A Validated Reverse Phase HPLC Technique for the Determination of TATB Assay

Sibes Chandra BHATTACHARYYA,[1,2*] Rajendra Shivaji PATIL,[2]
Mada S.S.N.M. SANTOSH,[2] Bikash BHATTACHARYA,[3]
Ranjan Kumar MALIK,[1] Anurag MEHRA[1]

[1] *Indian Institute of Technology Bombay,*
   Powai, Mumbai – 400076, India
[2] *Advanced Centre for Energetic Materials (ACEM),*
   P.B. No. 11, CIDCO Post Office, Nasik − 422 009, India
[3] *High Energy Materials Research Laboratory (HEMRL),*
   Defence Research & Development Organisation,
   Sutarwadi, Pune − 411 021, India
E-mail: sibes_bhatta@iitb.ac.in; sc.bhattacharyya@acem.drdo.in

Abstract: The main hurdle for the estimation of the purity of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is its insolubility in most of the known organic solvents. In the conventional method, TATB is digested with steam in a modified Kjeldahl digester and the ammonia evolved is estimated quantitatively. To do away with this cumbersome method, a simple, rapid HPLC technique using a reverse phase C-18 column has been established for quantitative determination of the purity of TATB. A sharp and symmetrical peak with a retention time of 2.92 min at 355 nm is obtained for pure TATB when the flow rate is 2.0 mL/min. The linearity of the detector response has been studied with sample concentrations ranging from 10 to 50 mg/L. The method addresses two important issues of sample preparation and the precision of measurement. Unlike the previously reported HPLC techniques which mainly aimed at the detection of TATB, the present work is a validated account of a quantitative estimation of purity. Regular production batch samples have been assayed by this method and the results are compared with those obtained from the conventional analysis. The HPLC method is convenient and reliable for quality control of the product at the plant level.

Keywords: TATB, HPLC, HPTLC, explosive, LOQ, LOD

1 Introduction

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) has become important since it is regarded as the industry standard [1] for insensitive high explosives (IHE). TATB has attractive properties such as high thermal stability, extreme insensitivity towards external stimuli, high density and its explosive performance is better than that of trinitrotoluene (TNT). On account of this remarkable combination of properties, TATB has received a great deal of attention in recent years. TATB can be combined with a plastic binder to produce a plastic-bonded explosive (PBX) composition, which is heat-resistant and highly insensitive [2-6]. It is insoluble in organic solvents and has a melting point above 400 °C. These characteristics favour its use in military applications. Breslow *et al.* [7] and Nasielski-Hinkens *et al.* [8] have reported non-military applications of TATB. For rocket propellants, it is desirable to have a low pressure exponent (between 0.2 and 0.5) of the burning rate. Bhattacharya and co-workers [9] have recently reported a novel application of TATB as a pressure exponent suppressant.

TATB was first reported in the chemical literature by Jackson and Wing [10] in 1888, and subsequently various synthetic routes were reported [11-14]. However, the synthesis using 1,3,5-trichlorobenzene (sym-TCB) has been adopted for pilot-plant scale production worldwide [15, 16]. HEMRL has also set up a pilot plant for the production of TATB on the kilogram-scale [17, 18]. The reaction scheme adopted for our pilot plant is shown below (Figures 1 and 2):
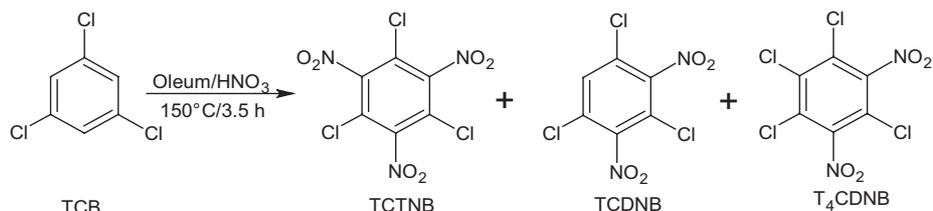
Figure 1.   Nitration of sym-TCB.
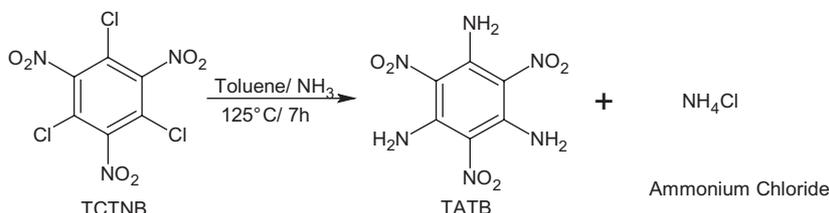
Figure 2.   Amination of TCTNB.

The main impurities associated with TATB depend on its synthetic route. During the nitration of TCB, two by-products, namely 1,3,5-trichloro-2,4-dinitrobenzene (TCDNB) and 1,2,3,5-tetrachloro-4,6-dinitrobenzene (T₄CDNB), are formed along with the main product, 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) [19, 20].

The crude product from sym-TCB nitration, TCTNB is filtered off, washed with water, dried and then dissolved in toluene before being subjected to the amination reaction under pressure. That the impurities in TCTNB, namely TCDNB and T₄CDNB, remain unreacted during the amination process was confirmed by the gas chromatographic analysis of the toluene effluent and also from the analysis of the residue after recovery of the toluene. The only by-product of the amination reaction is ammonium chloride.

The main hurdle for estimating the purity of TATB is its insolubility in most of the known organic solvents. Walter Selig [21] studied in detail the solubility of TATB in various solvents. The insolubility of TATB causes difficulty in sample preparation for analytical techniques [22, 23]. Its insolubility is related to the strong intra- and inter-molecular hydrogen bonds (between the nitro and amino groups) present in the molecular packing of the crystal lattice [24].

1.1 Determination of the chloride content

Chloride impurities in TATB are harmful as the decomposition of ammonium chloride produces hydrogen chloride and ammonia, which react with the weapon components [25]. The contamination of TATB by ammonium chloride is of considerable interest. Methods reported for the chloride estimation are based either on the decomposition of TATB crystals in presence of alkali or on combustion of a sample in a Parr bomb calorimeter [26]. Mehilal and co-workers [27] have reported a method based on conventional analysis for the determination of the chloride content in TATB.

1.2 Determination of the purity by conventional methods

Rigdon [28] estimated the purity of TATB by the determination of the total amino and nitro functional groups. At HEMRL, the purity is determined by conventional analysis using the amino group estimation method. This method is described below.

The total amino functional group estimation was carried out for the determination of the assay of regular production batch samples [29] using a modified Kjeldahl apparatus designed in-house. Accurately weighed TATB (0.1 g to 0.11 g) was transferred to a 500 mL two-neck round-bottomed flask. DMSO-water (1:1, 20 mL) was added to disperse the sample. 0.1N H₂SO₄

(40 mL) was accurately transferred to a 250 mL conical flask using a burette and the volume was made up to 100 mL by adding water. The apparatus was then assembled as shown in Figure 3. Water was boiled in the steam generator. When steam generation had stabilised, the tubing was connected to the steam distillation assembly as shown in the figure. 40% aqueous NaOH (15 mL) was added slowly to the round-bottomed flask using a dropping funnel. Some NaOH solution (1-2 mL) was kept in the dropping funnel to act as a seal. TATB was thus converted to 1,3,5-trihydroxy-2,4,6-trinitrobenzene (trinitrophloroglucinol, THTNB) with quantitative evolution of three equivalents/moles of NH_3 gas, which was collected in the H_2SO_4 solution. The reaction scheme is shown in Figure 4. The distillation was continued for 45 min in order to collect 75-100 mL of condensate. Care was taken to avoid any bubbling out of the steam/ammonia through the solution. After the distillation, the condenser and receiver were washed carefully and the washings were collected in the H_2SO_4 solution. This solution was then titrated with 0.1N NaOH using methyl red indicator. A blank determination was carried out following the entire procedure without TATB. The escape of ammonia gas affects the accuracy and precision of this method. Equation 1 was used for the calculation of the purity by this method.
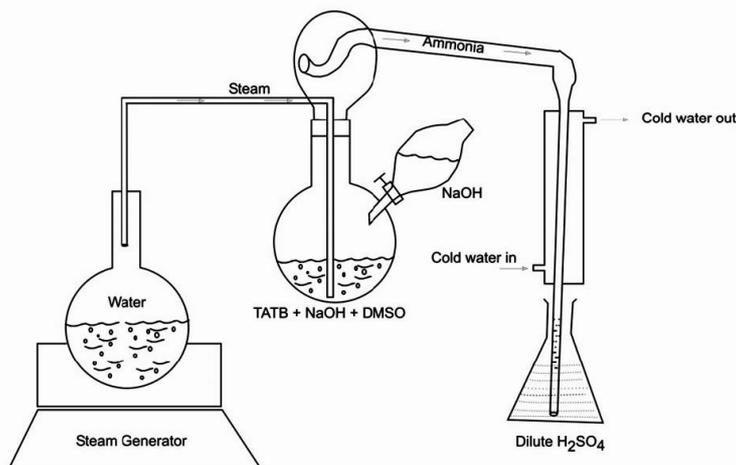
Figure 3.   Experimental arrangement for the assay of TATB by the total amino group estimation method.
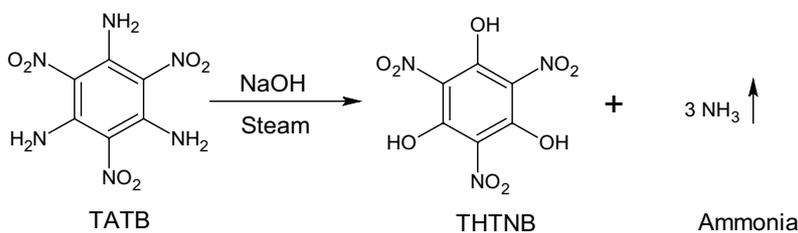
Figure 4.   Conversion of TATB to THTNB.

$$\text{Purity of TATB (\%)} = \frac{(V_2 - V_1) \times N \times M \times 100}{W \times n \times 1000} \tag{1}$$

V_2 – blank reading of 0.1N NaOH titre,
V_1 – sample readingof 0.1N NaOH titre,
N   – normality of NaOH,
M   – molecular weight of TATB,
W   – weight of sample,
n   – 3 (number of amino groups present in TATB).

The main drawback of this method is the time required for testing. It has been observed that only one test is possible per day which makes it unsuitable for qualification of regular production batches. The outcome of this test is dependent on the analyst and hence not robust. This method also lacks accuracy due to positive interference from ammonium chloride.

1.3 Motivation for the development of an HPLC method for the assay of TATB

Schaffer [30] reported the assay of TATB by HPLC using DMF as the sample solvent. He later reported the analysis of water and soil for the detection of TATB [31]. Kayser [32] reported the analysis of a synthetic mixture of 14 explosive materials including TATB. He used DMSO as the sample solvent. Later Bellamy *et al*. [14] quantified the impurities in TATB by HPLC. The TATB they used was synthesised from 1,3,5-trimethoxy-2,4,6-trinitrobenzene and contained impurities which are not present in the TATB obtained from sym-TCB. Dressen *et al*. [33] presented a pilot plant synthesis from a novel process with phloroglucinol as the starting material, and reported an assay by HPLC without any details. This synthesis, again, was not from sym-TCB and the purity estimation was not validated. Similarly Yu *et al*. [34] presented an HPLC analysis for microwave irradiated TATB without any details of the method. Table 1 presents a summary of the reported methods for the assay of TATB.

Table 1.   HPLC methods for TATB analysis

Authors	TATB source or quality	Column	Injection solvent, concentration of TATB	Buffer	Mobile phase	Flow rate [mL/min]	Detector wavelength	Precision, accuracy, Limits of detection
Schaffer [30]	DSC not reported. Both recrystallised TATB and composite mixtures of impurities were analysed.	μ-Bondapak NH$_2$ 300×4 mm	DMF, 0.04 mg/mL	-	1.5% DMF, 43% toluene and 55.5% heptane	0.8	355 nm	Not studied
Kayser [32]	DSC not reported. 14 component synthetic mixture was used.	C-18 column Radial Pack with RCM-100 radial compression module	DMSO 10^{-5}-10^{-7} mol/L (0.0258 mg/mL)	-	50:50 methanol / water	2	254 nm	Accuracy, precision not reported. LOD: 4.1 µg/mL
Schaffer [31]	DSC not reported. Detection of TATB contamination in water and soil was studied.	4.6 mm × 25 cm Alltech Hypersil C18 column (5-µm mean particle size)	DMF 0.025 mg/mL	50 µM phosphoric acid	75% Buffer + 25% mixture of (57.5% DMF/ 42.5% acetonitrile)	2	350 nm	LOD: 5.8 ppm (5.48 µg/ mL)
Bellamy *et al.* [14]	DSC exotherm at 335-346 °C. TATB was synthesised from 1,3,5-trimethoxy-2,4,6-trinitrobenzene and contained impurities.	C18 μ-Bondapak	DMSO, concentration not mentioned	EDTA (0.1 mM)/ citric acid (20 mM)	MeOH (50%): water (50%)	1	254 nm	Not reported

From Table 1, it is clear that different methods for the assay of TATB by HPLC have been reported during the last thirty years or more. However, details of the sample preparation, calibration, instrumental precision, validation of the technique with the limits of quantification were not clearly brought out. In none of the reports was the accuracy of the assay by HPLC determined by comparing the results obtained from a different analytical method. It has been reported that TATB obtained from the pilot plant via the sym-TCB route of preparation yields the purest product [29] and this is evident from the DSC exotherm data. Impure TATB [29, 30], with a low DSC exotherm (< 350 °C), has no bearing on the material under evaluation in the present context. It is therefore the validation of the technique, concentration of the sample and the accuracy of the method that still remain the real issues and not the separation of impurities from a synthetic mixture [31, 33] as reported previously. Silva and Mattos [15] have therefore concluded that chromatography is not practicable for TATB analysis.

2   Experimental

2.1 Reagents

HPLC grade methanol, water and DMSO were obtained from Merck, India. EDTA dipotassium salt dihydrate GR grade and citric acid anhydrous were also procured from Merck, India. The TATB used for the analyses was synthesised in the laboratory and the standard sample was prepared by repeated recrystallisation from DMSO. The pre-processing of TATB is detailed below.

2.2 Pre-processing of TATB

Production-grade TATB was obtained from HEMRL, Pune, pilot plant. The production grade TATB was separated from its impurities in four steps as follows:
1. Firstly, the as-synthesised product was digested in hot water at 90 °C for 2 h in a sealed reactor, in order to dissolve the ammonium chloride by-product.
2. The TATB was then filtered off and washed, with cold water several times and finally with hot water.
3. It was then washed with toluene to separate the organic impurities.
4. Finally it was washed with acetone and dried in an oven until the moisture content met the specification [29].

After the purification, TATB and its precursor 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) were extracted in methanol. While TCTNB dissolves completely in methanol, TATB is not soluble. Both the TCTNB and the TATB production batch sample were analysed by high performance thin layer

chromatography (HPTLC) with the following conditions:
(i)   HPTLC plate size: 20.0×10.0 cm
(ii)   Material: HPTLC plates silica gel 60F 254
(iii)   Spray gas: inert gas
(iv)   Sample solvent: methanol
(v)   Dosage speed: 150 µL/s
(vi)   Predosage volume: 0.2 µL
(vii)   Syringe size: 100 µL
(viii) Application position, Y: 8.0 mm
(ix)   Band length: 8.0 mm.

A chromatogram of track 1 (TCTNB) scanned at 254 nm is shown in Figure 5, and shows two compounds. The two peaks correspond to TCTNB and T$_4$CDNB. Quantitative data is given in Table 2. It is seen from the analysis that the TCTNB component at R$_f$ 0.52 constitutes 86.46% of the mixture.
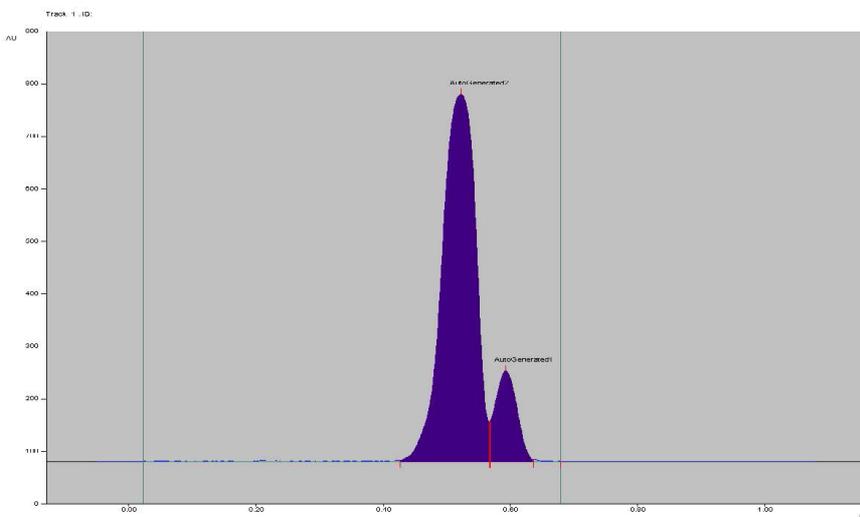
Figure 5.   Chromatogram of crude TCTNB scanned at 254 nm.

Table 2.   Quantitative data for the TCTNB sample

Peak	Start position (Rf)	Start height (AU)	Max. position (Rf)	Max. height (AU)	Max [%]	End position (Rf)	End height (AU)	Area (AU)	Area [%]
1	0.42	3.3	0.52	700.0	80.17	0.56	75.9	26737.6	86.46
2	0.56	77.9	0.59	173.2	19.83	0.63	4.3	4187.1	13.54

A chromatogram of production-grade TATB is shown in Figure 6. Here no peaks are observed and hence no impurity is detected by HPTLC. From the chromatogram, it is also clear that no TATB was dissolved in the methanol, and was not detected within the instrumental limits of detection.
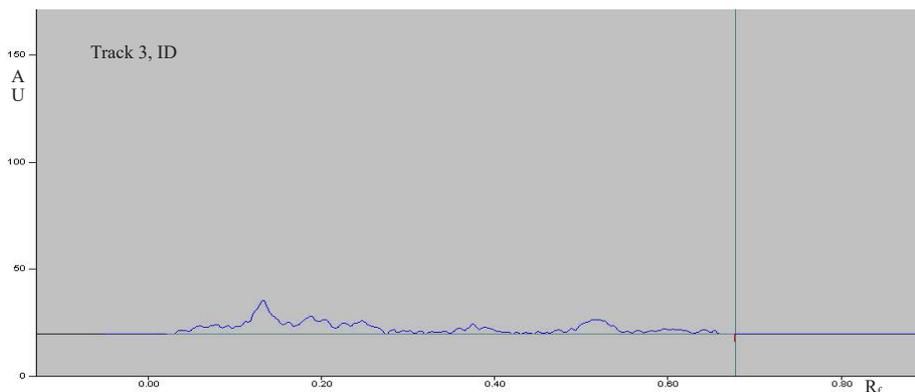
Figure 6.   Chromatogram of TATB scanned at 254 nm
NOTE: NO PEAK FOUND

2.3 Procedure

The TATB was further purified by repeated re-crystallisation using HPLC grade dimethyl sulphoxide (DMSO). The recrystallised TATB was dissolved in DMSO and the UV spectrum was recorded as shown in Figure 7. TATB shows UV absorption at λ_{max} 355 nm. Thus an HPLC method using a UV detector was found suitable for its assay.

Pure TATB (6 mg) was accurately weighed and dissolved in HPLC grade DMSO (100 mL), followed by ultrasonication for 10 min. The resulting concentration of this stock solution was 60 mg/L. Several aliquots of the stock solution were pipetted into 20 mL volumetric flasks and the volume was made up to the mark in each flask with DMSO, so as to prepare 10, 20, 30, 40 and 50 mg/L dilutions. The resultant solutions were filtered using a syringe filter (0.45 μm) before injection.
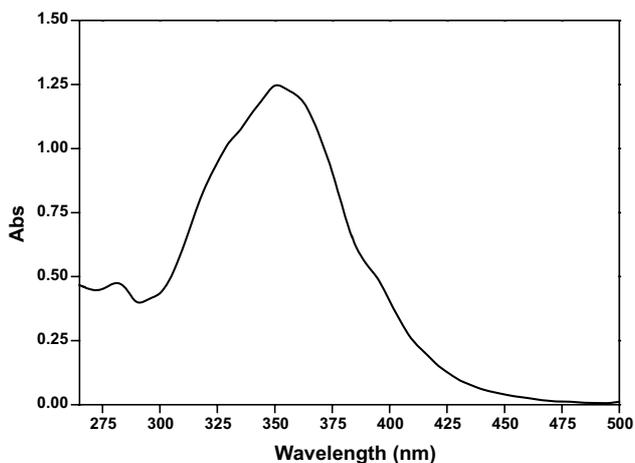
Figure 7.   UV spectrum of TATB.

2.4 Instrumentation

The chromatographic separation was conducted on a Dionex Ultimate-3000 Intelligent HPLC system consisting of LPG-3400A pump, WPS-3000 auto sampler, TCC-3000 column compartment, Photodiode Array (PDA) 3000 detector, Chromeleon 6.80 chromatography management system. A μBondapak™ C18 reverse phase column (3.9×300 mm C18 cartridge 10 μm, 125 Å) was used as the stationary phase, as used in Ref. [14]. The elution was carried out using methanol/EDTA buffer (0.1 mM EDTA dipotassium salt and 20 mM citric acid in water, pH 2.3) (50:50 v/v). The detailed analytical conditions are shown in Table 3 and a typical HPLC chromatogram of TATB is shown in Figure 8.

Table 3.   HPLC analytical conditions

Column	μBondapak™, 3.9×300 mm C18 cartridge, 10 μm, 125 Å
Mobile phase	Methanol/EDTA buffer (50:50 v/v)
Flow rate	2 mL/min
Injection volume	20 μL
Detection	Absorbance at 355 nm
Column temperature	30 °C
Run time	10 min
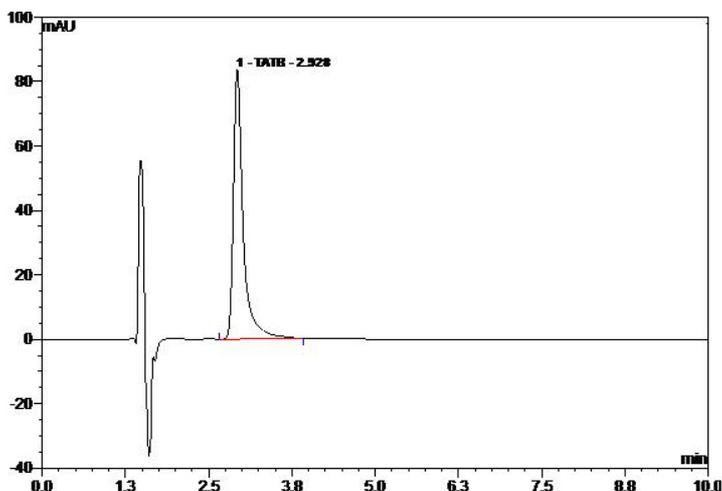
Figure 8.   HPLC chromatogram of TATB.

2.5 Calibration

The calibration curve was generated with four concentrations (10, 20, 30 and 40 mg/L) and the analysis was repeated seven times for each dilution. Before injecting the solutions, the column was equilibrated for at least 30 min with the mobile phase flowing through the system. Evaluation of the peak was done by the PDA detector at 355 nm and the peak areas were recorded for all solutions. The linearity was evaluated by linear regression of the data. The correlation graph was constructed by plotting the peak area obtained at the wavelength of detection versus the concentrations of the TATB solutions. The calibration curve is shown in Figure 9.
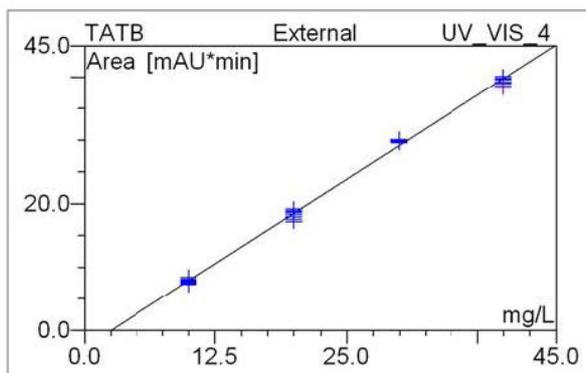
Figure 9.   Calibration curve of TATB.

It was observed that the response is linear up to 40 mg/L. The results showed an excellent correlation between the peak area and the concentration of TATB, with a linear regression coefficient (R^2) of 0.998.

Attempts were also made to inject a higher concentration of TATB (> 40 mg/L) solution into the HPLC system under identical conditions, but it was observed that the response became disturbed with successive injections and a standard deviation of 10% or more was recorded. This clearly indicates that the response is linear only up to a concentration of 40 mg/L.

3 Results and Discussion

3.1 Estimation of TATB purity

HPLC conditions were maintained as for the optimised conditions. TATB was run in the mobile phase composition of 50% methanol and 50% EDTA buffer (0.1 mM EDTA dipotassium salt and 20 mM citric acid in water, pH 2.3) with the C-18 column (μBondapak, 10 μ 125 Å, 3.9×300 mm). This gave a sharp and symmetrical peak with a retention time of 2.92 min, with detection at 355 nm, when the flow rate was 2.0 mL/min.

The Match Factor expresses the similarity of two curves. A peak purity match factor can be expressed for both the UV spectra. The match factor for UV spectra (UV match factor) refers to the correlation between the spectrum at the peak maximum and the spectra on the leading and trailing edges. Ideally, none of the spectra between peak start and peak end should deviate from the spectrum at the peak maximum. In which case they correspond to 100% correlation; that is, the match value is 1000. The match factor for TATB HPLC analysis is shown in Figure 10. The match values were 991.69 (99.17%) at peak start, 1000 (100%) at 2.93 min and 989.00 (98.9%) at peak end. This demonstrated that the peak was pure and the peak represented TATB only, and that there was no co-elution of impurities.
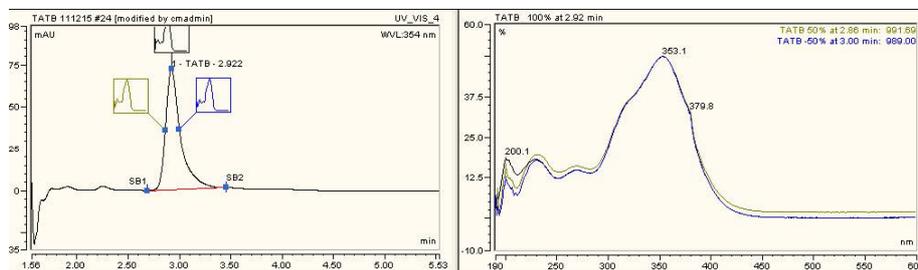
Figure 10. Peak purity and match factor.

3.2 Validation of the technique

The limit of detection (LOD) and the limit of quantification of the proposed method were determined by injecting gradually lower dilutions of the TATB standard solution into the same apparatus. The lowest concentration of the sample that gave a detectable response (LOD) was 0.06 µg/mL. The lowest concentration for a quantifiable response (LOQ) was 0.2 µg/mL.

3.3 Comparative studies

To compare the assay values obtained from the HPLC method and the conventional method, four production batches were identified for study. The material was prepared in the HEMRL pilot plant and samples were withdrawn after preprocessing the crude TATB. The material was tested for its moisture content, chloride content and DSC exotherm, as per the specification document [29]. The chloride content estimation has been described in the previous section. The test results of the four production batches are presented in Table 4. It is again seen from the data that the DSC exotherm for all of the batches is above 380 °C and proves that the TATB obtained from the pilot plant was pure.

Table 4.   Analysis report for the TATB production batches

Sample ID	Moisture content [%]	DSC exotherm, peak max [°C]	Chloride impurity [%]
A	0.08	385.15	0.65
B	0.13	383.31	0.39
C	0.13	386.6	0.57
D	0.18	385.73	0.45

All four batches were analysed for assay by the conventional method described in an earlier section, and were analysed in triplicate. The reported purity values were compared for reproducibility.

Subsequently, samples from the same four production batches were tested for assay by HPLC at ACEM, Nasik. From the production grade batches of TATB, samples were prepared at various strengths in DMSO. 20 µL of each sample solution was injected into the HPLC seven times and the responses were recorded. The standard deviation and standard error were calculated as given in Table 5. The standard TATB was labelled as 100% pure, while the purity of the production grade TATB was determined by HPLC.

Table 5 also presents the purity of TATB determined by different methods in the two laboratories.

From Table 5, it is evident that the comparisons of the purity results for the

production batches by the two different techniques at the two laboratories are satisfactory. We feel that the accuracy of the HPLC method justifies its use for qualification of production batches of TATB.

Table 5. Purity analysis by different methods

Sample ID	Purity by conventional (Kjeldahl) analysis [%]	HPLC analysis			
		Purity [%]	Standard deviation	RSD [%]	Standard error
A	98.27	98.48	0.095	0.096	0.043
B	98.35	98.33	0.042	0.042	0.019
C	98.26	98.53	0.034	0.035	0.015
D	98.60	98.55	0.015	0.012	0.006

3.4 Method precision

The method precision was determined by the analysis of four batches from the pilot plant. The analyses were performed with six replicates. As shown in Table 5, the RSDs of the production batch analyses ranged from 0.012% to 0.096%.

4 Conclusions

In the present study, the assay of TATB has been quantitatively estimated by a method based on reverse phase HPLC. The method is simple, stable, fast and offers good resolution within a short analysis time. The method records a linear response up to a concentration of 40 mg/L with DMSO as the solvent for sample preparation. The lowest concentration for a quantifiable response is 0.2 µg/mL while the lowest concentration for a detectable response is 0.06 µg/mL. The HPLC method was found to be accurate when the results were compared with a conventional technique. Several production batches have been assayed. The method of analysis scores over the conventional procedure in terms of accuracy and the time required for the estimation. The validated HPLC method for TATB assay is suitable for qualification of pilot plant batches of TATB.

References

[1] Rice S.F., Simpson R.L., *The Unusual Stability of TATB: a Review of the Scientific Literature*, Lawrence Livermore National Laboratory, Livermore, CA, Report, UCRL-LR-103683, **1990**.

[2] Tarver C.M., Koerner J.G., Effects of Endothermic Binders on Times to Explosion of HMX- and TATB-based Plastic Bonded Explosives, *J. Energ. Mater.*, **2007**, *26*, 1-28.

[3] Burgess C.E., Woodyard J.D., Rainwater K.A., Lightfoot J.M., Richardson B.R., *Literature Review of the Lifetime of DOE Materials: Aging of Plastic Bonded, Explosives and the Explosives and Polymers Contained Therein*, Amarillo National Resource Center for Plutonium Report, ANRCP-**1998**-12.

[4] Dobratz B.M., *Insensitive High Explosive Triaminotrinitrobenzene (TATB): Development and Characterization – 1888 to 1994*, Los Alamos National Laboratory Report LA-13014-H, University of California Report UC-741, **1995**.

[5] Kumar R., Sood D., Bhardwaj V., Biswas I., Singh M., Analysis of the Impact Sensitivity of TATB-Viton and HMX-Viton, *Proc. 9th Int. High Energy Materials Conference and Exhibits*, HEMCE, Trivandrum, India, **2014**.

[6] Singh A., Kumar M., Soni P., Singh M., Srivastava A., Mechanical and Explosive Properties of Plastic Bonded Explosives Based on Mixture of HMX and TATB, *Def. Sci. J.*, **2013**, *63*, 622-629.

[7] Breslow R., Maslak P., Thomaides J.S., Synthesis of the Hexaaminobenzene Derivative Hexaazaoctadecahydrocoronene (HOC) and Related Cations, *J. Am. Chem. Soc.*, **1984**, *106*(21), 6453-6454.

[8] Nasielski-Hinkens R., Benedek-Vamos M., Maetens D., Nasielski J., A New Heterocyclic Ligand for Transition Metals: 1,4,5,8,9,12-Hexaazatriphenylene and its Chromium Carbonyl Complexes, *J. Organomet. Chem*., **1981**, *217*(2), 179-182.

[9] Bhattacharya B., Singh P.P., Mehilal, Kurva R., Jawalkar S.N., Bhattacharyya S.C., Rao A.S., *A Novel Composite Propellant Composition with a Reduced Pressure Exponent*, Indian Patent Application No. 393/DEL/2010, **2010**.

[10] Jackson C.L., Wing J.F., On Tribromotrinitrobenzol, *Am. Chem. J.*, **1888**, *10*, 283-287.

[11] Benziger T.M., *Method for the Production of High-purity Triaminotrinitrobenzene*, Patent US 4032377, **1977**.

[12] Mitchell A.R., Coburn M.D., Lee G.S., Schmidt R.D., Pagoria P.F., Hsu P.C., *Synthesis of Trinitrophloroglucinoland Triaminotrinitrobenzene (TATB)*, Patent US 7057073 B2, **2006**.

[13] Pagoria P.F., Mitchell A.R., Schmidt R.D., 1,1,1-Trimethylhydrazinium Iodide: a Novel, Highly Reactive Reagent for Aromatic Amination via Vicarious Nucleophilic Substitution of Hydrogen, *J. Org. Chem*., **1996**, *61*, 2934-2935.

[14] Bellamy A.J., Ward S.J., Golding P., A New Synthesis Route to 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), *Propellants Explos. Pyrotech.*, **2002**, *27*, 49-58.

[15] Silva G., Mattos E., Synthesis of 2,4,6-Triamino-1,3,5-trinitrobenzene, *J. Aerosp. Technol. Manag.*, **2011**, *3*, 65-72.

[16] Agrawal J.P., Past, Present and Future of Thermally Stable Explosives, *Cent. Eur. J. Energ. Mater.*, **2012**, *9*(3), 273-290.

[17] Bhattacharyya S.C., Narasimhan V.L., Indigenous Development of the Insensitive High Explosive: TATB, *Proc. Propex Seminar*, Ordnance Factory Bhandara, India, **2002**, 30-38.

[18] Nandi A.K., Kasar S.M., Thanigaivelan U., Ghosh M., Mandal A.K., Bhattacharyya S.C., Synthesis and Characterization of Ultrafine TATB, *J. Energ. Mater.*, **2007**, *25*(4), 213-231.

[19] Yasuda S.K., Simultaneous Determination of 1,3-Dinitro-2,4,6-trichlorobenzene and 1,3-Dinitro-2,4,5,6-tetrachlorobenzene in 1,3,5-Trichloro-2,4,6-trinitrobenzene, *J. Chromatogr. A*, **1973**, *76*(2), 331-335.

[20] O'Keefe D.M., Gurule F.T., *The Synthesis of Symmetrical Trichlorotrinitrobenzene*, Dept. of Energy, Sandia Laboratories Report, SAND 78-1001, **1978**.

[21] Selig W., *Estimation of the Solubility of 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) in Various Solvents*, Lawrence Livermore Laboratory Report UCID-17412, **1977**.

[22] Foltz M.F., Ornellas D.L., Pagoria P.F., Mitchell A.R., Recrystallization and Solubility of 1,3,5-Triamino-2,4,6-trinitrobenzene in Dimethyl Sulfoxide, *J. Mater. Sci.*, **1996**, *31*(7), 1893-1901.

[23] Talawar M.B., Agarwal A.P., Anniyappan M., Gore G.M., Asthana S.N., Venugopalan S., Method for Preparation of Fine TATB (2-5µm) and its Evaluation in Plastic Bonded Explosive (PBX) Formulations, *J. Hazard. Mater.*, **2006**, *B137*, 1848-1852.

[24] Cady H.H., Larson A.C., The Crystal Structure of 1,3,5-Triamino-2,4,6-trinitrobenzene, *Acta Cryst.*, **1965**, *18*, 485-496.

[25] Kohn E., *Determination of Inorganic Chlorides in TATB*, Mason and Hanger-Silas Mason Co., Inc. Pantex Plant, Amarillo, Texas 79177, MHSMP-75-5K, **1974**.

[26] Faubion B.D., *Chemical Analysis of TATB*, Mason and Hanger-Silas Mason Co., Inc. Pantex Plant, Amarillo, Texas 79177, MHSMP-75-5J, **1974**.

[27] Mehilal, Prasad U.S., Survey R.N., Agrawal J.P., Determination of Chlorine Content in 1,3,5-Triamino-2,4,6-trinitrobenzene by Converting it into 1,3,5-Trihydroxy-2,4,6-trinitrobenzene by Treatment with Aqueous Sodium Hydroxide, *Analyst*, **1998**, *123*, 397-398.

[28] Rigdon P., Stephens F.B., Harrar J.E., Precise Assay of TATB by the Determination of Total Amino and Nitro Functional Group, *Propellants Explos. Pyrotech.*, **1983**, *8*, 206-211.

[29] *Provisional Specification for TATB*, High Energy Materials Research Laboratory, Pune, India, No. HEMRL/CEPP/PS/364, **2005**.

[30] Schaffer C.L., *Assay of TATB by HPLC*, Mason and Hanger-Silas Mason Co., Inc. Pantex Plant, Amarillo, Texas 79177, Report No. MHSMP-78-65, **1978**.

[31] Schaffer C.L., *Analysis of Soil and Water for TATB Content*, Mason and Hanger-Silas Mason Co., Inc. Pantex Plant, Amarillo, Texas 79177, Report No. MHSMP-92-40, **1992**.

[32] Kayser E.G., *Analysis Methods for Explosive Materials – I. Polynitro Compounds*, Naval Surface Weapons Center, Virginia, 22448 Report NSWC TR 81-123, **1982**.

[33] Dressen S., Merrill D., Sanderson A., Velarde S., Pilot Plant Synthesis of TATB from a Novel Process, *IM/EM Technical Symposium*, San Francisco, CA, Nov. 15-17, **2004**.

[34] Yu W., Zhang T., Huang Y., Yang L., Li G., Li H., Li J., Huang H., Effect of Microwave Irradiation on TATB Explosive, *J. Hazard. Mater.*, **2009**, *168*, 952-954.