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Assay of the Insensitive High Explosive FOX-7 by Non-Aqueous Titration

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Abstract: A non-aqueous titration method was developed to assay the insensitive high explosive 1,1-diamino-2, 2-dinitroethene (FOX-7). The weak acidic nature of FOX-7 (pK_a 10.6) was exploited in the assay method. The sample was dissolved in the protophilic solvent N, N-dimethylformamide and titrated against sodium methoxide solution in benzene/methanol using azo violet as indicator. FOX-7 samples obtained from regular batch operations were assayed by this method and the results were compared with that of a recrystallized sample. The method is simple, rapid and has good accuracy and precision.

Keywords: 1,1-diamino-2,2-dinitroethene, FOX-7, non-aqueous titration, N,N-dimethylformamide

Introduction

1,1-Diamino-2,2-dinitroethene (FOX-7) has received increasing interest as a high explosive due to its lower sensitivity and comparable performance to RDX. Since it was developed in the late 1990's [1], research and development work on FOX-7 has been continued with great interest in process development and scale up to pilot plant [2-6], as well as the evaluation of its properties [7, 8] and performance [9-11]. This laboratory has also established the manufacturing technology for FOX-7 at pilot plant scale [12]. This demands a good analytical

method for assaying the product. Although an HPLC instrumental method has been reported [13, 14] using a special porous graphite column, the method was applied using a sample which was a synthetic mixture of FOX-7 and its possible impurities rather than actual batch samples obtained from different batch operations. An HPLC method was also developed by Polish scientists (B. Buszewski et al.) for purity analysis of FOX-7 (obtained under different recrystallization conditions using solvents such as DMF, acetone, water etc.), as well as some intermediate products generated during the synthesis of FOX-7 [15]. A thin layer chromatographic (TLC) method was also developed by S. Cudziło et al. which was found effective for monitoring the synthesis of FOX-7 from the starting material 2-methylpyrimidine-4,6-dione (MPD) [16]. The present paper describes a simple and rapid, non-aqueous titration method for the assay of batch samples of FOX-7 obtained from the pilot plant of this laboratory.

Organic compounds having weakly acidic or basic properties, such as alkyl/aryl substituted phenols, and amines, are generally assayed by non-aqueous titration [17]. FOX-7 is also a weak acid (pK_a 10.6) due to the labile N–H bond [18]. The weakly acidic properties of the compound is enhanced by dissolving it in protophilic solvents such as N,N-dimethylformamide (DMF), ethylenediamine (ED) and titrated against the strong base sodium methoxide, prepared in benzene/methanol.

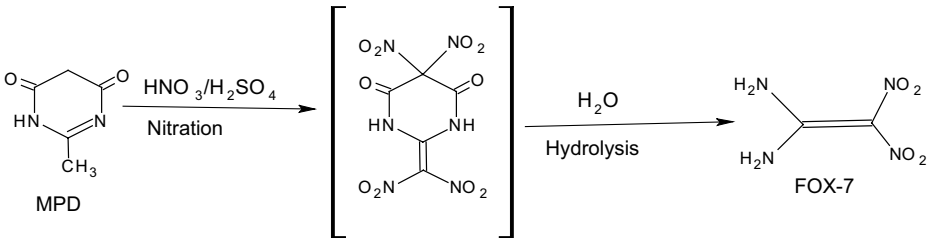
Materials and Methods

Chemicals and Reagents

The reagents DMF, ED, benzene, specially dried methanol, 30% sodium methoxide solution in methanol, azo violet (p-nitrobenzene-azo-resorcinol), thymol blue, and benzoic acid were of analytical reagent grade from M/s Merck Ltd., Mumbai, India.

FOX-7 Samples

FOX-7 samples were obtained in-house from the pilot plant (5 kg/batch level) of this laboratory. It was synthesized by nitration of the precursor 2-methylpyrimidine-4,6-dione (MPD) followed by hydrolysis of the tetranitro intermediate (2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione) in water (Scheme 1). Five batch samples were analysed and the results were compared with the purity of recrystallized FOX-7 (considered as the standard sample). The reported [19] cooling crystallization method using DMF as the solvent was adopted for the recrystallization.



Scheme 1. Synthetic route to FOX-7.

Preparation and standardization of the titrant [0.1 M sodium methoxide solution in benzene/methanol (9:1)]

30% Sodium methoxide solution in methanol (18 ml) was transferred to a 1000 ml standard volumetric flask. Methanol (138 ml) was added to it and the remaining volume was made up with benzene. This solution was standardized by titration against the primary standard benzoic acid.

Benzoic acid (120 to 150 mg) was weighed accurately to the nearest 0.02 mg and transferred to a dry 250 ml conical flask. DMF (50 ml) was added followed by 2-3 drops of azo-violet indicator (saturated solution in benzene). The flask was swirled to dissolve the benzoic acid and the solution became red in colour. This solution was titrated against 0.1 M $NaOCH_3$ solution (prepared in benzene-methanol). The titration end point is indicated by a sharp colour change from red to blue. The burette reading (Vs) was noted. A blank (V_b) was determined by performing the entire titration without benzoic acid. The blank usually consumed 0.25 to 0.35 ml of 0.1 M $NaOCH_3$ solution to neutralized the free HCl present in the solvent DMF.

Calculation:

$$\text{Strength of } NaOCH_3 \text{ solution (M)} = \frac{W}{(Vs - Vb) \times 0.122}$$

where W = weight of the sample (g).

Analytical method for the assay of FOX-7

FOX-7 (300 to 400 mg) was weighed accurately and transferred to a dry 250 ml specially designed flask (similar to a filtrate receiving flask used for slurry filtration using a Buckner funnel). DMF (50 ml) was added along with 2-3 drops of azo-violet indicator solution. The flask was swirled to dissolve the FOX-7 and the solution became brown in colour. A bar magnet was placed in the flask and the flask was placed on a magnetic stirrer. The burette and nitrogen gas pipe to the flask were fitted as shown in Figure1.

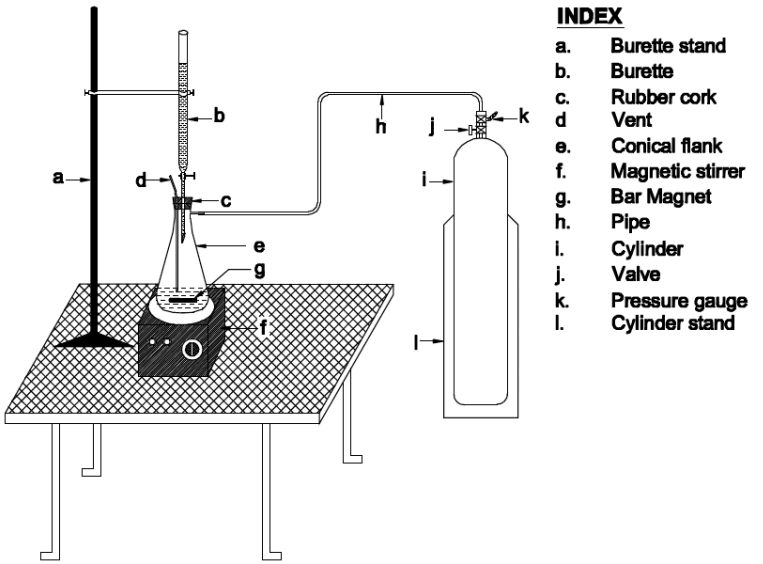


Figure 1. Experimental setup for estimation of purity: FOX-7.

This solution was titrated against 0.1 M $NaOCH_3$ solution in benzene/ methanol. The titration end point is indicated by a sharp colour change from brown to blue. The burette reading (Vs) was noted. The burette reading was generally between 18-25 ml. A blank (V_b) was determined by performing the entire titration without FOX-7. The blank generally consumes 0.1 to 0.3 ml titre.

Calculation:

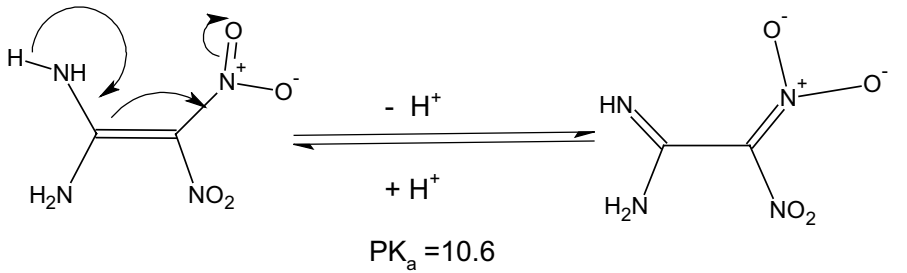
$$\% \text{ Purity of FOX-7} = \frac{(Vs - Vb) \times M \times 14.8}{W}$$

where: V = burette reading (ml), M = molarity of sodium methoxide solution, W = weight of the sample (g).

Results and Discussion

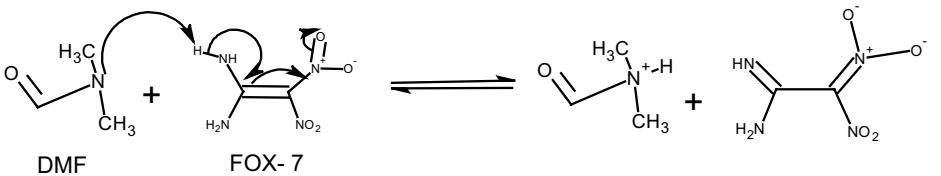
FOX-7 may be described as a push-pull ethylene molecule with two donor amino groups and two withdrawing nitro groups within its molecular framework [1]. Generally organic amines shows basic characteristics due to the lone pair electrons on the amine nitrogen. However, unlike other organic (alkyl or aryl)

amines, FOX-7 behaves as weak acid due to the labile N−H bond. The conjugate base of FOX-7 is stabilized by the strong electron withdrawing effect of the two nitro groups as shown in Scheme 2. The weakly acidic characteristics of FOX-7 have been exploited here in the assay method of non-aqueous titration.



Scheme 2. Acidic nature of FOX-7 molecule.

When FOX-7 is dissolved in the non-aqueous solvent DMF, the labile proton from the amino group is accepted by the solvent and the conjugate base of FOX-7 is released (Scheme 3), where the reaction equilibrium lies to the right. The protophilic solvent DMF exerts a levelling effect and enhances the acidic strength of FOX-7 sufficiently to permit titration with sodium methoxide in benzene-methanol using a visual indicator.



Scheme 3. Acid-base reaction between FOX-7 and DMF.

FOX-7 samples were assayed by the above described method and the results are presented in Table 1. Normal batch samples show a purity of ~99.5% whereas the same sample after crystallization shows a purity of ~99.6%. As standard FOX-7 was not commercially available, the recrystallized sample was considered as the standard (assumed 100% pure). A comparison of the experimental and theoretical values of purity indicates that the error involved is <1%.

Table 1. Assay results of FOX-7 samples

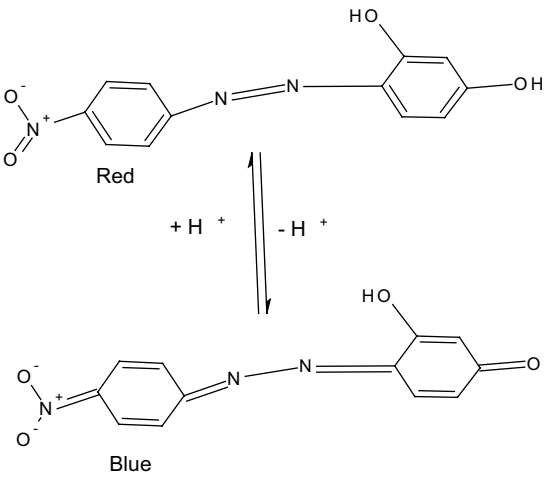
Sample	No. of replicates	Avg. purity (%)	STDEV (σ)
1	3	99.33	0.21
2	4	98.80	0.10
3	3	99.43	0.12
4	2	99.40	0.27
5	4	99.60	0.10
Recrystallised FOX-7	3	99.63	0.06

For the non-aqueous titration of weak organic acids, dimethylformamide is a recommended solvent and reasonably satisfactory results were obtained with DMF or ethylene diamine (ED). These two solvents are very sensitive to carbon dioxide present in the air. Thus, nitrogen [grade: ultra-high pure nitrogen, free from moisture and CO_2] flushing during the titration is essential to eliminate the positive interference caused by atmospheric CO_2. The same samples, when assayed without the nitrogen flushing facility showed a purity value greater than 100% due to the above fact. Positive interference is illustrated in Table 2. The titration with ED as the solvent shows a higher positive interference compared to DMF.

Table 2. Comparison of results without & with nitrogen atmosphere (in DMF solvent)

Sample	% Purity without N_2 (a)	% Purity with N_2 (b)	Difference (a-b)
1	101.50	99.33	2.17
2	100.11	98.80	1.31
3	100.92	99.43	1.49
4	101.52	99.40	2.12
5	101.86	99.60	2.26
Recrystallised FOX-7	100.68	99.63	1.05

Both azo violet and thymol blue indicators are suitable for this titration. The red colour of the azo violet indicator mixed with the yellow colour of FOX-7 resulted in a dark brown colour. The indicator gives a sharp colour change to blue at the end point. The blue colour arises from the quinoid structure of the azo violet indicator as shown in Scheme 4.



Scheme 4. Structural change in azoviolet indicator (p-Nitrobenzene azo resorcinol) under acidic and basic condition.

The product FOX-7 is formed by nitration of 2-methylpyrimidine-4,6-dione (MPD) followed by hydrolysis of the tetranitro intermediate in water (Scheme 1). The possible by-products of FOX-7 are reported in the literature [14]. These are 2-methyl-5-nitro-1H-pyrimidine-4,6-dione (MNPD), nitroform [$CH(NO_2)_3$] and dinitromethane [$CH_2(NO_2)_2$]. Dinitromethane and nitroform are highly soluble in water and expected to be removed completely from FOX-7 during the water wash. However, both MNPD and MPD are probable impurities in FOX-7 as they are water insoluble. The method was validated by performing titrations with pure MPD, MNPD and FOX-7 samples containing known percentage of these two impurities. Both MPD and MNPD do not respond to the titration and thus they do not cause any interference in the titration method.

Considering the toxic effect of benzene, the feasibility of performing this titration with toluene as the solvent (analytical reagent grade) instead of benzene was explored. Toluene was also found suitable for this titration method and hence may be used for this analysis.

The above FOX-7 samples were also analysed by an HPLC method (Ultimate 3000 HPLC system; Column: C-18 reversed phase; Column dimension: 250×4.6 mm; Mobile phase: water/methanol (60:40 v/v); Flow rate: 1ml/min; Injection volume: 10 µl; Temperature: 25 ºC; Detection wavelength: 254 nm) developed in this laboratory [20]. The HPLC method gives a single peak for FOX-7 in the chromatogram. This indicates the absence of any UV active impurities (detected by the HPLC detector) in the FOX-7 sample. The purity of

FOX-7 was calculated from the peak area realized with the batch sample with respect to the calibrated peak area (obtained from the standard FOX-7 sample). The purity values obtained from the HPLC method were found to be marginally (<1%) lower than the assay values obtained from the non-aqueous titration method (Table 3). The non-aqueous titration gives higher purity values due to the positive interference of trace impurities such as moisture, dinitromethane and mineral acids present in the FOX-7 samples.

Table 3. Comparison of assay results between HPLC and Non-aqueous titration method (with N_2 flushing)

Sample	Assay values of FOX-7 (%)		Difference
	Non-aqueous titration (a)	HPLC (b)	(a-b)
1	99.33	98.73	0.60
2	98.80	98.14	0.66
3	99.43	98.78	0.65
4	99.40	98.60	0.80
5	99.60	98.94	0.66

Conclusion

A non-aqueous titration method was developed to assay the insensitive, high explosive 1,1-diamino-2,2-dinitroethene (FOX-7). The weakly acidic nature of FOX-7 is enhanced by dissolving it in the protophilic solvent, N,N-dimethylformamide and titrated against sodium methoxide solution in benzene/methanol using azo violet indicator. The method is simple, rapid and economic. The accuracy and precision of this analytical method is found to be comparable with the existing HPLC method. The method may be useful for process quality control.

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