Assay of the Thermally Stable, Insensitive, High Explosive 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)

Amiya Kumar NANDI*, Nenavath THIRUPATHI,
Alok Kumar MANDAL and Raj Kishore PANDEY

*High Energy Materials Research Laboratory, Chemical Engineering
and Pilot Plant Division, Sutarwadi, Pune-411021, India*
*E-mail: nandi.ak@hemrl.drdo.in

Abstract: An aqueous titration method is described to assay the insensitive, high explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). TATB is initially quantitatively converted to the weak acid 1,3,5-trihydroxy-2,4,6-trinitrobenzene (THTNB) by base catalysed hydrolysis. Subsequently THTNB is assayed by acid-base titration. TATB samples obtained from regular batch operations are assayed by this method, and the results are compared with those obtained by the total amino functional group estimation method using a modified Kjeldhal apparatus. The method is simple and has good accuracy and precision.

Keywords: assay of TATB, acid- base titration, base hydrolysis, trinitrophloroglucinol, ammonium chloride

1 Introduction

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) is an aromatic high explosive of special interest because of its insensitivity, thermal stability (>350 °C), and respectable performance with respect to conventional high explosives such as TNT, RDX and HMX [1, 2]. Although several alternative routes for TATB synthesis have been reported [3-5], the large-scale production of TATB is still an adaptation of the Benziger route (Scheme 1) starting from 1,3,5-trichlorobenzene (TCB) [6-8]. This laboratory has also adapted this route and the process has been scaled up to pilot plant level [9-13].
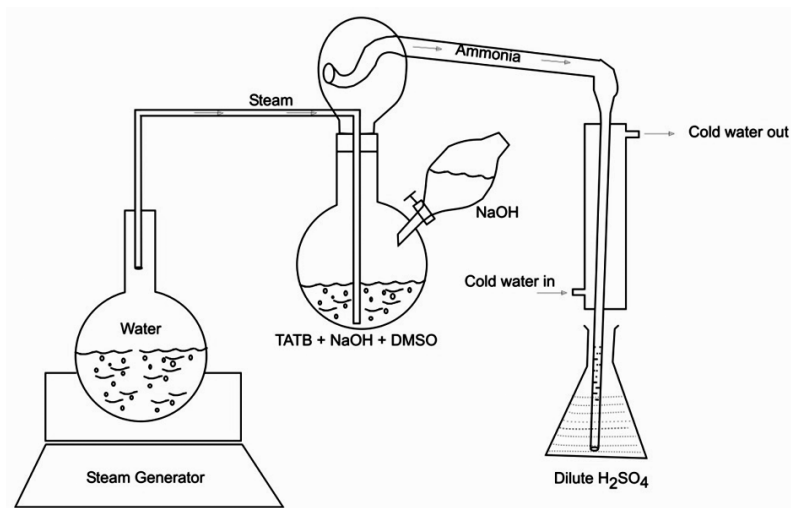
Scheme 1. Benziger route for TATB synthesis.

Unlike other military explosives (*e.g.* TNT, RDX, HMX *etc.*), TATB is virtually insoluble in most common solvents [14-19]. The insolubility of TATB is related to the strong intra- and intermolecular hydrogen bonds (between nitro and amino groups) present in the molecular packing of the crystal lattice [20, 21]. The insolubility of TATB is an issue for the assay of a representative sample. Some authors have developed HPLC method for the assay of TATB [22, 23]. However, the poor solubility of TATB is a limiting factor for achieving accuracy and precision by the HPLC method. Considering this issue, Rigdon *et al.* [24] later developed an assay method based on the estimation of the total amino and nitro functional groups present in TATB. The total amino functional group estimation (TAFGE) was carried out using a simplified Kjeldhal apparatus. The total nitro functional groups were estimated by electrolytic reduction using controlled-potential coulometry. This laboratory adapted the TAFGE method for assaying regular batch samples [25]. TATB is digested by steam with the slow addition of sodium hydroxide solution in an in-house designed, modified Kjeldhal apparatus (Figure 1). TATB is converted to 1,3,5- trihydroxy-2,4,6-trinitrobenzene (trinitrophloroglucinol) with quantitative evolution of three equivalents /moles of NH_3 gas. The liberated NH_3 gas is estimated by absorbing it in a known quantity of dilute H_2SO_4 solution. This is a cumbersome, wet-chemical method and needs very experienced hands to carry out the digestion and quantitative absorption of the evolved ammonia gas in dilute H_2SO_4 solution. The slow addition of sodium hydroxide solution (10 M) during the TATB digestion liberates ammonia gas at a slow rate, and thus, the evolved ammonia gas effectively gets absorbed in the acid solution without any loss (escape by bubbling) [25]. The escape of ammonia gas affects the accuracy and precision of this method.

Figure 1. Experimental set-up for assay of TATB by the TAFGE method.

Earlier Nandi *et al*. [26, 27] reported acid-base titration methods for the assay of two insensitive high explosives, 3-nitro-1,2,4-triazol-5-one (NTO) and 1,1-diamino-2,2-dinitroethylene (FOX-7). This paper describes a wet-chemical, acid-base titration method for the assay of TATB. TATB is initially quantitatively converted to the weak acid 1,3,5-trihydroxy-2,4,6-trinitrobenzene (THTNB) by the base-catalysed hydrolysis reaction. Subsequently, the THTNB is assayed by acid-base titration.

2 Materials and Methods

2.1 Chemicals
All of the chemicals used were analytical reagent (AR) grade from M/s Merck Ltd., Mumbai, India. Distilled water was used for the preparation of aqueous solutions.

2.2 TATB samples
TATB samples were obtained from regular batches produced in the pilot plant of this laboratory. TATB was synthesized by the Benziger route [7]. TCB is first nitrated to 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB), and the product TATB is synthesized in a second step by the amination of the intermediate TCTNB in toluene (mixed with 5% water) using ammonia gas (Scheme 1).

2.3 Titration method

2.3.1   Preparation and standardization of 0.1 N sodium hydroxide solution in water

0.1 N NaOH solution was prepared by dissolving 4 g sodium hydroxide flakes in water in a 1000 mL volumetric flask and making up to the mark with water. The solution was standardized [28] using the primary standard potassium hydrogen phthalate (well dried) using phenolphthalein indicator.

2.3.2   Preparation and standardization of 0.05 N and 0.1 N HCl solutions

0.05 N and 0.1 N HCl solutions were prepared by dilution of 4.1 mL and 8.2 mL concentrated HCl (12 N) respectively in a 1000 mL volumetric flask. The 0.05 N solution was standardized by titration against the above mentioned standard 0.1 N NaOH solution using phenolphthalein indicator [28].

2.4 Analytical method for the assay of TATB

TATB powder (200 to 250 mg) was weighed accurately and transferred to a conical flask (250 mL). 50.0 mL standard NaOH (0.1 N) and 25 mL DMSO were added to it. The mixture was heated on a hot plate, with occasional swirling. The TATB was converted to the sodium salt of THTNB (trinitrophloroglucinol) with the evolution of ammonia gas resulting in a dark brown coloured solution. Heating was continued until the evolution of ammonia gas ceased (checked by wet litmus paper). The solution was then cooled to room temperature and a few drops of bromophenol blue indicator solution were added to it. 25.0 mL 0.1 N HCl (accurately measured by pipette) was added to it. The mixture was titrated against standard 0.05 N HCl solution and the end-point was indicated by a sharp colour change from greenish-brown to yellow. The burette reading (V_s) was noted. A blank titration (V_b) was also carried out without TATB.

$$\text{Calculation: \% Purity of TATB} = \frac{(V_b - V_s) \times N \times 25.8}{m}$$

where: V = burette reading (mL), N = normality of sodium hydroxide solution, m = mass of the sample (g).

3   Results and Discussion

Harris *et al.* [29] studied the base hydrolysis of TATB to develop a qualitative high explosive spot test. TATB undergoes a base (OH$^-$) catalysed hydrolysis reaction which proceeds via a nucleophilic aromatic substitution (S_NAr) reaction [30].

Three NH$_2$ groups are stepwise replaced by HO$^-$ with the liberation of 3 moles of NH$_3$ gas (Scheme 2). Thus, TATB (I) is quantitatively converted to THTNB (IV) which is a weak acid. Subsequently, THTNB consumes one mole of base (OH$^-$) and is converted to its conjugate base (V). The conjugate base is stabilised due to delocalization of the negative charge by the –R effect of the –NO$_2$ group. The resulting brown colour is due to the quinoid structure of the conjugate base (V_b). During titration of the solution, the conjugate base (V_a /V_b) is converted back to the yellow coloured THTNB. The difference in burette reading with respect to the blank titration gives the amount of base (NaOH) consumed by THTNB. Thus, the % purity of the TATB is estimated.
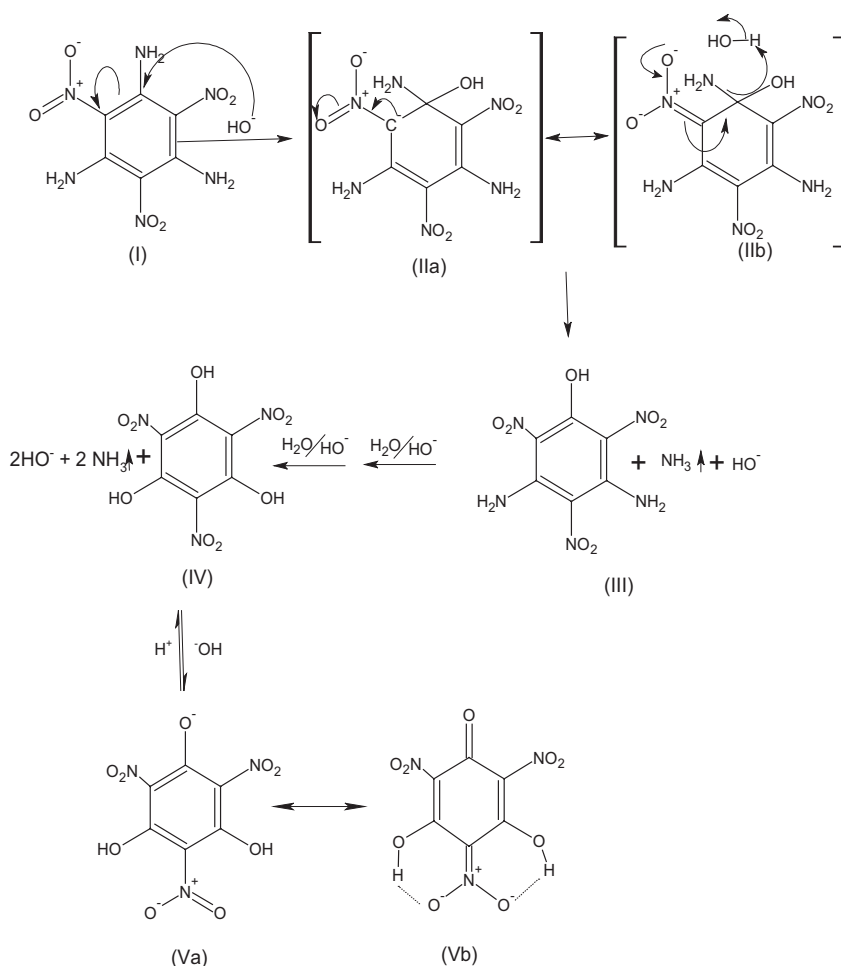
Scheme 2. Mechanism for base hydrolysis reaction of TATB.

It is interesting to note that TATB consumes no base in the hydrolysis process to convert it to THTNB. This indicates that the hydrolysis is a base catalysed reaction. The proposed reaction mechanism is shown in Scheme 2. No base ($^-$OH) is consumed during the stepwise replacement of NH_2 groups by OH. The consumption of base occurs during the neutralization of the weak acid THTNB. Although THTNB has three ionisable hydrogen atoms (from the corresponding three hydroxyl groups), only one is ionised by dilute base (0.1 N). This may be due to engagement of the other two hydrogen atoms in intramolecular hydrogen bonding, giving extra stability to the conjugate base (V_b).

Addition of DMSO in water helps the hydrolysis process by imparting organic character and also changing the overall polarity of the solvent. The hydrolysis reaction takes a longer time to become complete without DMSO. Gentle heating on a hot plate (until the evolution of ammonia gas ceases, which is checked by litmus paper) is required to realise better accuracy and precision of the assay method. Boiling on the hot plate was avoided as it may cause decomposition of the THTNB resulting in a lower assay value. A higher concentration of NaOH also causes decomposition of THTNB and thereby affects the accuracy of the method. Incomplete reaction, which is indicated by a suspension of yellow TATB particles after titration, also affects the accuracy. Bromophenol blue indicator (pH 5.6-2.5) was found suitable for this titration. The brown colour of the conjugate base (V_b) mixes with the blue colour of the indicator resulting in a greenish-brown coloured solution. However, the colour of both compounds change to yellow at a lower pH resulting in a sharp colour change at the titration end point. Other indicators such as phenolphthalein, methyl orange, methyl red and bromocresol green were found to be unsuitable for this titration. Initial neutralization of the NaOH-digested solution by 25 mL 0.1 N HCl (accurately measured by pipette) was necessary to keep the burette reading within 50 mL. The addition should be accurate and the same for both blank and actual (with sample). One may use HCl of higher concentration (> 0.1 N); in that case there will be a magnification of the analytical error if the volume is not measured accurately to be the same for both blank and actual.

As already mentioned, TATB was synthesized by the Benziger route. In the TCTNB amination process, the product TATB and the by-product NH_4Cl crystallize out (co-precipitation) simultaneously, resulting in the formation of crude TATB with a high chloride impurity content (~24%) (Scheme 3). This chloride impurity is largely removed by boiling the crude product in hot water (due to the very high solubility of NH_4Cl in water). However, crude TATB contains a small percentage of ammonium chloride (< 1%) which is occluded in the TATB crystal lattice [31-34]. This occluded ammonium chloride is

not removed by boiling the crude product in water. Thus, TATB prepared by the Benziger route invariably contains a small percentage of NH_4Cl impurity [7]. Chloride is an undesirable impurity in TATB. It causes compatibility problems with certain ammunitions, and thereby reduces the storage life. Thus, it is recommended practice to estimate the chloride impurity in each TATB batch sample, and to report the data along with the assay value (purity). This laboratory has adopted an in-house developed method for the estimation of the chloride impurity in TATB [35]. It is estimated by the potentiometric titration of an acidified, digested TATB solution (digested in 10 N NaOH solution) using a Ag/AgCl electrode (DG141) in a Mettler Toledo Autotitrater (Model: DL55).
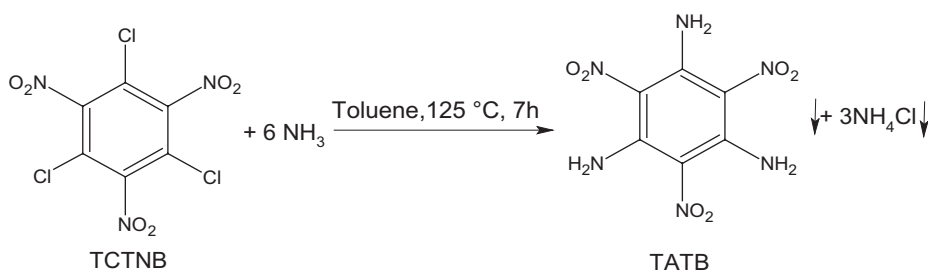
Scheme 3. Formation of TATB along with by-product NH_4Cl during amination process.

Table 1. Assay results for TATB samples

Sample	Acid-base titration method		TAFGE method		Chloride impurity (%)
	Purity (%)	STDEV* (σ)	Purity (%)	STDEV* (σ)	
1	98.6	0.19	98.7	0.39	0.6
2	98.8	0.21	98.4	0.51	0.5
3	99.0	0.18	98.5	0.68	0.4
4	98.8	0.25	98.6	0.75	0.7
5	99.0	0.27	98.4	0.47	0.35
Dry aminated TATB	101.5	0.18	101.1	0.88	1.8
Recrystallized TATB (free from chlorine)	99.5	0.28	99.1	0.38	0

* Number of replicates was 3 for all samples.

Assay values of a few TATB batch samples with chloride impurity data are shown in Table 1. The assay values are compared with those obtained by the

TAFGE method. A standard sample (free from chloride) was prepared in-house from production grade TATB by a literature reported, acid recrystallization method [16]. The accuracy and precision of the developed acid-base titration method was found to be better. The accuracy and precision of the TAFGE method are largely affected by the escape of evolved ammonia gas (by bubbling) during its absorption in the dilute H_2SO_4 solution.

The presence of ammonium chloride impurity in TATB causes positive interference to this assay method. NH_4Cl also reacts with NaOH during the base hydrolysis of TATB with evolution of ammonia gas. Thus, some amount of base is consumed by NH_4Cl. As the molecular weight of NH_4Cl (53.5) is much lower than that of TATB (mol. wt. 258), the positive interference becomes prominent in the presence of a small percentage (> 1%) of this impurity. Similar interference was also observed for the TAFGE method [24]. However, this interference is not prominent for samples with very low chloride content (< 1%). Dry aminated TATB (amination of TCTNB carried out in toluene in the absence of water) shows a purity > 100% by both methods due to the positive interference from occluded ammonium chloride (> 1.0%) (Table 1).

Some authors reported the presence of some organic impurities in TATB such as TCTNB, 1,3,5,6-tetrachloro-2,4-dinitrobenzene (T_4), 1,3,5-trichloro-2,4-dinitrobenzene (T_3) and their mono, di, and triamino derivatives [36]. These impurities may cause negative interference in the acid-base titration method (the molecular wt. of these impurities is higher than that of TATB). However, they are generally present in the sample at trace level (< 0.2%) and hence, their effects are negligible.

4   Conclusion

An aqueous, acid-base titration method was developed for the assay of TATB. TATB is initially quantitatively converted to the weak acid 1,3,5-trihydroxy-2,4,6-trinitrobenzene (THTNB) by a base catalysed hydrolysis process. Subsequently, THTNB is assayed by acid-base titration. TATB samples obtained from regular batch operations were assayed by this method and the results were compared with those obtained by the TAFGE method using a modified Kjeldhal apparatus. The method is simple and has good accuracy and precision. However, the presence ammonium chloride impurity in TATB shows a positive interference in this assay method.

5   References

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