sample across 5 measurements of each sample. The larger RSV for T4A is due to the amount being near trace levels and closer to the detection limit of the system. Also, note the minor variations in the total weight are dominated by the TATB contribution which is about 500 times the T4A contribution.

Several other compounds can be detected by HPLC-DAD and, by using known compound concentrations, the concentrations can be estimated. Table 2 shows the concentrations of TATB, T4A, F1, FX1, Br-T4A, MN-TATB, and HO-TATB in a PBX 9502 sample. The concentrations for TATB, T4A, and FX1 are determined using pure compound standards. Because the only pure standards available are for TATB, T4A, and FX1, the concentrations of F1 were determined using the FX1 calibration data; Br-T4A is determined using the T4A calibration data; and MN-TATB & HO-TATB were determined using TATB as the calibrant.

The results in Table 2 are from a single thermal aging experiment but represent two separate groups of samples at different conditions within the experiment. Replicate samples PBX 9502-1 through -6 are PBX 9502 that was contained in a metal mesh basket inside a thermal aging vessel. Samples PBX 9502-7 through -12 are replicates of the same source of PBX 9502 but mixed with pieces of an inert polymer and contained in a separate mesh basket in the same vessel during the experiment. The summation of all the components indicates the overall composition determined for these two sets is the same within experimental error. However, there are differences in the concentrations of the trace components, particularly T4A, FX1, and HO-TATB. The origin of these differences is possibly a localized concentration effect and will be discussed below.

Table 2. Concentrations of replicate samples of PBX 9502 determined by HPLC-DAD method.

PBX 9502 #	ppm[a]	Wt% TATB[b]	T4A[c]	F1[d]	FX1[d]	MN-TATB[b]	HO-TATB[b]	Br-T4A[c]	Σ[e]
9502-1	40.7	94.431	0.140	0.015	0.001	0.100	0.198	0.010	94.894
9502-2	42.7	95.674	0.142	0.017	0.002	0.103	0.207	0.017	96.162
9502-3	42.8	94.498	0.134	0.016	0.001	0.097	0.206	0.015	94.965
9502-4	43.2	94.885	0.131	0.016	0.001	0.102	0.201	0.011	95.349
9502-5	45.7	93.847	0.139	0.016	< LOD	0.100	0.200	0.011	94.313
9502-6	45.8	93.384	0.139	0.015	0.001	0.098	0.199	0.013	93.850
Average		**94.453 ± 0.008**	**0.138 ± 0.004**	**0.016 ± 0.001**	**0.001 ± 0.000**	**0.100 ± 0.003**	**0.202 ± 0.004**	**0.013 ± 0.003**	**94.922 +/− 0.805**
9502-7	39.9	95.011	0.139	0.024	0.017	0.089	0.166	0.003	95.448
9502-8	40.8	96.200	0.183	0.020	0.015	0.097	0.183	0.020	96.718
9502-9	41.0	93.710	0.185	0.019	0.019	0.094	0.165	0.017	94.208
9502-10	44.1	94.263	0.165	0.018	0.017	0.097	0.172	0.015	94.746
9502-11	45.2	94.781	0.185	0.019	0.021	0.090	0.179	0.018	95.294
9502-12	47.4	96.020	0.154	0.019	0.016	0.095	0.189	0.028	96.520
Average		**94.997 ± 0.970**	**0.169 ± 0.019**	**0.020 ± 0.002**	**0.018 ± 0.002**	**0.094 ± 0.003**	**0.176 ± 0.010**	**0.017 ± 0.008**	**95.489 ± 0.980**

[a] Prepared solution concentration; [b] Calibrated using TATB pure standard; [c] Calibrated using pure T4A standard; [d] Calibrated using FX1 pure standard; [e] Sum of weight % values for all components, does not include nominal 5 wt.% Kel-F 800.

There are variations within each set of data. The T4A and the Br-T4A concentrations for PBX 9502-7 are lower than the rest of the samples from this group. Again, it is reasonable to assume localized differences in the concentrations of the compounds cause this difference.

As in Table 1, the samples in Table 2 should have 5 wt.% binder in the bulk PBX 9502, and therefore the sum of the measured compounds should be 95 wt.%. The variation in the wt.% of the primary compound (TATB) is presumed to be variations in the amount of binder present and not due to contaminants. For the 12 samples in Table 2, the average total of accounted for compounds was 95.206 ± 0.867 wt.%. Thus, matching the expected outcome.

The ability to measure the trace-level compounds strengthens the presumption that the variations are due to the concentration of the binder, by showing there are no detectable compounds responsible for the variation. Note: when comparing a replicate containing higher amounts of TATB to a replicate containing lower amounts of TATB, the minor components will be higher in concentration as well, as would be expected if the differences were external to the TATB crystals, such as the amount of binder. A good example is PBX 9502-8 which has higher wt.% TATB than PBX 9502-7.

These samples were prepared with the limited solubility of TATB in DMSO [30–32] as the determining factor. Due to the low concentrations involved, without a stable method with sufficient separation outfitted with a modern highly sensitive DAD, these types of trends would not be detectable. The invariant positions in the chromatograms at these very low concentrations allow for possible determination of the reaction chemistry with the formation of trace-level compounds.

3.2 Structural Identification of Trace Compounds in DMSO Extracts

HPLC-DAD profiles of trace components. The HPLC-DAD method was successful at detecting several compounds other than TATB and T4A. Table 2 lists some of these compounds with approximate concentrations but not all. The DMSO extractions are relatively dilute because of the limited solubility of TATB. Past HPLC detection methods reported in the literature have not been able to detect many of the trace-level compounds. Recent improvements in DAD sensitivity and the HPLC method used here have enabled the detection of additional compounds of interest.

Figure 2 shows a typical chromatogram monitoring 354 nm for detection with the proposed chemical assignments. Note that the figure has been expanded to highlight the low concentration species. Several compounds related to TATB are detected in trace levels–F1, FX1, MN-TATB, HO-TATB, Br-T4A, Triazole, and Nitrile-TATB. The assignments are made based on retention time and structural analyses by HPLC-MS of the components eluting at a corresponding retention time. The mass spectral results are discussed below.

Compounds detected by HPLC-DAD. Table 3 summarizes the trace components typically found in the DMSO extracts showing the identification, formal naming, high-resolution negative ion masses, and formulas. Figure 1 shows the structure of these components. The formulae of these compounds are known with a high degree of confidence given the high-resolution mass spectral data. The structures of these compounds are derived from their formula, based on the high-resolution mass of the compound, and an understanding of the synthesis of TATB and formulation processes that produced the PBX 9502.

UV-vis Absorbance Spectra. Most of the TATB related compounds discussed in this study have strong absorbances at 354 nm wavelength. Figure 3 shows the UV-Vis absorption spectra of TATB, F1, and FX1 in wavelengths be-

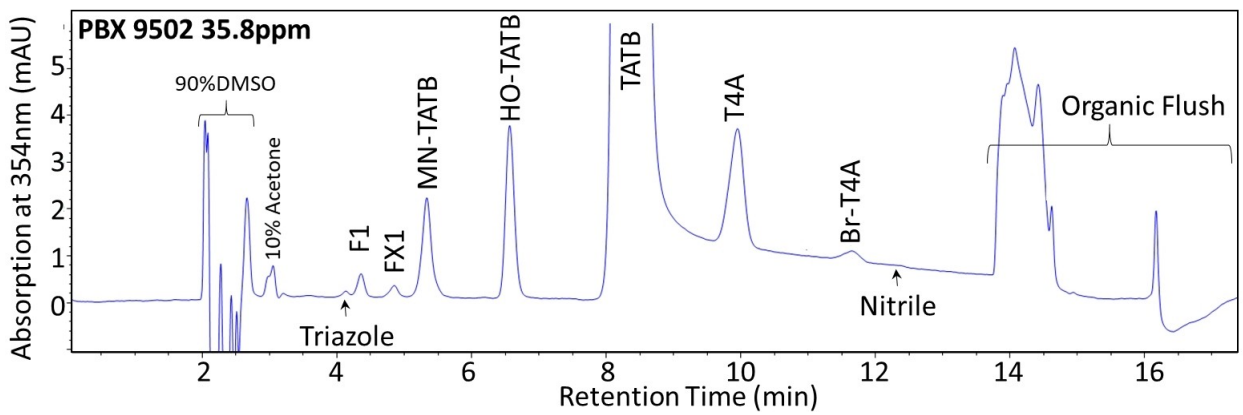

Figure 2. Separation UV-Vis chromatogram of DMSO extract of a PBX 9502 sample while monitoring 354 nm; scale expanded to highlight compounds in very low concentration in the sample.

Table 3. Compound list with high resolution ion mass for the $[M–H]^-$ ions and the formula of the M compound.

ID	IUPAC Designation	Ion Mass	Formula
Triazole	5,7-dinitro-2H-benzo[d][1,2,3]triazole-4,6-diamine	$[238.0331]^-$	$C_6H_5N_7O_4$
F1	5,7-dinitrobenzo[c][1,2,5]oxadiazole-4,6-diamine	$[239.0169]^-$	$C_6H_4N_6O_5$
FX1	5,7-diamino-4,6-dinitrobenzo[c][1,2,5]oxadiazole-1-oxide	$[255.0110]^-$	$C_6H_4N_6O_6$
MN-TATB	2,4-dinitro-6-nitrosobenzene-1,3,5-triamine	$[241.0322]^-$	$C_6H_6N_6O_5$
T3A	2,4-dinitrobenzene-1,3,5-triamine	$[212.0423]^-$	$C_6H_6N_5O_4$
HO-TATB	3,5-diamino-2,4,6-trinitrophenol	$[258.0119]^-$	$C_6H_5N_5O_7$
TATB	2,4,6-triamino-1,3,5-trinitrobenzene	$[257.0271]^-$	$C_6H_6N_6O_6$
T4A	2-chloro-4,6-dinitrobenzene-1,3,5-triamine	$[246.0037]^-$	$C_6H_5N_5O_4Cl$
Br-T4A	2-bromo-4,6-dinitrobenzene-1,3,5-triamine	$[289.9535]^-$	$C_6H_6N_5O_4Br$
Nitrile-TATB	3,5-diamino-2,4,6-trinitrobenzonitrile	$[267.0125]^-$	$C_7H_4N_6O_6$

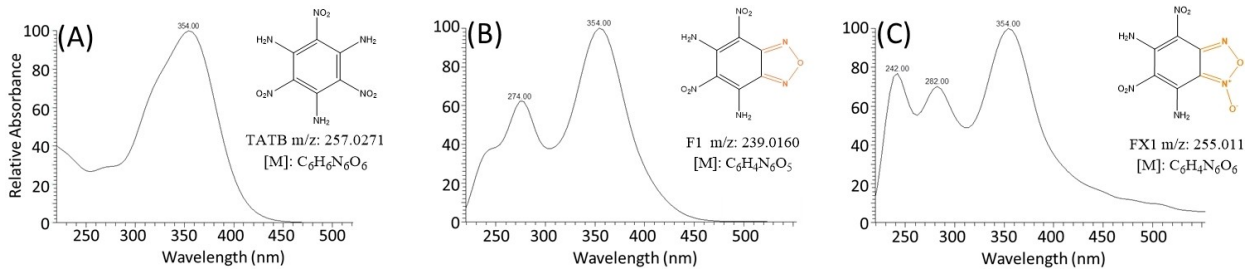

Figure 3. Example UV-vis absorption spectra of TATB, F1, and FX1.

tween 190 and 640 nm. Figure S-2 in the supplemental material shows the UV-vis spectra for all the materials above. The other compounds in Figure S-2 have absorption maxima shifted from 354 nm but have sufficient intensity at 354 nm to be used in this method. Nitrile-TATB has a weak absorbance at 354 nm which is one reason it is usually not noted by DAD methods.

Variations in Trace Compounds-HPLC-DAD Profiles. To further illustrate some of the trace compounds detected in these samples, Figure 4 shows how the relative amounts of the minor compounds vary across different lots of TATB and the formulations made using those lots. TATB Lot A and Lot B were synthesized using different processes and therefore have different distributions of the minor compounds most notably MN-TATB and T4A. Note that the concentration of the samples in Figure 4 are nearly identical thus differences in the amounts are primarily due to the pedigree of the material and not the concentration of the sample. The source

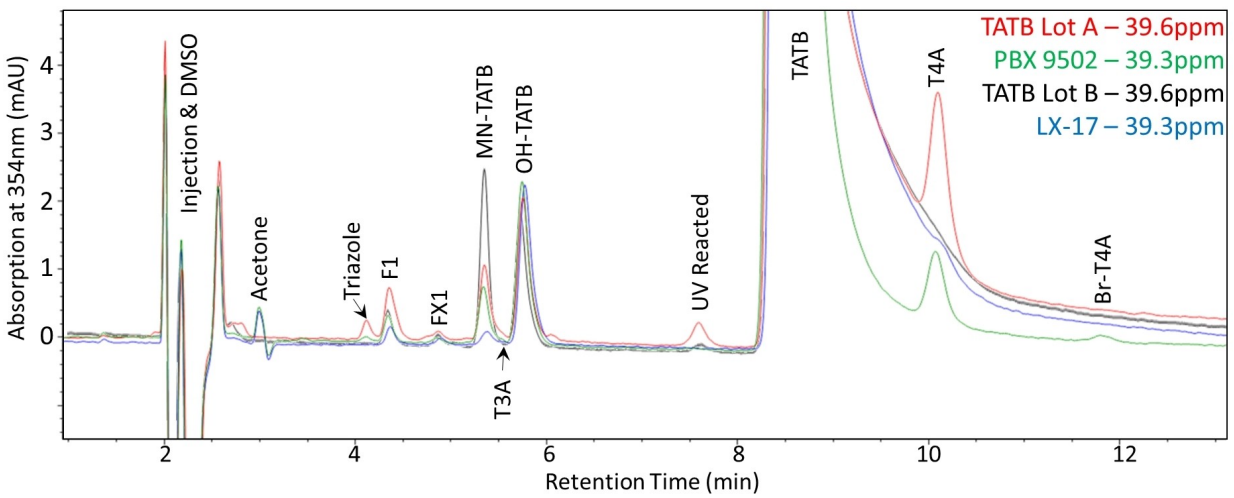

Figure 4. DAD chromatograms of compounds of interest in two different preparations of TATB and two different formulations of TATB (PBX 9502 & LX-17).

material for LX-17 was TATB synthesized the same way as the Lot B material and thus has nearly undetectable amounts of T4A. The source material for PBX 9502 was TATB lot A and thus has detectable amounts of T4A.

The "UV Reacted" compound with a retention time of 7.5 min noticeable in both the Lot A and Lot B material is a degraded form of TATB produced when TATB is exposed to UV light. This compound reacts with the DMSO solvent used to dissolve the sample forming the compound detected at that retention time. A detailed description of this compound and others like it are beyond the scope of this manuscript and will be discussed in future publications.

Figure 4 demonstrates the ability of the method to separate trace-level compounds thus enabling the tracking of their concentrations across different source materials, synthesis routes, formulation processes, and environmental influences such as light exposure and heat. More detail about the sources and possible reactions that lead to the minor compounds is discussed further in Section 4.

3.3 Mass Spectral Evaluation of TATB and non-TATB Compounds in DMSO Extracts

The identity of the trace components in the HPLC-DAD chromatograms was further analyzed by HPLC-MS. The HPLC method used for the MS analysis, as mentioned above, is the same as that of the HPLC-DAD method with two exceptions. 1) The flow is slower to accommodate the spray conditions of the HESI and APCI ionization sources and thus the retention times are longer. 2) The mobile phase is not acidified because TATB and its related compounds form negative ions and acidification would suppress the ionization of the compounds. Without acidification, the retention time of the HO-TATB is shorter and typically is the first to elute. Otherwise, the elution order is unchanged.

All compounds targeted exhibited precursor ions that have lost one proton to form the $[M–H]^-$ ion, listed in Table 3, one atomic mass unit (amu) lower than the molecular weight of the compound. The loss of the proton is typical for HESI and APCI ion sources for compounds forming negative ions and having protons to lose. Compounds forming positive ions typically form $[M+H]^+$ ions and would be one amu higher than the molecular weight. As mentioned in the instrumentation section, the positive ion spectra were collected as well as the negative ion spectra; however, none of the species contained in the samples favored positive ion formation. For all the compounds reported here, the $[M–H]^-$ ions signal was intense enough for almost unequivocal assignment of the molecular formula. Figure S-3 shows the high-resolution MS of the compounds in Table 3.

The identity of some of the trace components is solidified by the MS/MS of the parent ion. Figure 5 shows the MS/MS spectra of TATB, T4A, and Nitrile-TATB. The spectra exhibit useful information for structural identification because the MS/MS indicates how the compound fragments. Each exhibits strong precursor ions, the previously mentioned $[M–H]^-$ ion. There is a typical sequential loss of two oxygen and two hydrogens in each spectrum, typical of these compounds. It is important to note the fragmentation pattern in the MS/MS spectra is from Collisional Induced Disassociation (CID) occurring in a vacuum, not the original APCI or HESI ionization that ionized the precursor, which occurred at atmospheric pressure. The MS/MS fragments are typically different and can be complicated. However, the use of MS/MS is recommended for unequivocal identification of many of these compounds. The CID fragmentation pattern of TATB agrees with previously published MS/MS studies on TATB and other explosives [13,14]. Figure S4 has the MS/MS spectra for all 10 compounds and Table S1 lists all the fragment ions.

The assignments of TATB, T4A, T3A, F1, and FX1 have been verified by comparisons to standards. T4A is further verified through the isotopic pattern in the mass spectra of chlorine-containing compounds. The isotope pattern also verified the presence of Br-T4A. Figure 6A shows the Cl isotope pattern of $C_6H_6N_5O_4Cl$ as dictated by Cl natural abundance [33]: ^{35}Cl, 75.77%; ^{37}Cl, 24.23%, which is clear in the figure. Figure 6B shows the Br isotope pattern for $C_6H_6N_5O_4Br$ as dictated by Br natural abundance [33]: ^{79}Br, 50.686%; ^{81}Br, 49.314%. The mass separation and relative

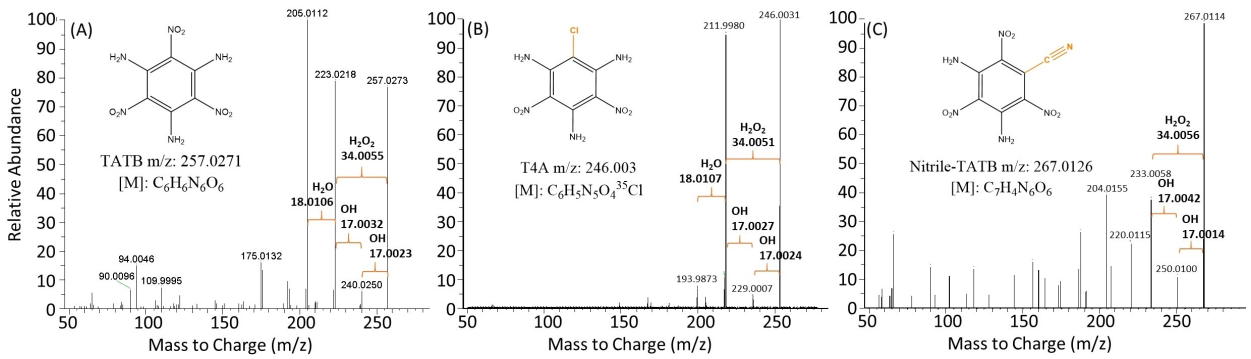

Figure 5. MS/MS spectra of TATB (A), T4A (B), and Nitrile-TATB (C). The mass provided is the ion mass.

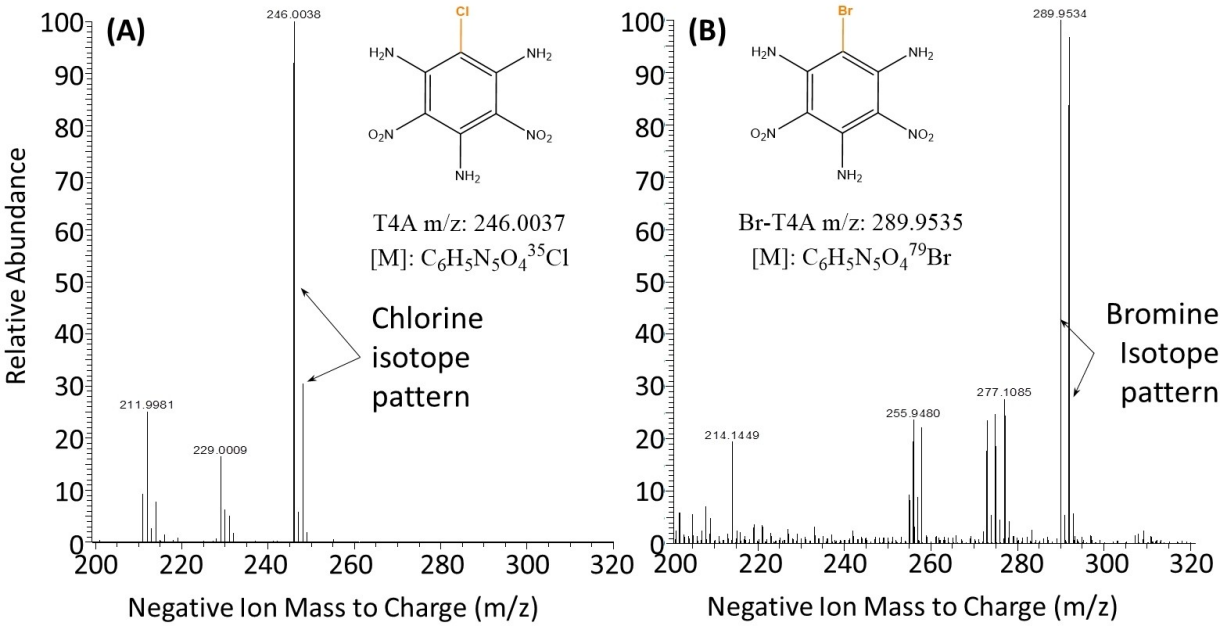

Figure 6. MS of a) T4A and b) Br-T4A showing Cl and Br isotope effects, respectively.

concentrations of ions confirm the presence of these two compounds.

3.4 Mass Spectral Detection Methods

Ionization Sources. The HPLC-MS assay detects many more compounds than the HPLC-DAD assay described above. The list of compounds varies because of many factors including the ionization technique used. Figure 7 illustrates the differences in ionization technique response for six of the compounds mentioned in the previous section. The compounds in Figure 7 A–C, clearly favor the use of HESI, with FX1 at or near noise levels when APCI was used. HESI is generally a softer ionization technique and is therefore slightly better for most TATB related compounds. FX1 easily fragments, through the loss of oxygen, when subjected to APCI conditions. When using APCI, FX1 is detected using the fragment ion of 239.0169 which is the same mass as F1 but the FX1 fragment has a different retention time than the F1 compound. The other compounds, Figure 7 D–F, clearly favor APCI ionization. In most samples, T4A is not detectable using HESI and requires the use of APCI. The retention time shift in the early eluting peaks was due to a column change between the two runs. The same type of column was used both times.

All TATB related compounds exhibit essentially no fragmentation or adduct ion formation when using HESI. The mass spectra consist of the $[M–H]^-$ ions with only low-level fragmentation. This is not true when using APCI. As mentioned above, the FX1 precursor mass often fragments to near-noise levels when using APCI. The compounds favoring APCI generally elute after TATB.

As with all mass spectral techniques, some care must be taken to determine the compound's precursor mass. The apparent major mass of the compound may be a fragment or the result of an adduction. The compounds reported here have been verified using standards when available. If none are available, the spectra have been scrutinized to determine if logical higher masses are present and if the spectra indicate the formation of an adduct has occurred. No adduct formation was detected and precursor fragmentation was only significant for FX1 when using APCI. Figure S3 shows MS spectra using HESI for all the compounds in Figure 1.

Overall, a total of 34 compounds were detected in PBX 9502 using HESI and APCI. APCI-MS detected around 35% of the complete compound list with 15% of them overlapping those detected by HESI-MS. Thus about 20% of the compounds detected in PBX 9502 would not have been detected without the use of APCI. For the 15% that overlap, HESI-MS produced stronger signals most of the time with notable exceptions being MN-TATB, TATB, and T4A which produced one to two orders of magnitude more signal when using APCI. Br-T4A was only ionized using APCI and not detected in HESI spectra. These results demonstrate the utility and necessity of using both ionization techniques to fully characterize TATB-based explosives.

Nitro-based explosives are a class of compounds preferring to form negative ions in ionization sources and their degradation products tend to follow the same behavior [12, 13, 34, 35]. All compounds detected using HPLC-MS were detected as negative polarity ions, with almost no

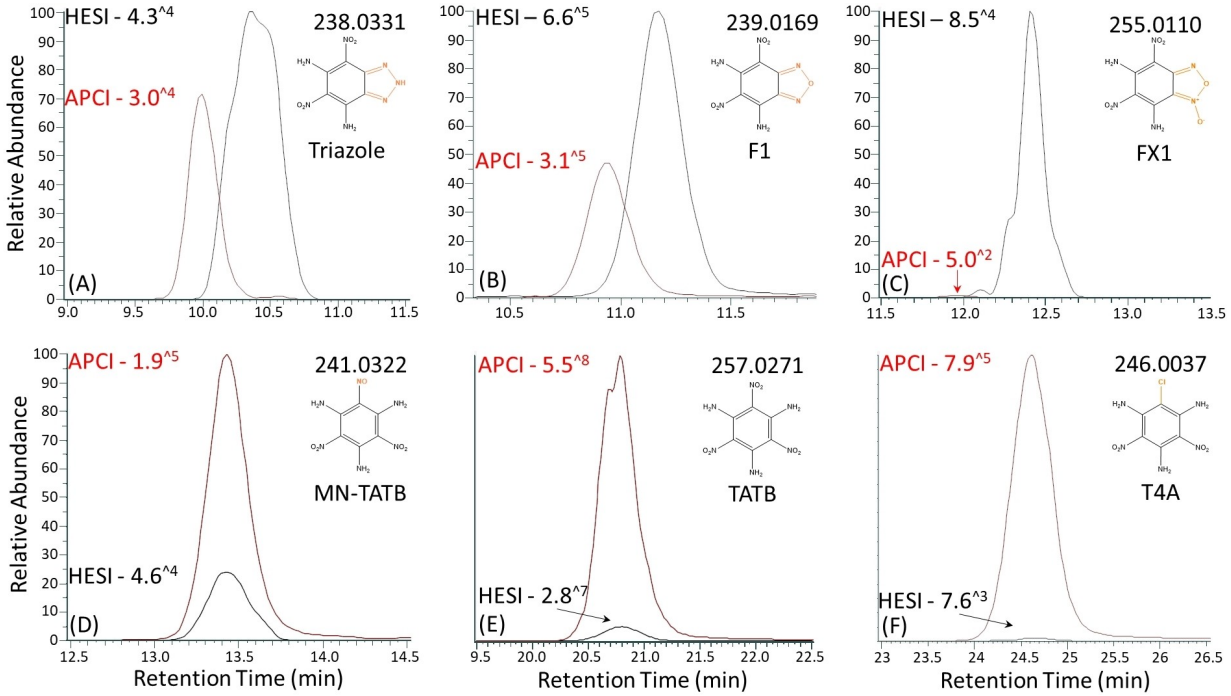

Figure 7. LC-MS chromatograms comparing HESI and APCI ionization techniques for selected compounds. (A) through (C) produced larger signals when HESI is used and (D) through (F) when APCI is used; listed numbers are the peak height of the ion signal.

compounds observed to form positive polarity ions. For compounds producing both positive and negative ions, the negative ion signal was greater and therefore used for identifying the compound. Polarity switching was used so that both positive and negative polarity mass spectra were collected throughout each HPLC-MS run for completeness. With modern systems, polarity switching provides high-quality data for both polarities with little loss of fidelity in the data and remains a good strategy to ensure compounds are not missed.

Ion Chromatograms of PBX 9502. Figure 8 shows an example of Extracted Ion Chromatograms (EIC) from PBX 9502 to further demonstrate the need for this chromatographic method to resolve the individual compounds separated in the DMSO samples using the two different ion sources. The EIC shows 10 ions representing the 10 compounds listed in

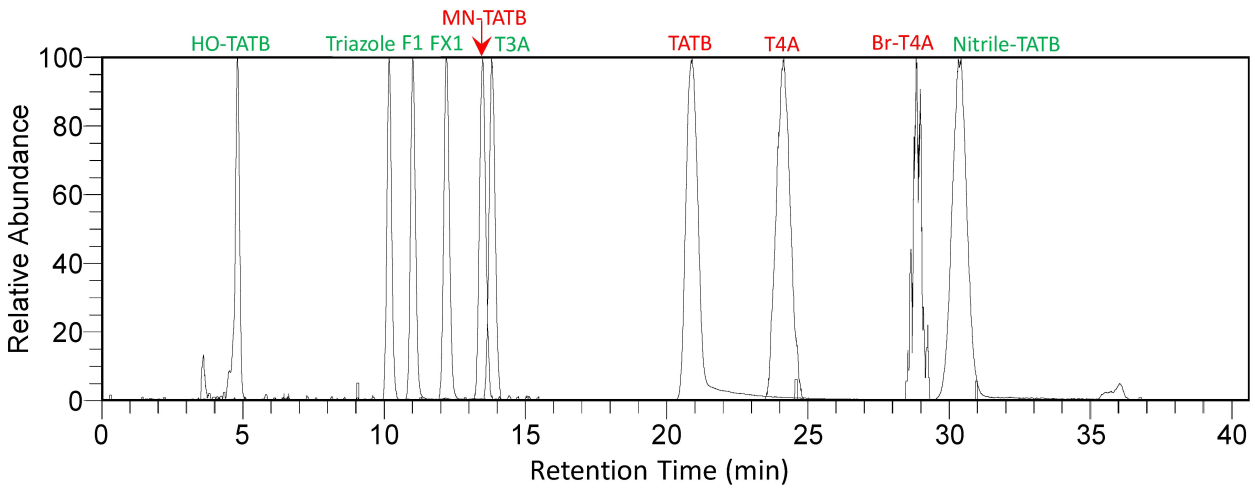

Figure 8. Extracted Ion Chromatograms for the main compounds detected in PBX 9502 (ion masses listed in Table 3); red text indicates compounds requiring or favoring the use of APCI; green text indicates compounds requiring or favoring HESI ionization; all plots are independent scales.

Table 3. Ions labeled with red text favored the use of APCI as the source; those labeled with green text were strongest using HESI as the source. To fully analyze the extract, both ion sources are necessary to produce the highest quality data.

The ions shown in Figure 8, except for Nitrile-TATB, were also detected by the HPLC-DAD method described above. However, an additional 24 compounds have also been detected in the same PBX 9502 using the MS. A full discussion of these compounds is beyond the scope of this article and will be covered in future publications. The nature of many of the additional compounds are not fully identified but appear to fall into four categories, (1) synthesis byproducts, (2) binder related, (3) degradation products and/or dimers or trimers of degradation products, and (4) reaction products of the previous three with DMSO used to solvate the HE and/or possibly ethyl acetate used in the formulation process.

4 Discussion

4.1 Trace Components Detected

There are precedents in the literature for the existence of the materials detected here and their suggested structures. Several of the components have been synthesized and isolated as pure materials.

For triazole-TATB, the only structure fitting the exact mass is the triazole structure in Figure 1. There were no Cl, Br, or S isotopes present, eliminating those elements. The nominal mass of 238 had been detected using low-resolution mass spectrometers in the past. Structures for compounds producing an $[M–H]^-$ ion mass of 238 were considered but were ruled out once the high-resolution mass (238.0330) was measured. Figure S5 shows the structures considered. The formation of triazole has some precedents in highly acidic solutions from the Boulton-Katrizky rearrangement reaction [36] which also supports this identification.

F1 and FX1 have been linked to the thermal decomposition of TATB by many studies [37 and references therein] and have been reported in thermal treatment products [21–23]. FX1 is stable enough to be isolated pure [26] on a large scale [27] and is used as a standard in this study. F1 is reported in the literature as a pure stable compound [38, 39]. However, the synthesis of a pure compound has yet to be accomplished by the reported method.

Triazole, F1, and FX1 are the only compounds suggested here that have a multi-ring structure through the joining of nitro and an amine group and thus have similar affinities to the C18 column. They are also the only ones that do not fragment with the loss of two oxygens and two hydrogens as shown in Figure 5. The other 7 compounds do, as shown in Figure S4 and Table S1. It is likely the formation of the second ring and the loss of an $–NO_2$ and an $–NH_2$ group is why they do not fragment in the same fashion as TATB and the other related compounds.

The MN-TATB has been identified previously in TATB synthetic mixtures and can be synthesized by manipulation of experimental conditions [40]. The mono-nitroso moiety has also been considered as a thermal decomposition pathway for nitro-aromatic compounds [41] and has been observed in DMSO extractions of products from the thermal cook-off of LX-17 [23] and thermally sensitized LX-17 [21, 22].

The structure for ion mass 258.0119 is the proposed HO-TATB not $[TATB]H^+$ as suggested in some previous studies [37, 42, 43]. The protonated form has been ruled out in some of these past studies, but not by exact mass properties. The high-resolution MS utilized here is accurate enough to unequivocally rule out a protonated form and to confirm that nitrogen was lost, and oxygen gained. The proposed structure is the only way to accommodate this change by losing an $–NH_2$ group and replacing it with an -OH group.

The process leading to the formation of HO-TATB is still unclear. TATB can, under base-catalyzed hydrolysis [6], form hydroxylated species through the loss of amine groups. Kelly & Brown (2021) [20] have proposed that nitro groups may be replaced with the OH functional group during ionization for TCTNB and its contaminants in DMSO. We believe it unlikely that the HO-TATB, reported here, is being formed during ionization. No known leaving group has been identified and it is unlikely that a chlorine or a nitro group were present at the amine site prior to ionization. However, the possibility cannot be ruled out. HO-TATB has been ruled out as a reaction product between TATB, or one of its contaminants, with DMSO because of its presence in acetone extracts of TATB (not reported here), with which there is no DMSO. This compound is also water-soluble and has been observed in water extracts of TATB conducted in our lab (not reported here). Although not proven, and a subject of future reports, the mechanism of formation is likely nucleophilic aromatic substitution [44].

Br-T4A is probably a result of impure trichlorobenzene (TCB) starting material. In the TATB synthesis, T4 is generated in the TCB nitration step as a low percentage byproduct, with TCTNB as the majority product. Any T4 present in the TCTNB then becomes T4A during the final amination step. The same chemistry extends to any Br substituted TCB. Further, tribromo-trinitrobenzene (TBTNB) is a stable compound [45]. The end synthesis result with the Br analogues is the formation of TATB and Br-T4A.

The Nitrile-TATB is the only structure that fits the high-resolution ion mass of 267.0125. The loss of two hydrogens and the gaining of a single carbon necessitates the triple bond between the nitrogen and the carbon and that the carbon is attached to the core ring.

4.2 Calibration Methods

In this study, only 3 pure standards were available by synthesis, TATB, T4A, and FX1. Figure S-1 shows the calibration behavior of these materials and Tables 1 and 2 use the fits of the calibrations for absolute concentrations. These calibrations were also used for semi-quantitative assessments of F1, MN-TATB, HO-TATB, and Br-T4A, with Table 2 showing the results. Although it would be better to have calibrations from standards for these latter materials, the synthesized materials that we have are not pure enough to be used for calibration. Structural similarities were used when choosing which calibrant for these latter compounds. MN-TATB and HO-TATB have structural similarities with TATB; F1 has structural similarities with FX1; Br-T4A has structural similarities with T4A.

4.3 Localized Concentration Differences

If the instrument was working reliably, RSV for the main constituent in a single replicate sample was below 0.5%. We saw values typically below 0.2%. It was common for trace level compounds to have higher RSVs because their signal was very low or near the detection limit of the system. For example, T4A is often at 3–5% RSV because it is a minor component. The RSV for a lot, or set of samples, depends on the homogeneity of the sample but was typically below 2% when preparing samples at the 10-mg scale.

The results in Table 2 are from a single experiment where two separate groupings of "identical" PBX 9502 material were prepared using slightly different experimental conditions. The two groups were then scrutinized separately: PBX 9502-1 through -6 and PBX 9502-7 through -12. Variations in the trace levels of compounds were found. The differences can represent the heterogeneity of the material at the 10-mg level leading to localized differences in concentrations. The formulation is a heterogeneous process, where particles of the energetic material are coated with the polymer co-addition, usually by forcing the polymer out of solution in the presence of the explosive [46,47]. As a result, localized ratios of energetic materials to polymer can vary.

Localized variations in concentrations of the starting materials can lead to results as shown in Table 2. Even though the overall concentrations of the TATB and T4A are within experimental error, the minor components show notable differences in concentrations. For example, FX1 is about 1/10th the concentration in PBX 9502-1 through -6 compared to PBX 9502-7 through -12, while the HO-TATB shows the opposite trend (although not the same magnitude). There are also variations within a set. The T4A and the Br-T4A concentrations for PBX 9502-7 are lower than the rest of the samples from this group. Again, it is reasonable to assume localized differences in the concentrations of the explosive and binder particles in the sample cause this difference. With the method reported here, trace concentrations can now be determined showing these differences on a localized level. The ability to track trace-level compounds in explosives furthers the refinement of sampling issues with heterogeneous systems.

4.4 Comparison with Previous Methods

Previous studies on TATB and formulated materials have detected species resulting from the synthesis of TATB, formulating PBX 9502, storage, handling, and analyses. Most of these compounds are chlorinated aromatics mixed with amino- and nitro-substitution. Efforts reported in the open literature in the 1970s and 1980s identified roughly 15 different combinations in extracts or solutions [7,8,15–17,48]. Table S-2 shows a complete list of these compounds. These compounds were separated, usually by chromatography (e.g., LC and TLC), and detected using spectroscopic (e.g., optical), and spectrometric (e.g., NMR and/or MS) methods. Later work includes focusing on specific impurities in pilot-plant processing [18] and recently, developing standards [20]. Additional methods have been developed, but usually for the quantitation of TATB, not focusing on impurities [5,6]. However, other than T4A, the trace species detected here have not been reported in more recent work that involves relatively pure TATB or formulations. The added sensitivity of modern instrumentation has led to big advances in detection. A few of the lots of TATB studied by our group still contain ultra-trace-level amounts of the chlorinated synthesis byproducts listed in Table S2. These can be extracted from the TATB using an acetone extraction technique and detected using traditional GC-MS techniques as well as the LC-MS technique reported here. The acetone extracts and the GC-MS work will be discussed in future publications.

5 Conclusions

C18 columns with isocratic conditions work well at separating the minor compounds in TATB. The enhanced sensitivity of modern instrumentation has made it possible to detect these species at very low concentrations necessitated by the solubility limitations of TATB.

Solvating samples in DMSO and separating the constituents using HPLC with a DAD detector allows for accurate quantitation of TATB and its minor contaminants even in polymer blended formulations. This technique allows for the direct quantitation of T4A and FX1 found as minor impurities. The T4A and FX1 calibrations were used to semi-quantitate the remaining UV-active contaminants. Ultimately, complete quantitation by HPLC-DAD or HPLC-MS of other minor components will occur when pure standards are synthesized and purified.

The origin of some of the reported trace components in TATB is not completely clear but they are stable and do not appear to change over time as the material is stored, either as a solid or already solvated in DMSO. The relative amount of the minor compounds varies based on synthesis starting materials, synthesis routes, the formulation process to create plastic bonded forms, and environmental exposure to light and heat.

High-resolution mass spectrometry and standard materials were used to identify the compounds reported here. High-Resolution MS and MS/MS were critical in identifying proposed chemical formulas and structures. Knowledge of the synthesis and degradation reactions permits high confidence in the assigned formulas and structures. The compounds reported herein PBX 9502, except for Br-T4A, are commonly observed in TATB and its related plastic bonded forms.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Thanks go to Alan DeHope, Elizabeth A. Glascoe, and Evan M. Kahl of LLNL for useful discussions and the standard materials used. (LLNL-JRNL-825102).

Data Availability Statement

Data available from the corresponding author upon reasonable request.

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Manuscript received: July 30, 2021
Revised manuscript received: January 26, 2022
Version of record online: ■■, ■■■

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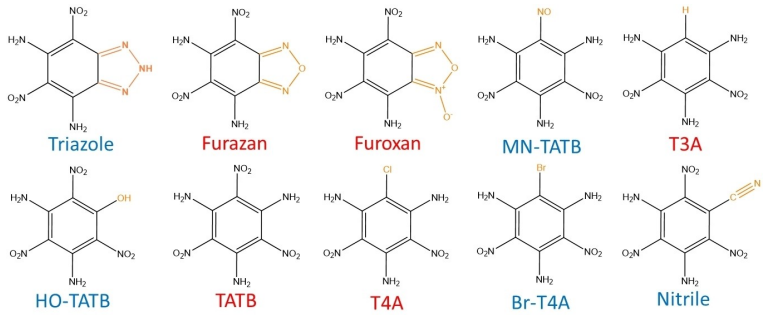

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Trace Compound Analysis in TATB by Liquid Chromatography coupled with Spectroscopic and Spectrometric Detection