Development of Methodology to Determine Stability of Single Based Propellant Through High Performance Liquid Chromatography

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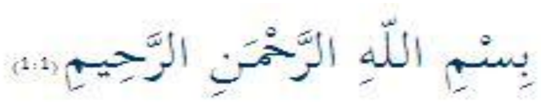
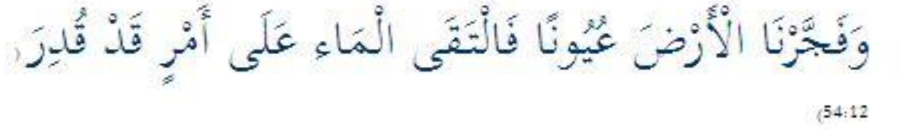


بِسْمِ اللّهِ الرَّحْمَنِ الرَّحِيمِ (1:1)

IN THE NAME OF ALLAH

THE MOST MERCIFUL

THE MOST BENEFICIENT



وَفَجَّرْنَا الْأَرْضَ عُيُونًا فَالْتَقَى الْمَاء عَلَى أَمْرٍ قَدْ قُدِرَ

(54:12

And we made the earth burst forth with springs and the waters met for a purpose that was preordained.

(Surah-Al-Qamar)

Dedication

I dedicate my work to

My parents, wife, my sons Shahwaiz and Shahmeer

and my prestigious Corps of Ordnance

Abstract

The level of concentration of diphenylamine present in propellant samples reveals valuable information which can help in determining safe shelf life of propellants. Till to date, Abel heat test is a primary investigative technique being used for stability monitoring of propellants in our country. This testing technique inherits some drawbacks and may mislead to erratic results. Diphenylamine is the most commonly used stabilizer in single based propellants. The aim of this research is to suggest such methodology to investigate stability levels of single based propellants in order to estimate the safe shelf life accurately in accordance to international standards.

Samples of propellants M1 and M6 were selected for this study. Diphenylamine is used as stabilizer in these propellants. Initial concentration of stabilizer in these propellants is 1 %. Chromatographic conditions were set up according to newly developed method. External standard method was used for calibration. Four solutions of different concentrations of diphenylamine in acetonitrile were prepared. Calibration curve was made by plotting HPLC readings of these solutions on graph. Diphenylamine was extracted from the propellant sample by dissolving samples in acetonitrile assisted by ultrasonic bath. Nitrocellulose was also removed from propellant sample by precipitation before analysis by adding aqueous solution of calcium chloride. Acetonitrile and water were used as mobile phase in HPLC analysis. C-18 bounded silica was used as stationary phase. Analysis of both naturally aged propellant sample and artificially aged sample was carried out. Artificial ageing of samples were realized at 90°C for 3.43 days so as to simulate 10 years of natural ageing at 25°C. The results show that after artificial aging of samples, stabilizer contents in M1 propellant is reduced from 0.84% to 0.48% and in M6 propellants reduced from 0.87% to 0.55%. It means that the particular lots of these propellants will remain stable for another 10 years in storage thus can be sentenced serviceable for 10 years.

Experimental methods at each step are more elaborated deliberately so that methodology may be adopted in service without complications.

Acknowledgements

All commendations to **Almighty Allah**, The most beneficent, the most merciful, who blessed me with intellect, resoluteness and determination to accomplish this research project and to contribute to my country. All the respects to His Holy Prophet Hazrat Muhammad (PBUH), who enabled us to recognize our creator.

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I pay my homage, sweet sensation of love and respect to my family including my father, mother, my sisters and specially my wife and my sons, Shahwaiz Hassan and Shahmeer Hassan, who understood me for not sparing much time for them during my studies. Special thanks to my younger brother Ali who has always been supportive and helping hand. They all prayed for my success and helped at every step of mine in every possible manner. My parents taught me the value of hard work and provided me enormous support throughout my life. It would not have been easy without their encouragement, cooperation and prayers.

(Shah Rukh Hassan)

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Chapter 1
General Introduction

1. This chapter explains the propellants degradation, role of stabilizers in propellants, techniques used to determine stability of propellants and need of this study.

1.1. **Introduction and Background**

Single based propellants contain nitrocellulose as their main component. Nitrocellulose is infact a type of nitrate ester which is prone to degradation with time evolving nitrogen oxides. If these nitrogen oxides are not removed from the propellant mix, they further accelerate degradation process. Resultantly, chances of autoignition of propellants at this stage cannot be ruled out. Autoignition of propellants have caused several catastrophes in past e.g. In Poland, there were explosions in the magazines of Warsaw Citadel in 1924 and at Witkowise in 1927, and in France at Bergerac in 1928. Massive fires in Finland [1], Australia [2] and Sweden [3] were also caused by the spontaneous ignition of gun propellants.

In order to prevent these incidents from happening, a chemical with stabilizing properties "stabilizer" are added to propellant mix. Stabilizers are the compounds which reacts easily with nitrogen oxides and prevent autoignition. The reaction of these compounds is complex with the formation of many daughter products. Some of these daughter products also act as stabilizer and others do not. There is always depletion of effective stabilizer with relation to time. Therefore stabilizer contents of propellants must be monitored periodically to assess remaining "safe life" of propellants and to dispose of those lots that are likely to undergo autoignition.

The Army is unique in terms of the volume of samples processed and in terms of the number of propellant formulations required to be analyzed annually. The quantity and diversity of the samples tested directly influences the choices made in establishing these procedures. Different techniques are being used around the globe to routinely monitor the levels of stabilizer in the Army's propellant stockpile to assure that ageing propellant remains safe for continued storage. These monitoring techniques have been used from the years in different countries but with passage of time most of the old techniques were found outdated and inaccurate. The advent of modern analytical instruments such as **High Performance Liquid Chromatography** has provided a way to monitor propellant degradation more accurately than ever before. Efficient measuring of stabilizer contents ensures safety of man and material so it is essential to integrate modern instrumentations and analytical techniques into existing propellant stability monitoring programs.

1.2. Propellants

A propellant is a substance or combination of substances which burns at an extremely rapid but regular rate producing a large volume of gas and evolution of heat. These gases may be used to accelerate a projectile in the bore of the gun, or to propel a rocket or similar missile. Propellants should be distinguished from high explosives, the reaction occurring on detonation of the latter being altogether too violent for use in normal gun or rocket system [4]. Combustion generally involves reaction with oxygen or with some substance containing oxygen, an essential feature of conventional propellants is that they carry their own oxygen supply chemically combined in one or more ingredients and they do not therefore require a supply of atmospheric oxygen as required for internal combustion engine.

1.2.1. Properties of Propellants

A solid propellant should ideally possess the following properties:-

- Its burning properties should not change under any condition of temperature and humidity which may be experienced in service use.
- It should not cause excessive erosion or wear when used in guns.
- It should ignite readily, burn uniformly at the surface only and not break up during burning.
- It should not give unacceptable flash or smoke.
- It should be chemically stable under all conditions of storage and transport likely to be encountered in service.
- Its physical properties must be such that the propellant is not likely to deform or flow under load to an excessive extent.

1.2.2. **Type of Propellants**

Propellants may be divided into three main types according to their composition.

1.2.2.1. **Single Based Propellants**

A propellant which consists of nitrocellulose (NC) as the only explosive component is known as single based propellant. The formulation consist of 90 % of NC with nitrogen contents of 12.50 %-13.25 %. NC is gelled with help of plasticizer such as dibutyle phthalate and stabilized with stabilizer like diphenylamine (DPA) or ethyl centralite (EC). The energy contents of SB Propellants (Q value) varies from 3100 – 3700 Jg^{-1}[4].

1.2.2.2. **Double Based Propellants**

This type of propellants also consist of nitroglycerine (NG) in addition to nitrocellulose (NC). Double based Propellants are more energetic than single based propellants having Q value between 3300-5200 Jg^{-1}. There are two main disadvantages of double based propellants: high erosion of gun barrel due to higher flash temperature and presence of muzzle flash which discloses gun position.

1.2.2.3. **Triple Bases Propellants**

Nitroguanidine is also added to propellant mixes along with nitrocellulose and nitroglycerin in order to reduce flash temperature and muzzle flash. The triple based propellants have Q values ranging from 3200–3700 Jg^{-1}intermediate between single based propellants and double based propellants.

1.2.3. **Propellant Ingredients**

In order to evaluate degree of propellant degradation and quantification of stabilizer contents, it is essential to know regarding various components of propellants.

1.2.3.1. **Nitrocellulose (Cellulose nitrate)**

Nitrocellulose is a major energetic component of all propellants. It is made by treating purified cellulose with a mixture of H_2SO_4 (sulphuric acid) and HNO_3 (Nitric Acid) under controlled environment. The cellulose is found in form of paper, cotton, wood pulp, etc. Each unit of nitrocellulose contains the long chain of the cellulose molecules. Each molecule of cellulose is made up of three hydroxyl (OH) groups in addition to other items. During acid treatment these molecules are replaced by nitrate (ONO_2) groups (see figure 1.1). Proportion of replacement of OH group is varied by altering the temperature and acid concentration. The extent to which this reaction has proceeded is readily expressed in terms of the nitrogen content of the nitrocellulose.

When all the groups have been nitrated the nitrogen content is 14.14%, but for propellants, it is customary to use nitrocellulose of rather lower nitrogen content i.e 12.5% to 13.25 %.

All forms of nitrocellulose in this range of nitrogen content are soluble in acetone, and those below 12.8 % nitrogen are appreciably soluble in 2:1 ether alcohol solution by volume. Nitrocellulose always contains a small proportion of calcium carbonate (chalk) which is added during the purification process to neutralize traces of acid and forms part of the final composition of most of the propellants.

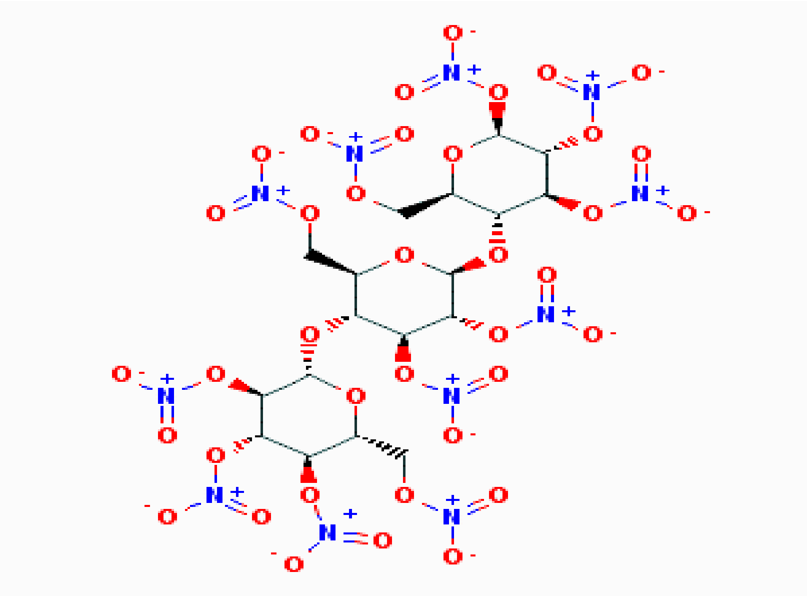


Figure 1.1 : Chemical structure of nitrocellulose [5]

1.2.3.2. **Nitroglycerine (Glyceryl trinitrate)**

Nitroglycerine is obtained by the reaction between glycerine and a mixture of nitric and sulphuric acids. In this case, in contrast to nitrocellulose, all the OH groups react with acid to produce a compound of definite chemical composition. Nitroglycerine is a liquid, colorless when pure but normally found in yellow color. It crystalizes in two forms, a normal form melting at 13°C and another form melting at about 3°C. It is an extremely sensitive explosive which must always be handled with the greatest care. Owning to its liquid form special precautions have to be taken whenever it is used.

Nitrocellulose will dissolve in nitroglycerine to form a viscous colloidal solution, the physical properties of which depend very markedly on the type and proportion of nitrocellulose employed. This process of solution is often termed gelatinization. Like nitrocellulose, nitroglycerine also decomposes spontaneously under certain conditions. The storage of nitroglycerine is normally avoided, but when it is necessary, periodic examinations for its stability are carried out in order avoid accidents.

1.2.3.3. **Stabilizers**

As described in para 1.1, the addition of stabilizers is essential to any propellant containing nitrocellulose, nitroglycerine, or any other nitric ester and their effect to react with the decompositions products to form harmless compounds [6]. Before 1925 the commonest stabilizer in British Service was mineral jelly, which act as stabilizer by virtue of the unsaturated hydrocarbons it contains. If mineral jelly is subjected to the heat treatment known as “cracking” the proportion of unsaturated hydrocarbon is increased and the stabilizing action is also enhanced. It was found that cordites which were stabilized by mineral jelly were not completely satisfactory, in that they were particularly liable to develop severe localized decompositions during storage. Carbamite (often known as centralite, ethyl centralite, or centralite 1, and chemically as symmetrical diethyl-diphenyl-urea) was introduced in order to confer a greater degree or stability. This substance is a solid (melting point 72 °C), and it has a very important additional property in being a powerful gelatinizing material for nitrocellulose. Diphenylamine is another important stabilizer which is very suitable for use with nitrocellulose. Its use with nitroglycerin is restricted due to fact that it accelerates rather than retards decomposition of nitroglycerine.

1.2.3.4. **Plasticizer**

Plasticizer are the additives employed with propellants in order to improve physical properties. They may be used to act like binders or to give plasticity to energetic materials. Plasticizers are essentially used in propellant manufacture for improving the processability of the propellant slurry and mechanical properties of the cured propellant. The phthalates are the most commonly used plasticizer.

1.2.3.5. **Flash Reducers**

It was early discovered that certain salts, particularly potassium and sodium salts, were able to interrupt the chain and inhabit the reaction even when the salts were present in only small proportions.

One of the commonest methods of reducing gun flash is to add a small quantity (generally less than 4 %) of a potassium salt to the propellant, the commonest salts in British practice being potassium sulphate, nitrate or cryolite, the later being a complex potassium aluminum fluoride [4].

1.2.3.6. **Other Additions**

For various purposes other substances may be added to propellants, usually small proportions:

- Graphite.
- Carbon black.
- Candela Wax.

1.3. Degradation of Nitrocellulose

Nitrocellulose is a nitric esters. They have very low binding energy of CO-NO_2 bounds i.e. approximately 160 KJ/mole compared to 414 KJ/mole for a typical C-H bond. Due to which they are very sensitive to thermal stress. Consequently, the nitrate esters decompose even under normal storage temperatures (see figure 1.2). This homolytical splitting of the CO- NO_2 bond produces NO_2 which is very reactive radical, it is also a strong oxidizing agent and the alkoxy radical. [7]

$$R – O – NO_2 \rightarrow R - O\bullet + NO_2$$

These initial products are highly reactive. Consequently, this initial phase is rapidly followed by a series of secondary reactions. These reactions are exothermic since radical species are involved. As a result, heat is produced and the propellant temperature rises since propellants, being plastic materials, are not good heat conductors. This temperature rise increases the rate of the homolytic splitting of the nitric esters and the subsequent secondary reactions will in turn further increase the temperature. If nothing is done to stop this autocatalytic action the propellant temperature will increase until the occurrence of auto-ignition.

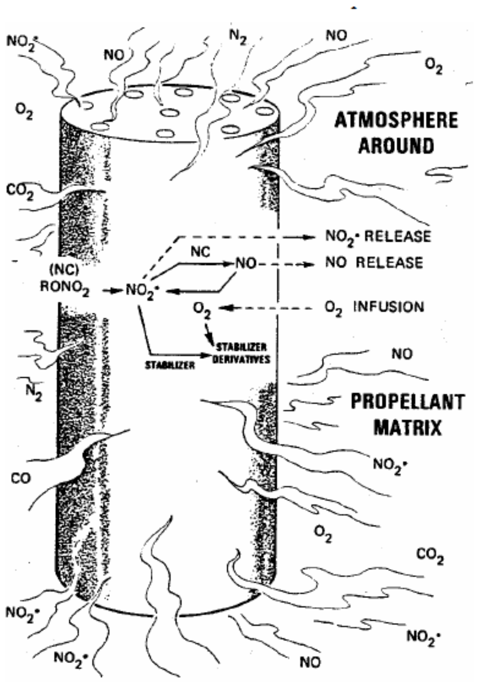


Figure 1.2: Schematic Chemical evaluation of nitrocellulose based propellants

One important feature of NO_2 is its capability to catalyze thermolysis of nitrocellulose [8]. As it accumulates, it accelerates further nitric ester decomposition. As a result more heat is produced and the temperature in the propellant rises. This accelerating action of NO_2 is called self-catalysis. If it were left to occur in an uncontrolled fashion, then the rate of heat generation could eventually become higher than the rate of heat loss to the surroundings, resulting in thermal explosion of the nitric ester after a certain induction period [9].

1.4. Role of Chemical Stabilizer in Propellants

It is a learnt fact that propellants degradation is a series of complex chemical reactions. Not only the initial decomposition, but all others subsequent chemical reactions which take place in the system. The resultant products of these reactions may accumulate and accelerate the rate of decomposition reactions. Although it is not possible to stop initial decomposition process but accelerated process may be delayed by addition of chemical substance which may stabilize propellants. Stabilizers react with resultant products of decomposition which mainly primarily oxides of nitrogen, nitrous and nitric acid [10].

Although stabilizers are the chemical species that have been used in propellants a very long ago. Although numerous studies have been conducted on role of stabilizer in propellants, even than the details of chemical processes undertaken with ageing are not fully known. It is due to complexity of decomposition of nitrocellulose and stabilizers. Along with the development of modern instrumental methods, especially the High performance liquid chromatography (HPLC) technique, introduced in the middle of the seventies [11] some other influents of chemical decomposition of stabilizer in propellants were also studied. Similar improvements in other experimental techniques, such as Thin layer chromatography, microcalorimetry and chemiluminiscence have further contributed to the elucidation of propellant and stabilizer degradation [12].

The stabilizers normally used in single based propellants are illustrated in following table

Table 1: *List of stabilizers used in single based propellants*

Name	**Other Name**	**Abbreviation**
Diphenylamine		DPA
2-Nitro-diphenylamine		2NDPA
Ethyl Centralite	Carbamite, centralite I N,N’-Di ethyle- N, N’ – diphenyl-urea	EC
Methyl Centralite	Centralite-II, N, N’-Dimethyl-N, N’- diphenylurea	MC
Akardite-II	N-Methyl-N’, N’-diphenylurea	AKA-II
p-Nitro-N-methylaniline		pNMA,MNA
Resorcinol		

1.5. Diphenylamine (DPA) and its Derivatives as Stabilizer

Diphenylamine (DPA) is the most commonly utilized stabilizer in propellants due to its excellent stabilizing behavior. It reacts with decomposition products of NC which mainly nitrogen oxides forming nitrated consecutive products with an increasing degree of nitration. Diphenylamine

(DPA) is a most common stabilizer which has been used in propellants from a long ago. The use of Diphenylamine (DPA) as stabilizer in order to suppress autocatalytic decomposition of of Nitrocellulose (NC) was proposed by Nobel in his German patent [13]. During ageing, DPA is also undergoes series of chemical reactions which results into various derivatives. These derivatives are known as daughter products. There are many studies in which reaction products of DPA are determined [14]. When DPA reacts with nitrogen oxides which evolves during process, various nitro and nitroso derivatives are formed.

An illustration of reactions path ways as shown in Figure 1.3 to show degradation of DPA was presented in 1949 [15]. This illustration is widely recognized for the mechanism of decomposition of DPA.

It is observed that reaction scheme contains both nitroso and nitro derivatives of DPA. It is shown that a single molecule of DPA can arrest six molecules of nitrogen oxide and before converting into picric acid. Apart from DPA itself, the mono nitro and nitroso DPA are the most important derivatives of DPA to stabilize propellants. The higher nitrated derivatives with two or more nitro groups do not become significant until the DPA has been consumed and thus the end of ballistic shelf life is reached. In studies of decomposition of DPA focused on DPA, 2-nitro-DPA (2NDPA), 4-nitro-DPA (4NDPA) and N- nitroso-DPA (NNODPA). At ambient temperatures the formation of higher derivatives is effectively hindered by the nitro groups already present in the aromatic ring [16].

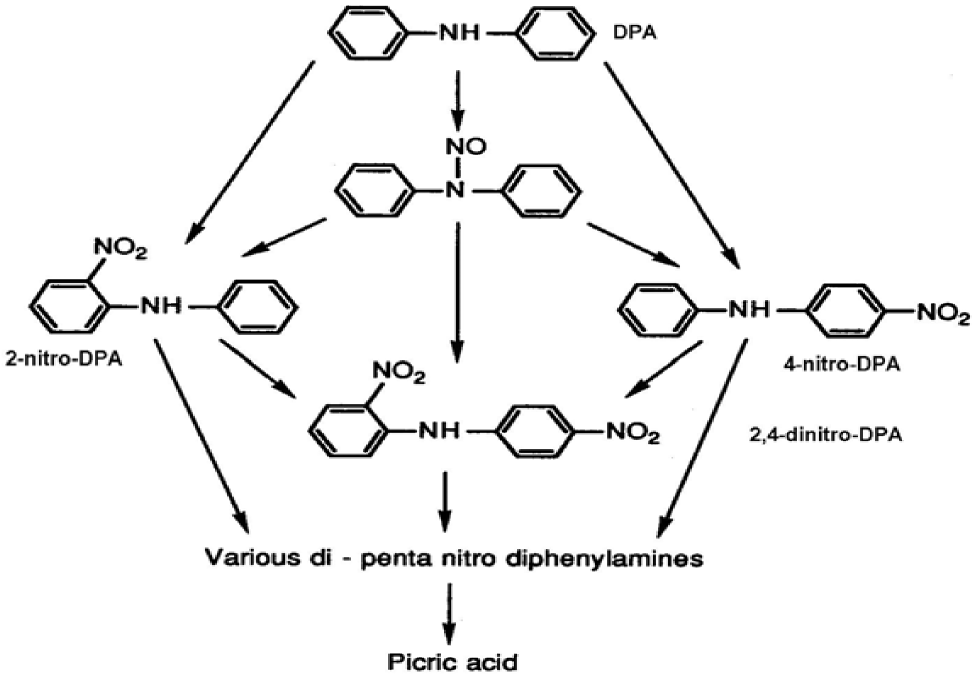


Figure 1.3: Schematic reaction routes for the degradation of DPA in an ageing propellant

1.6. Artificial Ageing

Generally ageing means change of properties of a material with respect to time and temperature. The purpose of artificial ageing is to expose propellants samples to elevated temperature for specified duration which accelerate rate of chemical reactions and ageing process in samples. The objectives of artificial ageing of propellants may be defined as follows [17]:

- To reach equivalent ageing in much shorter time than at target temperature.
- To find out ageing process(es) or other parameters to quantify the temperature dependence of the ageing.
- To use the temperature dependence describing parameters to predict the ageing at any time-temperature load.
- To simulate real ageing using time temperature profile.

1.6.1. Single Temperature Ageing Procedure

The single temperature ageing procedure is used for propellant consisting of well-known and generally used propellant components and stabilizers defined in Table 1.

1.6.2. Multi Temperature Ageing Procedure

For propellants with stabilizer not listed in Table 1, multi temperature ageing method is used. This ageing method also shows the kinetic parameter of stabilizer depletion method.

Majority of propellants in service are stabilized with stabilizer listed in Table 1. This work focuses on single temperature ageing procedure for single based propellants only. For the single-temperature ageing procedure, the "effective stabilizer" concept is used.

1.7. Measuring Decomposition of Propellants

Propellant decomposes with ageing. Number of chemical phenomenon occurs with ageing such as release of gases, molecular weight reduction of NC, depletion of initial stabilizer levels and evolution of heat. These phenomenon may be studied to estimate safe storage life of propellants. Considering the fact that under normal ageing conditions i.e at room temperature, these phenomenon proceed very slowly. Therefore artificial ageing (exposure of propellants to elevated temperature) is realized to reduce normal long ageing time. Various methods have been developed over the years to monitor propellants stability levels at regular intervals. These methods can be divided into following classes:

- Oxides production tests
- Molecular weight of NC
- Heat evolution
- Stabilizer contents analysis

1.7.1. Production of Oxides Test

This is an empirical test and dates back to almost a century. In this test propellant samples are heated at specific temperature and production of nitrogen oxides is monitored. Production of nitrogen oxides are detected with help of specially treated paper. This paper changes color when reacts with oxides of nitrogen. The sentencing of propellant is carried out on the basis of time paper takes to change its color. Abel heat test, Methyl violet paper test and Vieille test are included in this category [18].

Chemiluminescence is also used to monitor production of oxides of nitrogen. This method is capable of studying decomposition of propellants but no sufficient information is available with this method to predict future behavior of propellants [19].

1.7.2. **Molecular Weight of Nitrocellulose (NC)**

It is an established fact that reduction in molecular weight of NC reveals useful information regarding stabilizer degradation. This reduction in molecular weight can be established by gel permeation chromatography [20]. As molecular weight dependent on different variables such as raw material used for synthesis of NC, manufacturing and preparation methods, so this method cannot yield precise results required for synthesis.

1.7.3. **Heat Evolution**

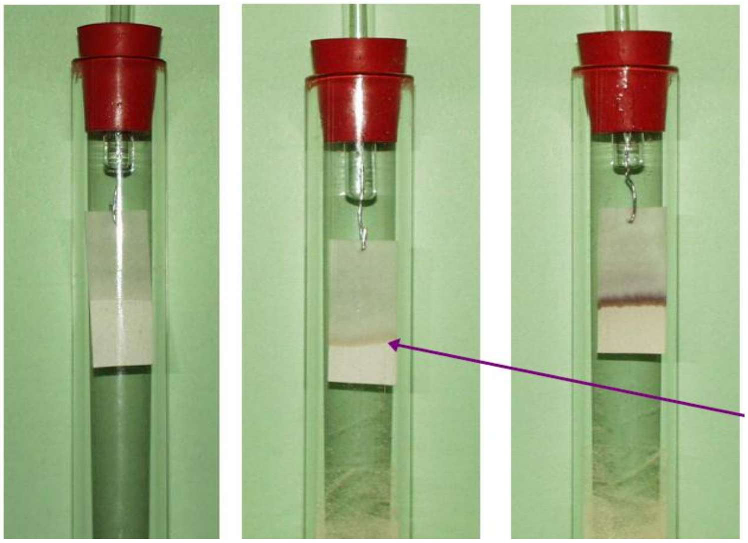
Heat flow from exothermal reactions involved in NC degradation can be measured by microcalorimetery. This method can be used to determine risk of self-ignition and critical diameter of propellants. In some countries this method is used as confirmatory test for the propellants sentenced unserviceable by chromatographic tests. Nevertheless this method remains area of interest in field of research from last two decades and has been used by many countries for propellant surveillance [17]. There are also few backdrops of this method including high cost of equipment and method, its limitation to handle large number of samples from quality point of view, results are highly dependent on the environmental conditions at time of experiment and comparison can only be done between results if similar conditions are maintained during results [20].

1.7.4. **Quantification of Stabilizer Contents**

In older methods, stabilizer was separated from propellant mix by digestion or steam distillation and then analyzed. The quantification of stabilizer was carried out by spectroscopy [21] or by gravimetric determination [22]. Due to inefficiency and lack of precision in results, these techniques were replaced with modern technique i.e chromatography. Initially separation and quantification of stabilizer contents were carried out with column chromatography which was a cumbersome process. By passage of time more efficient and accurate testing techniques were introduced and replaced older methods including thin layer chromatography, gas chromatography and high performance liquid chromatography [23].

1.8. Abel Heat Test

In our country, Abel heat test is used as primary testing technique to evaluate the serviceability of propellants. The principle of this technique is to detect nitrogen oxides released from propellants when they are heated at 65.6°C or at 71°C according to type of propellants. These oxides of nitrogen are detected by using starch-potassium iodide. The upper half of this paper is wetted before use with glycerin and water mixture. With time, a brownish tint appears at juncture of wet and dry halves. This procedure completes when tint matches to standard tint. Sentencing of propellants is being done on basis of the time taken to achieve this standard tint. [24]



Time taken to reach at this point for color change

Figure 1.4: Abel heat test results

1.8.1. Drawbacks of Abel Heat Test

There are various factors influencing Abel heat test including moisture contents, interference caused by impurities and no clarity in the end point of process. All these factors causes errors in results [24]. There were some incidents where propellants were declared unserviceable whereas, on later investigations they were found serviceable [25]. On the other hand, there were also incidents where Abel heat test results showed propellants stable whereas actually they were not [26]. Another disadvantage of this method is difficulty in recognition of standard tint color. It may vary person to person. Test papers (potassium iodide starch paper) and paper with standard tint has a very limited shelf life, i.e one year only. Acquiring new standard tint papers every year or non-availability of these papers cause hindrance in stability monitoring. Another drawback of this method is that propellants are sentenced serviceable for maximum three years, after three years re-test of the same lot of propellants is required to be conducted [27]. In this way more ammunition is consumed as compare to other techniques i.e HPLC which predicts serviceability of ammunition for 10 years.

1.9. **Aim of Study**

Propellant by their quantity are the largest energetic commodity held with Defence Forces of our country. Due to their sensitive nature, it is a established fact that regular and accurate monitoring of their stability is need of time. Presently, In our country propellant stability testing is based on Abel heat test which is an outdated technique and may mislead to inaccurate results under specific conditions. Such results are potentially dangerous and for such reasons, the obsolete testing technique must be replaced with by a modern technique i.e High Performance Liquid Chromatography. Therefore, an effective and modern surveillance technique for monitoring stabilizer contents of propellants is need of time. The aim of this study is to suggest such methodology to investigate stability levels of single based propellants through high performance liquid chromatography (HPLC) in order to estimate the safe shelf life accurately in accordance to international standards. Method so developed will not only predict safe storage life of single based propellant but also ensure safety of installations and subsequent disposal of dangerous munition.

1.10. **Objectives of Study**

The objectives of this study are as follows:

- To develop fast, reliable and efficient high performance liquid chromatography (HPLC) method for identification and quantitative determination of concentration of diphenylamine in single based propellants.
- To identify extraction technique which can extract diphenylamine completely from propellant sample and remove nitrocellulose.
- To carry out artificial ageing of propellants in order to ascertain stability of single based propellants after 10 years of storage at 25°C.

- To carry out sentencing of propellants based on stability test results and criteria given in Allied ordnance Publication (AOP 48) edition 2.

Chapter 2
Literature Study

2. This chapter is a systematic review of previous work reported in literature in the field of stability monitoring of propellants. This chapter is divided into 3 sections. 2.1 is discussion on degradation of Nitrocellulose, 2.2 is about role of diphenylamine as stabilizer, 2.3 is regarding artificial ageing of propellants.

2.1. **Degradation of Nitrocellulose**

Nitrocellulose is an important chemical having various industrial and lab applications. Owing to its uses, number of studies were conducted on its storage and decomposition under different conditions. Main reason of nitrocellulose degradation is due to the instability of nitrate ester groups in the polymer.

G. Gelernter, L.C. Browning [28] studies on the slow thermal degradation of cellulose nitrate in a current of inert gas and the decomposition at low pressures of cellulose nitrate tagged with isotopic N16 on the sixth carbon atom are described. The lower thermal stability of the nitrate groups in the second and third positions of the glucoside unit was established by the thermal decomposition studies with isotopic nitrogen and a chemical reaction sequence postulating early cleavage between the second and third carbon atoms formulated on the basis of the total experimental data obtained.

Sovizi et al. [29] studied that thermal decomposition of NC at nano and micro molecular level containing 13.9% nitrogen(see figure 2.1). DSC and TG-DTA were used for characterization of NC fibres. It was revealed that NC fibers in micro level showed thermal stability higher than fibers in nano level. Factors such as enthalpy, activation energy, critical explosion temperature and temperature of decomposition were involved. Assumption of first order kinetics was also made for calculating these factors.

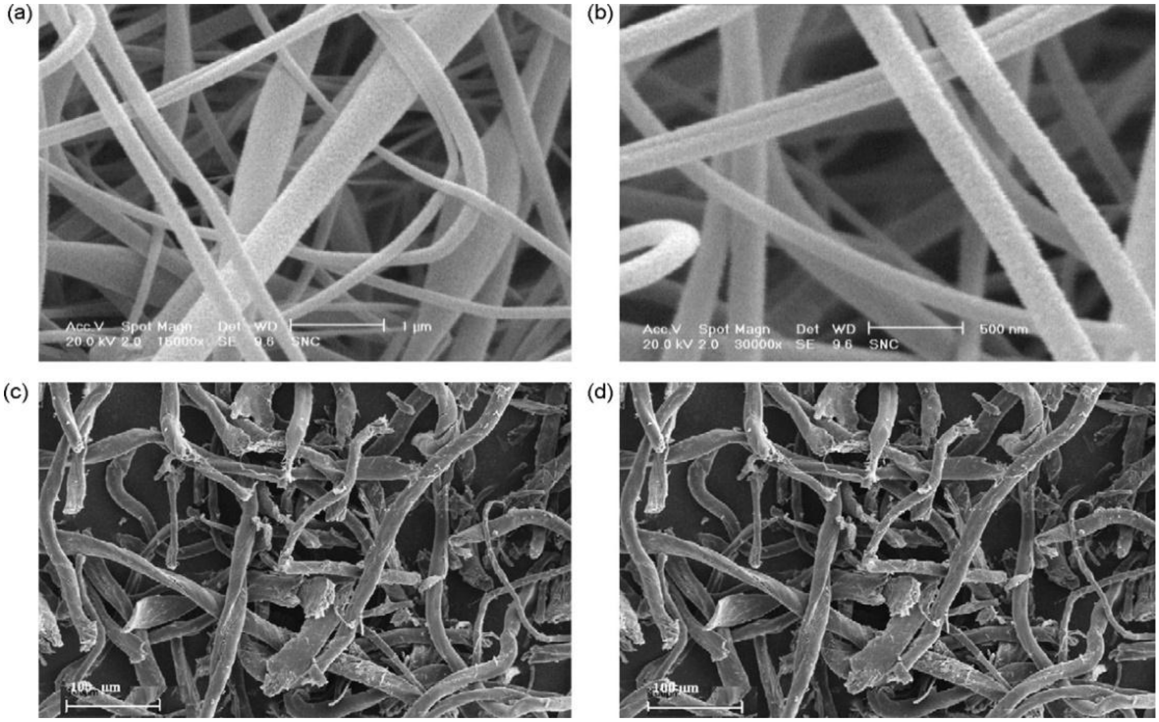


Figure 1.5: Comparison of nanofibers(a)(b) and microfibres(c)(d) of nitrocellulose.

Philips [30] studied mechanism and kinetics involved in decomposition of organic mono and poly nitrates on thermal basis. His study revealed that overall decomposition is in liquid and vapor phases due to primary fission of O – N bond to formulate NO_2. He also showed that due to early decomposition of numerous organic nitrates, nitrogen in gaseous form (NO_2) is wholly eliminated from the molecule. Based on these observation and identification of aldehydes among products suggest that the mechanism for methyl nitrate applies to organic nitrates.

Bergens [31] discussed the intermediary compound is believe to give the nitrocellulose the green color, However, he did not notice any color change in propellant covered with graphite. Working with pure NC after one day of storage at 70°C a faint green color was observed. With more ageing the green color gets more intense.

Becker and Hunold [32] also stated that in the presence of moisture the decomposition of nitrocellulose results in formation of nitrous and nitric acids. Nitrous acid changes the amine into nitrosamine, a process which often proceeds very rapidly and to some degree sets in during preparation of the powder. Under the influence of nitric acid, the nitroso group adheres to the amino nitrogen in the para position on the residual phenyl and is then simultaneously oxidized to the nitrogroup. As a result, 4-nitro-DPA is derived from N-nitroso-DPA.

R.I. Hiyoshi et al. [33] studied that the thermal degradation of nitrocellulose films (13% of nitrogen content) by pyrolysis (300 °C under 0.1 MPa) in air and Ar atmospheres using FTIR spectroscopy. The air atmosphere was created by combining 80% nitrogen and 20% oxygen, to avoid interferences provided by the strong IR absorption of CO2 present in natural air. The samples were analyzed by FTIR spectroscopy under both atmospheres. Products of decomposition in air and Ar were identified as CO, CO_2, NO, NO_2, H_2O, HCN, and CH_2O being CO the most widely produced. According to these results, it was obvious that the atmosphere did not interfere in the measurements.

De Angelis and Cardian [34] studied that decomposition process in propellants apparently seems two-step pseudo first order reaction in stabilizers with the second step rate-determining. Propellants which are stable can be taken as two-component system consisting of NC and stabilizer, other ingredients present in propellant mix are to be considered as inerts or only catalysts although while the other ingredients in formulation can be considered inert or catalysts.

2.2. Role of Diphenylamine as Stabilizer

Hale [35] studied the role of DPA and its general stabilizing action in propellants. He observed that first step in degradation of nitrocellulose is that it converts into NO which subsequently on contact with atmospheric oxygen converts into NO_2. Formation of NO_2 is an exothermic reaction which evolves heat. Both of these compounds accelerate further decomposition of nitrocellulose. This deterioration can also be observed by visual inspection. Decomposed propellant revealed discoloration and roughness of surface and edges.

Davis and Ashdown [36] studied that DPA included in propellants converted into N-nitroso-DPA. In their studies, it was concluded that under the influence of decomposed acidic products, DPA rearranged. It undergoes oxidation and nitration both and produce 2,4' and 4,4'-DPA subsequently these products nitrated to 2,4,4'-trinitrodiphenylamine.

Ovenston [37] studied that there are twenty four soluble ingredients in propellants which can be separated and identified by column chromatography. Some organic compounds such as mineral jelly, silica gel and celite are insoluble petroleum ether (b.p 40 - 50°C) mixed with ethyl ether or benzene is proved to be the best developing solvent.

2.3. Artificial Ageing of Propellants

Tranchant [10] studied ageing of propellants and changes in properties during storage. He termed ageing as a complex process in which number of physical and chemical process takes place such as diffusion of liquid nitrate esters.

Bohn [38] studied that accelerated ageing drastically effects stabilizer such as DPA. He found out that losses in DPA are higher if air is allowed to enter during ageing process. With further investigations, it was found that these losses correspond to number of oxygen molecules near DPA. The maximum loss in stabilizer occur during in initial phase of reaction. These losses are minimal in inert atmosphere.

Levitsky [39] studied the effect of accelerated ageing of propellant by keeping three different propellants at elevated temperature and at ambient temperature for fifty four weeks. All three propellants displayed some degree of ballistic instability over the period of time. This instability was determined by observing different spectra of methylene chloride extract of these propellants. The major change was attributed to diphenylamine depletion.

Chapter 3. Experimental Work – Materials, Analytical Techniques and Methodology

3. This chapter explains materials used in this study, analytical techniques and all the practical work carried out for determination of stabilizer contents in propellant samples.

3.1. Materials

3.1.1. Propellant samples

M1 and M6 were selected for analysis. Composition and status of these propellants are as given in table 2:

Table 2: Composition of propellants samples

Propellants	Type	Lot	NC %	Additives	Stabilizer	Initial DPA levels %
M1	Single based	2001	85 ±2	DNT, DBP, graphite	DPA	1% ±0.1%
M6	Single based	1998	85±2	DNT, DBP, graphite	DPA	1% ±0.1%

3.1.2. Chemicals

Accuracy of results depends on the purity of chemicals used, chemical required for HPLC analysis are of HPLC grade, chemicals required for calibration or extraction is of analytical grade. Details are given in table 3

.

Table3: List of chemicals used

Chemical	Manufacturer	Grade
Acetonitrile	Merck	HPLC
Water	Merck	“
Diphenylamine	Sigma-Aldrich	Analytical
Calcium chloride	Merck	“
Aluminum Chloride	Merck	“

3.1.3. **Equipment**

Sophisticated and state of the art equipment is used in this study. Details are as described in table 4:

Table 4: List of equipment

Equipment	Manufacturer	Model
HPLC binary chromatogram	Perkin Elmer	Flexar
Electronic Oven	Memert	UN-30
Ultrasonic bath	Elma	E-100

3.2. General Methodology

Method was developed for determination of stability of single based propellants in accordance with NATO Alliance ordnance publication (AOP 48) edition 2. In this study propellant M1 and M2 were selected to be analyzed. Step wise experimental procedures as shown in figure 3.1

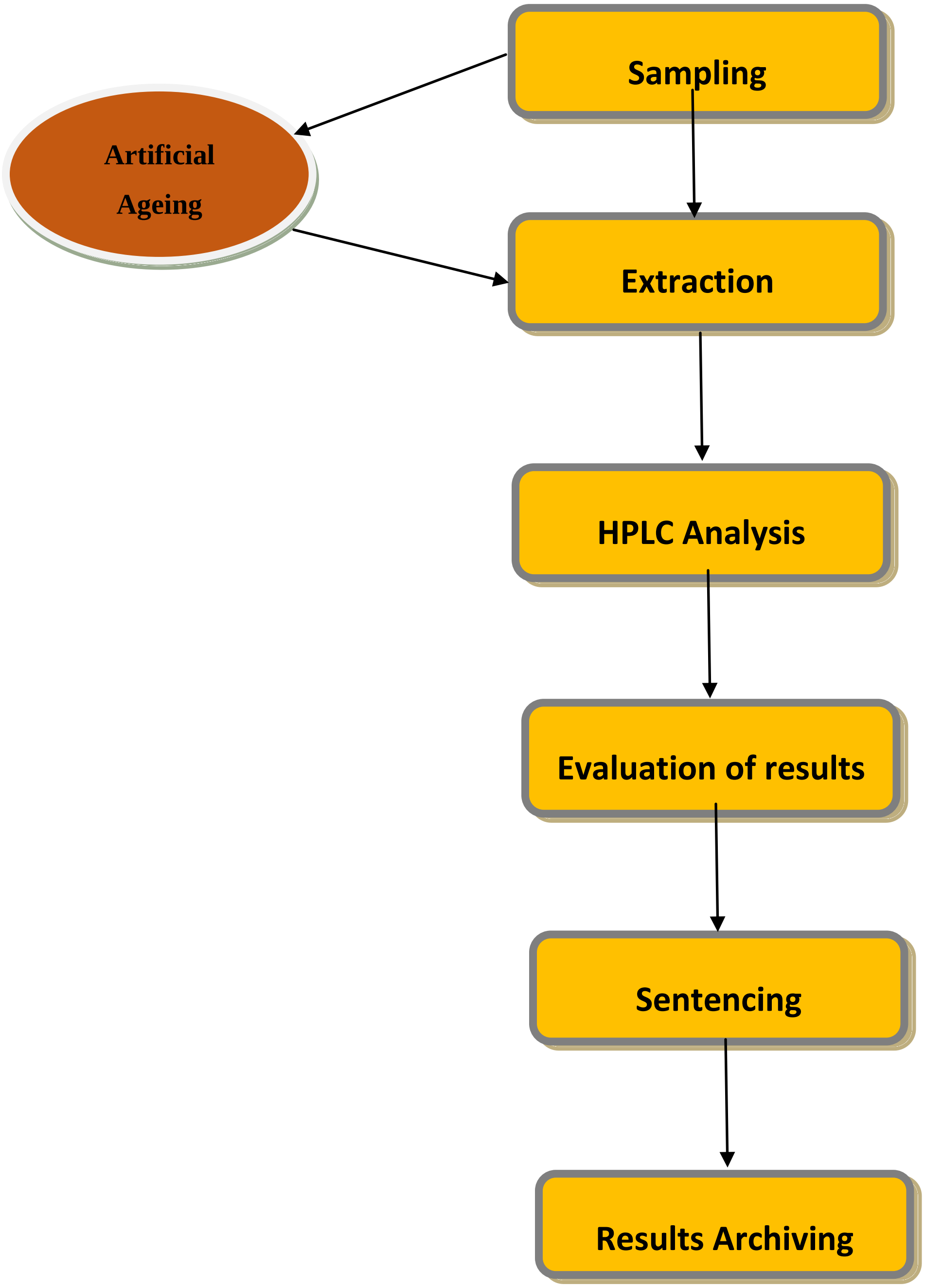


Figure 3.1: Diagrammatic layout of methodology for surveillance of propellants

Stability testing of nitrocellulose based propellant is carried out by determination of stabilizer depletion after artificial ageing of the propellants at temperatures and durations corresponding to 10 years of natural ageing at ambient condition (25°C). Steps involved in this methodology are shown in figure 3.1. **This testing should guarantee that the amount of stabilizer in the propellant would not drop below a safety level after its storage for 10 years.**

Extraction of stabilizer is carried out by dissolving of propellant in organic solvent and precipitating NC for removal. Stabilizer content in the samples of propellants are determined by High performance liquid chromatography. Sentencing of propellant is carried out accordance to AOP-48 [40].

3.3. Artificial Ageing of Propellants Samples

3.3.1. Ageing conditions

It is experimentally proved that both artificial ageing mechanism and ageing rate strongly depend on ageing conditions, which are as follows:

- Loading density (containers fully filled / party filled),
- Tightness of seal (containers unsealed / loosely sealed / airtight sealed)
- Size of propellant grains / blocks (propellant in original size / cut into pieces / ground).

The main reason of these limitations is change in reaction pathways due to higher oxygen levels in the sample (for lower loading densities or leaking seals) or due to reduced moisture levels (drying of propellant in case of unsealed containers or if seals are leaking).

The effect of these factors on ageing rate can not only be prominent but also go in both directions, with tendencies towards increased ageing rates with a higher loading densities, better tightness and larger propellant grain or block size. Therefore, conditions of sample preparation and artificial ageing should be as close as possible to the real ageing condition of the respective propellant in the ammunition system [41].

3.3.2. **Ageing Vials**

Ageing procedure in this study is carried out in glass vials that can be hermetically sealed. The vials must have a minimum volume of 5 ml / 10 ml. significantly larger volumes would be preferred. However, much larger vials, especially those mode of glass, often tend to leak if fully filled with propellant and if aged at high temperature, whereas the small heat flow calorimeter vials / glass vials have been found to almost always remain sealed during ageing.

The vials are filled with propellant up to the top so that the amount of air inside is minimal before sealing. The loading density is thus approx.0.8 to 1.1 g/ml. Alternatively, the loading density of the ammunition defined for the propellant in test may be used. The vials are then placed in an upright position in the oven in such a manner as to ensure that the entire volume of the vial is maintained at the specified temperature for the specified duration.

Materials of the sample container and seal used must not react with the propellants and their decomposition products. Their compatibility must be checked before ageing process. The ageing conditions (e.g. container type and loading density) chosen must be kept constant for all samples within the series in order to avoid fluctuations in the decomposition reactions between the different samples.

In case of large grain or tubular propellant and if the volume of the glass vial is too small to fit the large propellants, any of following measure may be adopted:

- Larger vials should be used, keeping in view the loading capacity.
- Multiple glass vials should be used for each ageing step.
- Sufficiently large amount of the propellant should be cut or ground and the sample should be taken from a well-mixed fraction in order to achieve the required sample homogeneity.

Grinding of propellant markedly changes ageing behavior and should be avoided whenever possible. Cutting into medium sized pieces, on the other hand, is a more acceptable alternative.

3.3.3. **Corresponding Temperatures**

The ageing can be performed at any temperature between 50°C and 90°C. Table 2 defined the corresponding ageing times which are considered equivalent to **10 years of storage at 25°C**. Ageing time is considerably shorter for higher temperature. Lower temperature, however, will better represent the ageing at ambient conditions. Due to the very conservative activation energy assumption made to circulate the ageing time in Table 6.

Table 5: Conditions for single temperature ageing procedure

Temperature [°C]	Ageing Time [days]
60	123
65	64.9
65.5	60.90
70	34.8
75	19.0
80	10.6
85	5.98
90	3.43

In this method, samples of propellant are exposed to single temperature ageing aggravated conditions of predetermined and controlled raised temperatures in labs in order to simulate storage conditions at ambient temperature (25° C) for 10 years.

3.3.4. **Electronic Oven**

It is the requirement of this methodology that ageing should be carried out in oven which must be capable of maintaining a specified mean temperature of ±0.2°C for the required duration for all aged samples. Careful selection of electronic oven should be considered.

After removing the samples from the oven, the effectiveness of the seal during ageing should be checked (e.g. by weighing the filled container before and after ageing) and noted. For longer ageing periods at higher temperature, absolutely perfect sealing is difficult to obtain, particularly of glass vials and glass tubes. In small glass vials weight losses of below 0.2% with respect to the total propellant weight is usually obtainable. It has to be taken into account that higher weight loss values means a considerable loss of moisture, residual solvents and other volatile components such as nitroglycerin, which changes the sample composition and likely effects ageing rate and reaction mechanism.

3.4. High Performance Liquid Chromatography(HPLC)

In recent times High performance liquid chromatography (HPLC) is proved to be the most reliable technique for determination of propellants stability. HPLC is a tool used for separation of molecules and ions. This equipment works on principal of partition, adsorption and ion exchange based on interaction of molecules of samples with stationary phase [39] [40].

3.4.1. Types of HPLC Column

HPLC column can be categorized into two types:

- Reverse Phase
- Normal Phase

3.4.1.1. Reverse Phase Chromatography

Reverse phase system has a non-polar stationary phase over which polar solvents are used as mobile phase; it is generally used for separation of polar species.

3.4.1.2. Normal Phase Chromatography

Normal phase system has a polar stationary phase over which non-polar solvents are used as mobile phase; it is generally used for separation of non-polar species.[38]. A detection system is coupled with HPLC to detect and quantify the constituents.

3.4.2. Method Development

HPLC is a state of art equipment which can separate and detect constituents of a particular mixture. In order to carry out qualitative and quantative analysis of particular consitituent, a method with specific chromatic conditions has to be developed. Developing a method for analysis is a function of the constituents of the analyte. Method development includes the following steps:

- Selection of the stationary phase
- Selection of a compatible mobile phase
- Dimensions of the stationary phase column
- Flow rate
- Wavelength of ultraviolet and visible rays for detection

In this study, mixture includes Nitrocellulose (NC), Diphenylamine and its derivatives. The method for analysis was developed based on the constituents of our analyte.

3.4.2.1. **Stationary Phase/Column**

In this study, reverse phase C-18 column was used for the analysis. This C-18 column is the most common of all and is efficient for separation of polar species.

3.4.2.2. **Mobile Phase**

Methanol, acetonitrile, water or any of their combination is generally reported to be compatible with reverse phase C-18 column. After extensive experimental trials, combination of acetonitrile (ACN) and water is used in ratio of 70:30 found to be best suited for carrying out analysis in this study.

3.4.3. **Column Dimensions**

25 cm column was selected because it gave better separation and delayed retention time for DPA, thus excluding the early peaks given with 10 cm column. Dimensions of the selected column were 25 cm length and 4.6 mm diameter.

3.4.4. **Flow Rate**

Flow rate of the mobile phase was adjusted to be 1 ml/min as it gives clear peaks around a retention time of 7-8 minutes.

3.4.5. **Wavelength**

Wavelength is adjusted as DPA gives maximum absorption of UV at 210 nm.

3.5. Calibration

In this study, external calibration was used to identify diphenylamine. Four solutions of different concentration of DPA was made in order to obtained calibration curve

3.6. Extraction of Diphenylamine from Propellant Sample

Efficiency of any surveillance technique depends on how stabilizer contents has been extracted from propellant mix. Presence of nitrocellulose fibers may cause congestion in column and may effect performance of column. So it is necessary to eliminate complete nitrocellulose from samples before injecting into HPLC. Calcium chloride has been used for this purpose. Samples should not be stored for more than 24 hours prior to analysis. If total analysis cannot be completed within this time period, samples may be stored for up to 5 days provided the condition described above are met and reference samples are also analyzed at regular intervals.

3.7. Methodology

3.7.1. Sample Selection

The practical work for this study started with selection of propellant sample for analysis. For accurate analysis, careful selection of sample was made.

3.7.1.1. Materials

Propellant extraction kit including non ferrous forceps, pre-clean and dried amber glass vial with hard top cap, Personal protective Equipment, portable electronic balance.

3.7.1.2. Sampling Procedure

Sample was selected so as to ensure that it was a close representative of complete lot of propellant under investigation. Initially ammunition cartridge was selected from the store house which represented average climatic condition of all other store houses of the facility. 20 gms of sample was extracted from middle of selected cartridge (see figure 3.2). Sample was immediately transferred to a pre-cleaned, sterilized amber glass vial (20 ml). Sample was handled with non-ferrous forceps and touching of propellant grains with bare hands were avoided to ensure safety.

Figure 3.2: Tared weighing of sample propellant M2

3.7.2. **Artificial Ageing**

Artificial ageing was realized at by exposing propellants at 90°C for 3.43 days in oven in order to simulate environment similar to ageing of propellant in store houses with mean temperature of 25°C.

3.7.2.1. **Materials**

Thermostatic electric oven (Memert-UN 30), 20 ml Glass vials (CNW) with hard top cap and PTFE septa, Teflon tape, Electronic balance.

3.7.2.2. **Ageing Procedure**

For ageing procedure larger volumes are preferred. However, much larger vials, especially those made of glass, often tend to leak if fully filled with propellant and if aged at high temperature, whereas the small glass vials have been found to be almost always remain sealed during ageing.

The sample was taken in three vials of equal volumes. The vials are filled with propellant up to the top so that the amount of air inside is minimal before sealing. The loading density was kept approx.0.8 to 1.1 g/ml. Teflon tape was used to ensure perfect sealing. Weight of vials with and without sample was noted. After weighing, vials were placed in an upright position in the oven in such a manner as to ensure that the entire volume of the vial is maintained at the specified temperature for the specified duration. Oven was preheated and stabilized at 90°C. Duration of ageing was set at 3.43 days according to corresponding temperatures. After completion of ageing duration, contents of vials are checked and weigh again for estimation of mass loss.

Figure 3.3: Thermostated electronic oven for artificial ageing.

3.7.3. **Calibration**

External standards calibration method was used.

3.7.3.1. **Apparatus**

Perkin Elmer HPLC Flexar, Supelco column 25 x 4.6, 5µm, Microliter injection syringe (Hamilton), Sample vials with screw threaded hard cap with septa (CNW), sampling gastight glass syringe 1 ml gas (Hamilton), Syringe filter PTFE 0.22 µm, ultrasonic bath 50 hz, electronic balance, glassware, non ferrous grinding mill.

3.7.3.2. **Chemicals**

Acetonitrile HPLC grade, water HPLC grade, methanol (analytical grade),
calcium chloride HPLC grade, DPA (purity 99.9 %)

3.7.3.3. **Procedure**

100 mg of DPA was taken in 100 ml volumetric flask then 100 ml of Acetonitrile was added to prepare stock solution of 1000 PPM (parts per million) concentration. From this stock solution, 4-5

solutions of concentrations ranging from 20 PPM to 150 PPM were prepared. Specific volumes of stock solutions were taken in 100 ml volumetric flask and remaining volume of flask was filled with acetonitrile as follows:

- 20 PPM solution was made by adding 2 ml of stock solution.
- 40 PPM solution was made by adding 4 ml of stock solution.
- 60 PPM solution was made by adding 6 ml of stock solution.
- 80 PPM solution was made by adding 8 ml of stock solution.
- 100 PPM solution was made by adding 10 ml of stock solution.

After running the sample in HPLC, area of peaks obtained from chromatogram were plotted in absorbance vs concentration graph, sample caliberation curve is obtained

3.7.4. **Sample Preparation and Extraction of DPA**

Efficiency of any surveillance technique depends on how stabilizer contents has been extracted from propellant mix. Presence of nitrocellulose fibers may cause congestion in column and may effect performance of column. So it is necessary to eliminate complete nitrocellulose from samples before injecting into HPLC. Method for determining the stabilizer contents of aged or non-aged propellant is the same.

3.7.4.1. **Apparatus**

Conical flask 250 ml, acetonitrile (HPLC grade) Merck, water (HPLC grade) Merck, calcium chloride (analytical grade) Merck, nonferrous grinding mill, Glass syringe 1 ml (Hamilton), PTFE 13 mm syringe filter 0.22 µm, ultrasonic bath.

3.7.4.2. **Procedure**

After homogenization, 3-4 gm of sample was taken. Grinding of sample was carried out in nonferrous grinding mill. After grinding, 1 gram of ground sample was taken in 250 ml conical flasks, 100 ml Acetonitrile was added. Flask was placed in ultrasonic bath for 2 hours in order to assist dissolution. Temp of water bath was kept under 40 ° C.

Figure 3.4: Propellant M1 after grinding

3.7.4.3. **Precipitation of Nitrocellulose by Calcium chloride**

After complete dissolution of propellant sample in Acetonitrile, 10 ml of 2 % aqueous solution of calcium chloride was added in flask in order to precipitate nitrocellulose from the solution. Solution was kept at static position for an hour for settling of solid particles completely.

Subsequently 1 ml of supernatant solution was taken with help of glass syringe. Sample was filtered through PTFE 0.22 µm syringe filter. Filtrate was taken into 4 ml glass vials and and then closely cap tight.

3.7.4.4. **Precipitation of Nitrocellulose by Aluminum chloride – Alternate Method**

During experimentation, different salts were tried for better precipitation of nitrocellulose from sample solution. it was found that calcium chloride can be replaced with aluminum. chloride salt for precipitation of nitrocellulose from propellant sample solution. 10 ml of 2 % aqueous solution of aluminum chloride was added in flask in order to precipitate nitrocellulose from the sample solution(see figure 3.5). After settling, 1 ml of supernatant solution was taken by glass syringe. After necessary filtration, HPLC analysis of this sample was carried out. Result shows that concentration of DPA remained same

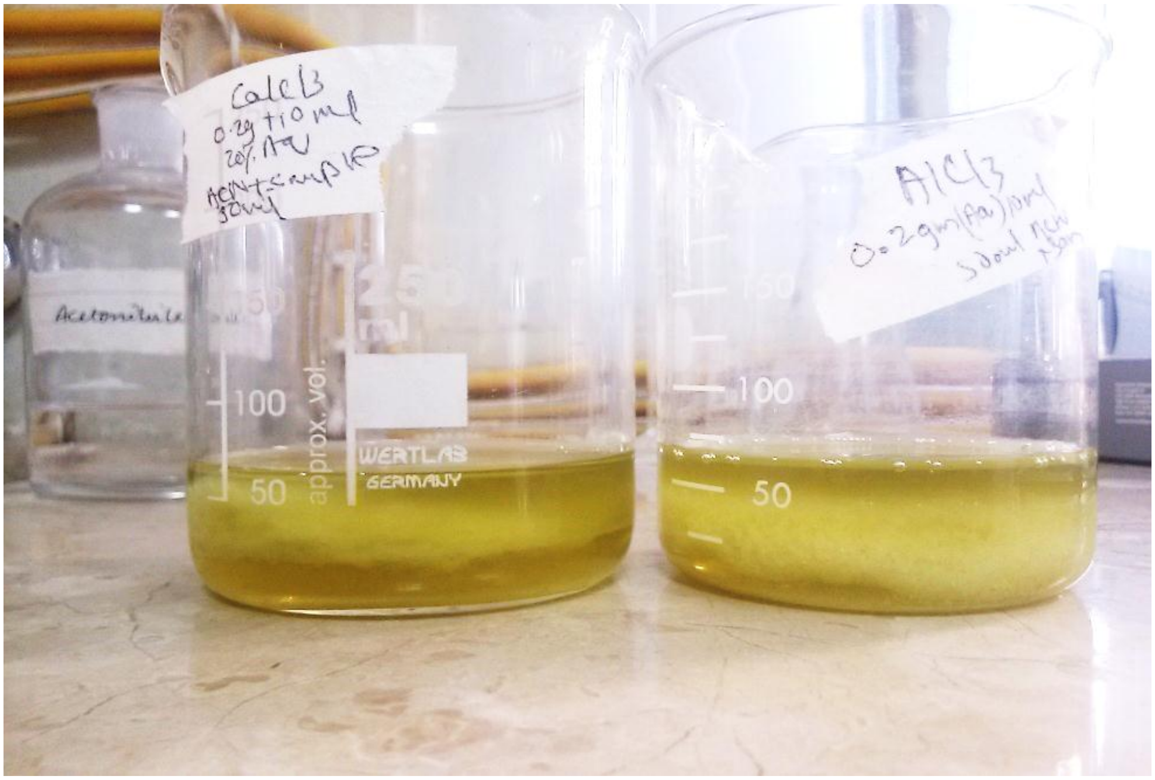


Figure 3.5: Precipitation of nitrocellulose by aluminium chloride

Previously, Precipitation of nitrocellulose from propellant sample solution by aluminum chloride has not been reported in literature.

3.7.5. Determination of Stabilizers by High Performance Liquid Chromatography (HPLC)

3.7.5.1. Apparatus

HPLC system Perkin Elmer flexar with binary pump, acetonitrile (HPLC grade) Merck, water (HPLC grade) Merck, sample injection syringe 100 µL, Hamilton

3.7.5.2. Chromatic Conditions for HPLC

Following chromatic conditions for HPLC have been found most suitable for determination of

DPA in propellants.

Mobile phase:	Acetonitrile: water (70%:30%)
Detector:	UV at 210 nm
Flow rate:	1 ml / min
Column Temperature:	35 º C
Calibration:	External standard
Total run time:	10 min

3.7.5.3. **Procedure**

Analysis was carried out by creating sequence in chromera software provided by firm Perkin elmer. Sequence consist of 3 steps and in each step 3 injections of sample were set. Each sample was analyzed 3 times in order to obtain average of all 3 run. Each run is followed by wash run in order to clear any ruminants in column.

After washing of syringe with acetonitrile 2-3 times, 30 µl of sample was taken from sample vial carefully so as to avoid air bubbles in samples. Injector handle of chromatograph was moved to load position and syringe needle was inserted fully inside the injection port and sample was injected slowly. Run started automatically after getting response from injection port. Three runs of the same sample was run to obtain mean value.

Chapter 4
Results and Discussion

4. This chapter explains the results obtained by experimental work carried in this study. Reprocessing and conversion of peak data into percentage of stabilizer is carried out in this chapter. Lastly, sentencing criteria is also discussed.

4.1. **Calibration**

Detection of samples in HPLC is shown as peaks in chromatogram. Peaks are identified by their retention time. In order to recognize peaks in relation to their retention time. Calibration of machine according to set method is carried out. In experimental part, DPA dissolve in acetonitrile in four different concentration was run. Chromatograms obtained are shown (see figures 4.1 to 4.4)

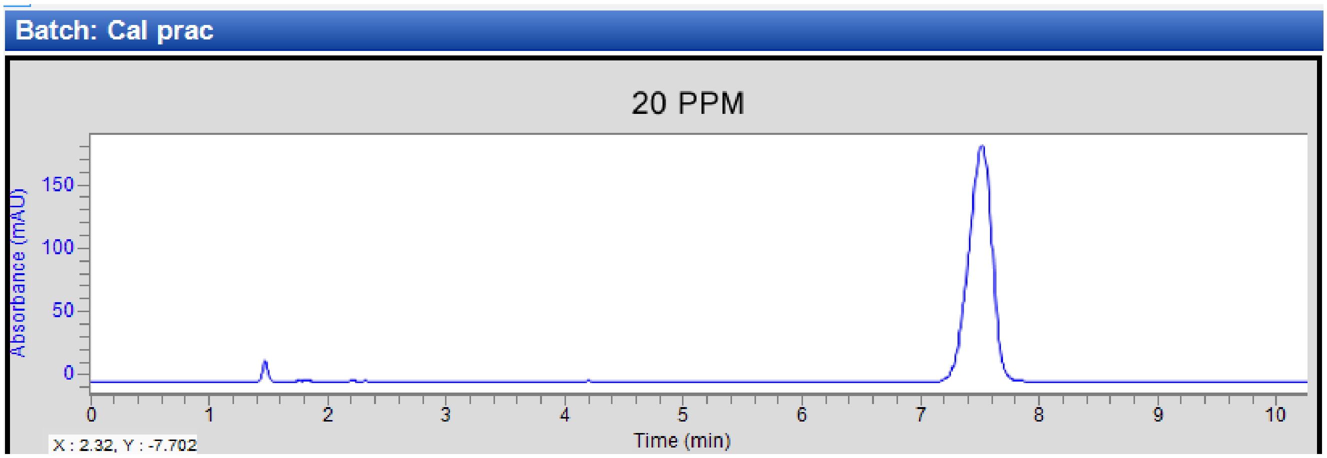


Figure 4.1: Chromatogram for 20 PPM solution DPA in acetonitrile

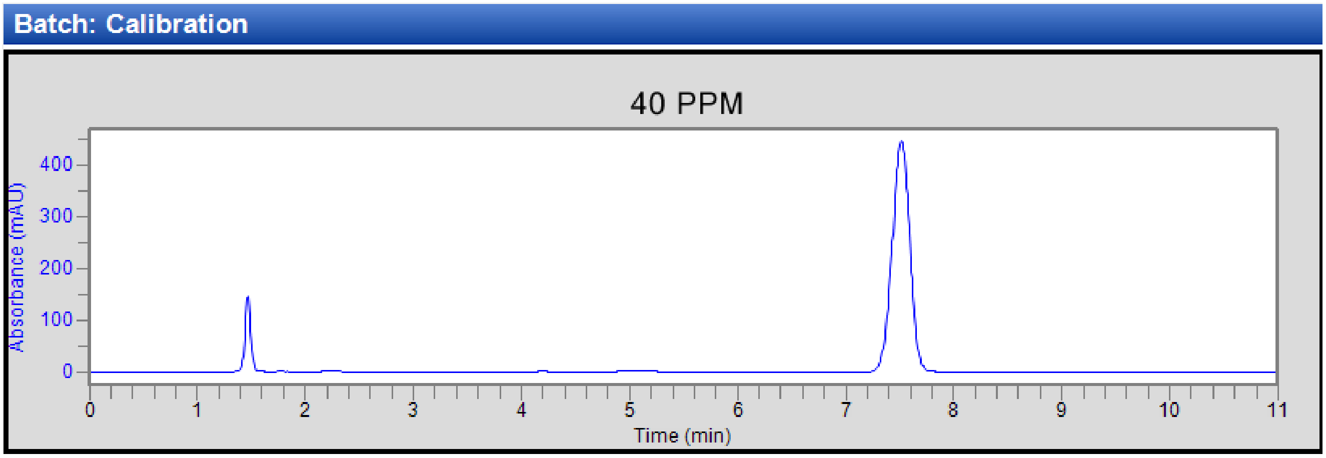


Figure 4.2: Chromatogram for 40 PPM solution DPA in acetonitrile

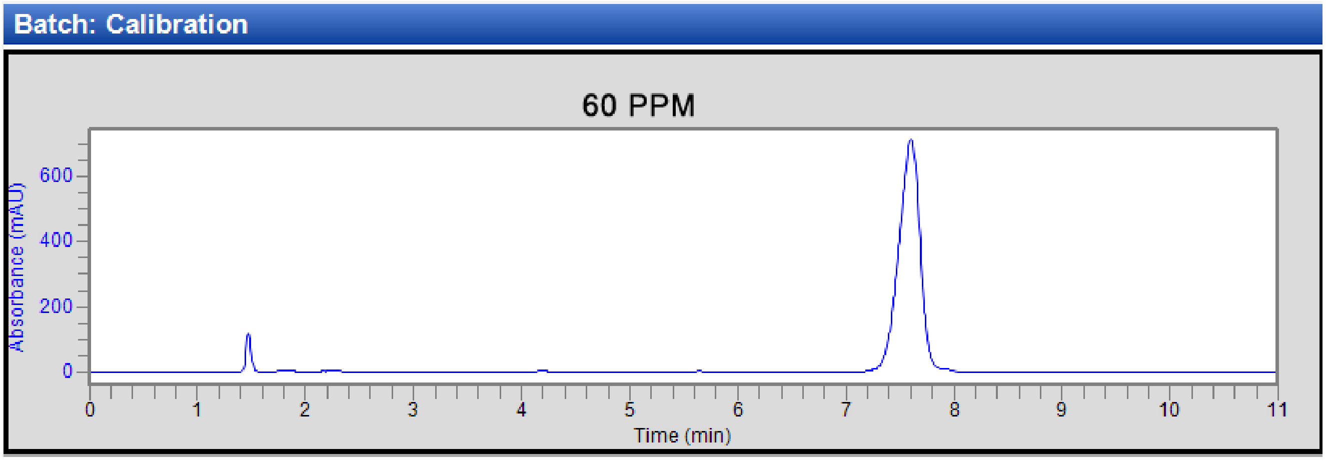


Figure 4.3: Chromatogram for 60 PPM solution DPA in acetonitrile

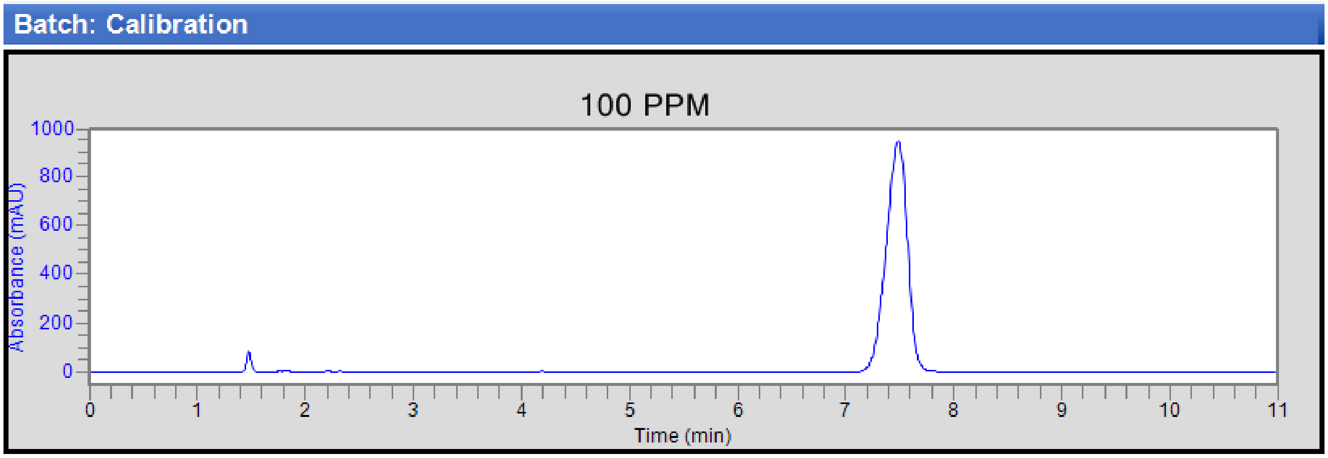


Figure 4.4: Chromatogram for 100 PPM solution DPA in acetonitrile

4.1.1. **Calibration Curve**

Retention time for DPA in preset conditions of applied method was found around 7.64 minutes. Area of peak shows concentration of DPA in solution (ref Table 6). Values were plotted in absorbance vs concentration curve (see figure 4.5).

Table 6: Calibration curve readings

Ser no	Conc(PPM)	Analysis 1	Analysis 2	Analysis 3	Ave	Std Dev
1	20	1389905.57	1349380.09	1357019.22	1365434.96	21533.62817
2	40	3518111.43	3544187.64	3569281.06	3543860.043	25586.38795
3	60	5617578.39	5667499.99	5666266.31	5650448.23	28472.79891
4	100	8418952.62	8414113.59	8414113.59	8415726.6	2793.815273

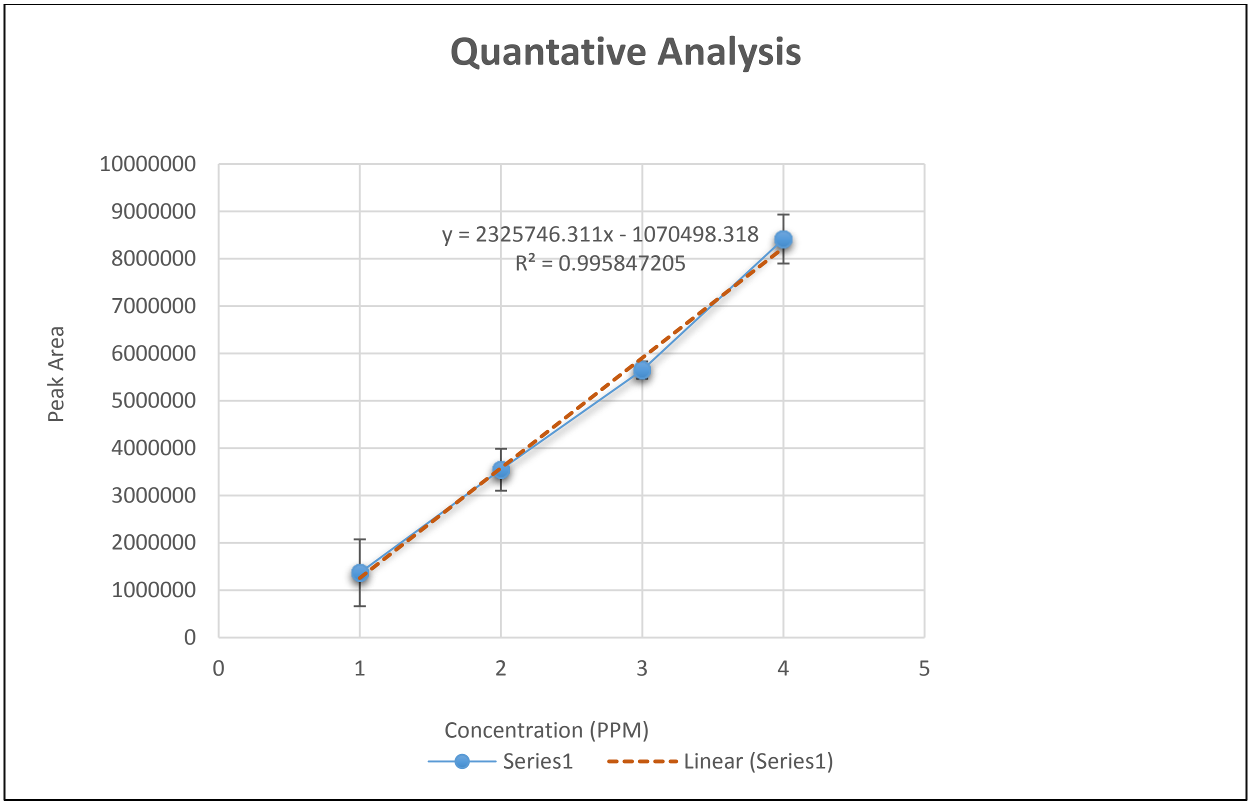


Figure 4.5: Peak area vs concentration curve

By joining 4 coordinates, a straight line is drawn with following equation. By putting in the value of Y axis (peak area), x-axis concentration is find out.

Y = 2325746.311x - 1070498.318 equation…. (i)

4.2. Finding Concentration of DPA in Sample

Analysis of single sample was carried out three times, in order to get average of three run values so that any error in calculation may be omitted. Following chromatogram(see figure 4.6 and 4.7) is obtained after analysis:

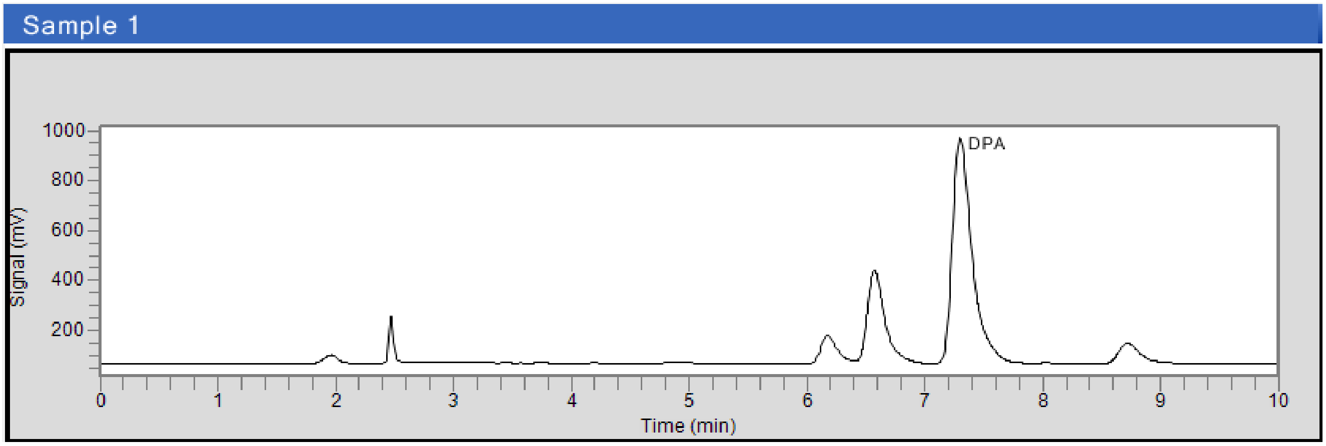


Figure 4.6: Chromatogram of M1 propellant (before ageing)

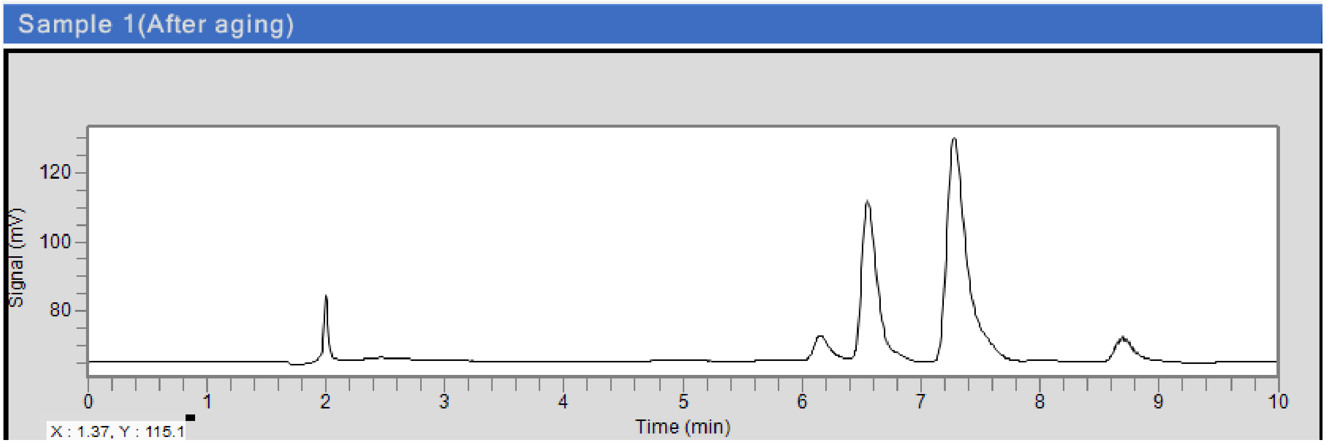


Figure 4.7: Chromatogram of M1 propellant (After ageing)

4.2.1. **Calculations**

Putting the peak value from sample in equation (i). instrumental data has been converted into DPA concentration (refer Table 7)

Table 7: Conversion of instrumental data into wt % of stabilizer

Sample	**Instrumental Reading (mAU)**	**DPA Conc (x)**	**DPA Wt (mgs)**	**Weight ratio %**
Sample 1	18512130	84 PPM	8.4 mg	0.84 %
Sample 1(after ageing)	10112130	48 PPM	4.8 mg	0.48 %
Sample 2	17112130	87 PPM	8.7mg	0.87%
Sample 2(after ageing)	8112130	55PPM	5.5 mg	0.55%

4.3. Sentencing Criteria

Nitrocellulose-based propellants will be sentenced according to the following criteria:-

- Criterion 1: Maximum decrease in effective stabilizer during ageing (in % of initial level)

  < 80 %

- Criterion 2: Minimum percentage of effective stabilizer remaining after ageing > 0.2%

The propellant will remain chemically stable for a minimum of 10 years of storage at an ambient temperature (25°C) if, after single temperature ageing both of these conditions are fulfilled.

4.4. Results

Keeping in view the above sentencing criteria, sample can be sentenced as serviceable for 10 years under ambient temperature of 25°C.

Chapter 5
Conclusions and Recommendations

5.1. **Conclusions**

Samples of M1 and M6 were selected for determination of remaining DPA contents in propellants. Artificial ageing of propellant sample was carried out to simulate 10 years of normal ageing in storage at 25ºC. A new HPLC method is developed and successfully tested for separation and quantification of components of propellants. HPLC readings were converted into weight ratio of DPA present in propellant. Serviceability of propellants lots used in this study may be determined based on these results. Results of artificial ageing may also be used to predict safe storage life for 10 years of storage.

5.2. **Recommendations**

Single based propellants make major chunk of propellants inventory of our country. Methodology developed in this study can be beneficial to keep majority of our energetic inventory safe during storage. Although it is recommended that research on developing testing procedures for stability testing of double/ triple based propellants may also be carried out. Data obtained with this methodology is beneficial to be used in other areas of research as well. It is also recommended that a new framework may be formulated at national level to incorporate new methodology. Framework may include central supervision of propellant stability testing, frequency of testing, scale of equipment and accessories for laboratories, training of manpower and economical disposal of discarded lots of propellants.

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