Reactions in the System Nitro-cellulose/ Diphenylamine with Special Reference to the Formation of a Stabilizing Product Bonded to Nitro-cellulose

BY

TORBJÖRN LINDBLOM
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Abstract

The methods HPLC, microcalorimetry and FTIR together with chemometry, provide good analytical tools to follow the degradation of nitro-cellulose.

The degradation products formed from diphenylamine (DPA) during storage can be followed with HPLC. FTIR, together with chemometry, also gives the precision needed for safety control of propellants.

Nitro-cellulose (NC) containing DPA obtained a green colour already after 1 day storage at 70°C. About 10% of the stabilizer, and its derivatives, added were not extractable giving an extended time to autocatalysis. This time could be extended up to 70 days at 70°C for an extracted sample compared to about 3 days for non-stabilized NC. This was not shown before.

Aged and extracted NC samples contained a non-extractable nitro compound. The most likely compound is 2,4-dinitroDPA, probably bonded to NC via the amine nitrogen. The bonding to NC occurs after the formation of NNODPA. This is something not described before.

Using another batch of nitro-cellulose to find out if a chemical bonding occurs gave inconclusive results as a blue NC was formed. Low molecular NC with high stability was obtained. A chemical bonding probably occurs when using NNODPA as a stabilizer, indicating NNODPA plays a key role.

The use of FTIR/chemometry is a promising method to use when studying small chemical changes. The described methodology should be used to find out more about the compound(s) being bonded to NC.

Keywords: Nitro-cellulose, NC, Propellant, Stabilizer, Diphenylamine, DPA, Stability, Shelf-life, Chemometry, FTIR, HPLC, Microcalorimetry

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PAPERS INCLUDED IN THE THESIS

This thesis summarises the content of the following papers, which are referred to by roman numerals, I to V, in the text:


II   Torbjörn Lindblom, Irreversible absorption of diphenylamine onto a straight phase and a reversed phase HPLC-column Symp Chem Probl Connected Stabil Explo 9th (1992) 205


Reprints were made with kind permissions from the publishers.
The experimental work in Paper I, concerning microcalorimetry, was made by L.G. Svensson and P. Lagerkvist. I was responsible for the rest of the work including writing the paper.
The experimental work in Paper III concerning gas analysis with FTIR was made by me.
In Paper IV I was responsible for the experimental work. Fred. O. Libnau and I performed the chemometric analysis together. Alfred A. Christy and I wrote the paper together.
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# Abbreviations

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<th>Abbreviation</th>
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<tr>
<td>2NDPA</td>
<td>2-nitro Diphenylamine</td>
</tr>
<tr>
<td>4NDPA</td>
<td>4-nitro Diphenylamine</td>
</tr>
<tr>
<td>2,4´-dinitroDPA</td>
<td>2,4´-dinitro Diphenylamine</td>
</tr>
<tr>
<td>AC</td>
<td>Autocatalysis</td>
</tr>
<tr>
<td>ACN</td>
<td>Acetonitrile (used for dissolution of NC)</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>CI</td>
<td>Centralite I, N,N´-diethyl-N,N´-diphenylurea</td>
</tr>
<tr>
<td>DPA</td>
<td>Diphenylamine</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane (used for extraction)</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared spectroscopy</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>MA</td>
<td>Multivariate Analysis</td>
</tr>
<tr>
<td>MC</td>
<td>Microcalorimetry</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>NC</td>
<td>Nitro-cellulose</td>
</tr>
<tr>
<td>NC Type I</td>
<td>Manufactured by Bofors</td>
</tr>
<tr>
<td>NC Type II</td>
<td>NC from a foreign source</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NNODPA</td>
<td>N-nitroso Diphenylamine</td>
</tr>
<tr>
<td>PC</td>
<td>Principal component (a “super” variable)</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal component analysis</td>
</tr>
<tr>
<td>PLS</td>
<td>Partial least square</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
</tbody>
</table>
1 Introduction

Nitro-cellulose (NC), a nitrate ester, is a very important derivative of cellulose used in many products. Common products are explosives, photographic films, protective varnishes and artificial leather. However, due to the thermal degradation of NC, devastating explosions in stores with old ammunition [1] has occurred, as well as fires in stores of old photographic films [2]. This last problem has initiated a restoration work where historic photographic films have been copied to a more stable type of film.

To increase the stability of NC explosives, stabilizers are added. An effective stabilizer must be able to react with liberated nitrogen oxides (NO, NO₂) as well as the acids formed from these, and it should preferably also be a good radical scavenger. The common stabilizers used today are various aromatic amines such as diphenylamine (DPA), 2-nitrodiphenylamine (2NDPA), N,N’-diethyl-N,N’-diphenylurea (Centralite I or CI) and N’-methyl-N,N-diphenylurea (Acardite II). Many other substances have also been tested [3].

Aim of this Thesis

This thesis is specially concerned with work and method developments at Bodycote CMK, earlier a department at Bofors, during the last 20 years. Developments in the different applied methods are discussed, since these methods constitute the foundation, the tools, on which the results rest.

The application of infrared analytical techniques for the determination of stabilizer additives and their degradation products in NC explosives is highlighted. Determination of stabilizers and their degradation products with HPLC is the standard method today to estimate the safe storage time of NC explosives.

This thesis is, among other things, concerned with the mechanism of the degradation, both what is occurring in the nitro-cellulose itself but also what is taking part in the stabilizer, DPA, and between stabilizer and NC. The last item has been overlooked to some degree earlier. Efforts have been made here to identify the intermediary compound proposed by Bergens [4]. This might be a reaction product between DPA and NC. In paper V also the direct reaction between NC and DPA is discussed. Results obtained (paper V) are further evaluated here and some new experimental results are presented.
2 Historical

In the beginning of the 19th century, the interest in treating various naturally occurring polymers with nitric acid grew [5]. In 1845, Schönbein, paid special attention to the properties of the product he obtained from cotton (cellulose) soaked with a mixture of nitric and sulphuric acid. He named it "guncotton" thus indicating the future use of the product. In the following years, much effort was made to scale up the process for the manufacturing of guncotton (NC). However, serious difficulties were discovered due to the chemical instability of the product. Accidents with explosions in NC factories occurred several times for example in Great Britain, France and Austria and the use of guncotton as an explosive was therefore limited for many years.

In 1868, Abel made significant progress when he managed to show that the accidents with NC were the result of inadequate purification of the guncotton. However, Alfred Nobel made an even more significant contribution by introducing DPA in 1889 as a stabilizing additive in NC based explosives. The NC formula developed by Nobel earned extensive use in both military and civilian explosives due to its remarkable stability. 1894 Nobel bought Bofors and built up a plant to produce nitro-cellulose. While working at Bofors Company many of the results presented here were performed, or research was initiated.
3 The degradation of nitro-cellulose

The wide use and practical importance of NC have initiated a number of investigations of the degradation mechanisms under different conditions [6-10]. The main causes for degradation of NC are rather well known today and can mainly be attributed to the unstable nitrate ester groups in the polymer. Chemical processes usually include nitrate ester decomposition, chemical stabilizers reactions, reactions with air oxygen and humidity, and decrease of nitro-cellulose molecular weight.

It is generally accepted that the primary step during the decomposition of nitrate esters is breaking of the O-NO$_2$ bond producing NO$_2$, since this bond has the lowest binding energy, 155 kJ/mole in comparison with C-ONO$_2$ 238 kJ/mole, [11]. Despite this, NO$_3$ a very strong oxidising agent has also been reported to occur [12]. When NO$_2$, a radical (sometimes written as $^\bullet$NO$_2$) due to its odd electron, is split off (Fig. 1), it leaves an alcoxy radical (RO$^\bullet$) in the NC-chain. The alcoxy radical formed may react very fast in a series of steps ultimately leading to the rupture of the C-C bond, chain fission [6, 10], which can be traced by GPC [13]. In [14] Phillips points out that. RO$^\bullet$ and $^\bullet$NO$_2$ can recombine. The dominating products due to the decomposition of NC are carbon oxides, nitric and nitrous oxides, methane, formaldehyde, water and nitrogen of which the nitrogen oxides are considered to be the most detrimental. These reaction will be treated more in detail under 6.1 Reactions in nitro-cellulose.

The intermediary compound discussed by Bergens [4] is believed to give the NC the green colour observed, although he didn’t notice any colour change as he worked with a propellant covered with graphite. Working with pure NC, (paper V) already after 1 day of storage at 70°C a faint green colour is seen. After 12 days the colour is deep green. With increased ageing the green colour gets still more intense.

The changes in propellant properties during production and storage are named ageing. Ageing is a complex process, in the course of which a series of physical and chemical processes take place. Of the physical processes taking place in the propellant diffusion of liquid nitrate esters e.g. nitroglycerine and ballistic modifiers play the most important role [15]. Also the distribution of stabilizer is important as discussed by Tranchant [16].
these processes result in changes of mechanical and ballistic properties of a propellant.

Chemical processes are characterised by the release of heat and gaseous products that are capable of accelerating the process of ageing. In extreme cases this ageing process may lead not only to deterioration of material properties below permissible limits but also to self-ignition, hazards that can jeopardize property and safety. From the producer’s viewpoint it is desirable to have a deeper knowledge of the character and nature of physical and chemical processes that may occur in propellants during ageing.

3.1 Shelf life

Discussing the stability in connection with propellants we consider their ability to maintain their ballistic properties. This is called the **ballistic shelf life**.

The time period during which the propellant can be safely stored without risk for self-ignition is defined as **storage life** or **safe shelf life**. This work deals mainly with the chemical stability and storage life of single base propellants. Normally the ballistic shelf life expires before the safe shelf life.

Rule of thumb: The amount of stabilizer should be ≥0.2% DPA before special attention is paid to the propellant. Normal starting value is about 1%, corresponding to about one DPA per 50 NC-units [16].

It is not uncommon that an uneven distribution of stabilizer in the propellant is observed. Normally this has no negative effects on the stability as the stabilizer migrates, even via gas phase, to the spot where it is needed [17].

Another type of problem that has been observed occasionally is that the depletion rate d(DPA)/dt of the stabilizer and its derivatives changes with time. The same propellant lot should therefore be analysed on several occasions. Self-ignition accidents with ammunition, due to this problem, have been reported. The amount of stabilizer at the last safety control was low but within the limits. Subsequent investigations, after the self-ignition, showed that the consumption rate of stabilizer suddenly was much greater. Ammunition (not ignited) from the same lot showed almost zero stabilizer. The reason for this is unknown.

Knowledge of primary stabilizer depletion kinetics is necessary for propellant storage life calculations.
4 Theoretical

The degradation of nitrate esters such as nitro-cellulose is complicated because many degradation reactions are superimposed on each other e.g. reactions in NC, stabilizer and NOx and between these.

In addition, secondary reactions of degradation products, interference with oxygen and water further complicate the degradation path.

Physical processes such as diffusion limitations and restricted solubility do also influence the degradation path. In general, chemical reactions and physical processes have different temperature dependencies (e.g. activation energies, E_a) which makes the comparison of experiments performed at different temperatures even more complicated.

Hydrolysis reactions [18], thermolysis, impurities [5] formation of N_2O_5 [3] degree of nitration [12] further complicate the picture. Different glucose units in the NC chains may break down by different pathways, both because initial bond breaking can occur at any of three sites and because the resulting alcoxy radical can be stabilised in a number of different and possibly competing ways [10]. Impurities and certain additives e.g. nitrates, cryolite [19] also have great negative impact on stability.

Thus, the sequence of reactions is probably so complex that it is unlikely that the total mechanism leading to gaseous products will ever be completely understood.

4.1 Nitrate ester decomposition

The nitrogen oxides, especially NO_2, are very reactive and capable of catalyzing a series of exothermic reactions, which are responsible for the self-ignition of NC [12, 21]. Self-ignition during storage can cause devastating accidents and it is therefore essential that the autocatalytic reactions be prevented. The presence of moisture together with nitrogen oxides forms reactive HNO_2 and HNO_3 that further deteriorates the stability.
In spite of the high stability of modern explosives, it is still important to study the aging behaviour of such compounds. The stabilizing additive will be consumed with time and the autocatalytic reactions responsible for the degradation of NC will then accelerate unhindered. Thus, the risk of self-ignition still exists if the degradation process is allowed to proceed unmonitored for too long a time, and the stability of the NC must therefore be continuously monitored.

Propellants are manufactured from a relatively complex mixture of various compounds. For single base propellants the critical factor for the storage safety is the instability of nitrate esters as it is their main component, up to about 99%. The nitrate ester reactions are possible to classify based on the nature of the reacting agent as: nucleophilic, electrophilic, redox and radical thermal decomposition. The plain ester hydrolysis to alcohol and nitric acid is probably not too common as nitrate is found only when the propellant is close to autocatalysis (paper III). The radical thermal decomposition of nitrate esters is discussed by Lurie [22]. Studies with $^{15}$N by Gelernter [8] showed that the nitrate group of the $2^{\text{nd}}$ and the $3^{\text{rd}}$ carbon position of the glycoside unit are more unstable than the $6^{\text{th}}$ carbon position. The initial attack thus starts at the nitrate groups on the $2^{\text{nd}}$ and $3^{\text{rd}}$ carbon (Eq. 1) by the general mechanism of vicinal dinitrates. The chain cleavage thus occurs between carbon 2 and 3 eventually forming aldehyde groups at these positions. Decomposition of the 6-nitrate group gives NO$_2$, formaldehyde and a further rearrangement of the residue, involving rupture of the cellulose chain.

According to Lurie [23] nitro-cellulose denitration occurs primarily at the ends of the NC molecule while the rest of the molecule remains practically intact.

$$\text{or } RCH_2ONO_2 \leftrightarrow RCH_2O' + \cdot NO_2$$

$$\rightarrow COx + NOx + HCHO + CH_4 + H_2O + N_2O + N_2 + \text{solid residues}$$

The reaction described in equation (1) is followed by a series of consecutive reactions. As possible reaction products Lurie [22] gives
aldehydes, alcohols, nitrous and nitric acid. The final products of this decomposition are primarily nitrogen dioxide, glyoxal, formaldehyde, and carboxylic acids. Gaseous products such as carbon dioxide, nitrogen, nitrogen oxide, nitrous oxide and carbon monoxide have also been identified above the sample e.g. by IR (paper III). See also paragraph 5.3 FTIR for an example.

From kinetic parameters, given by some authors, [22, 24, 25] for nitroglycerine, nitro-cellulose, and diethyleneglycol dinitrate (DEGDN) the values of activation energies and preexponential factors are dependent on the temperature range at which the constants have been determined. However, also constants obtained under comparable conditions show relatively large differences between the individual publications. Errors cannot be excluded during processing of the measured data because parameters of the Arrhenius equation are intercorrelated and data describing the same quantity can be achieved using a series of combinations of preexponential factor and activation energy. Data obtained from different works [22, 24], have been processed by Lurie by means of regression. From the results of these the Arrhenius equation constants for nitro-glycerine have been estimated:

\[ E_a = 171 \text{ kJ\cdot mol}^{-1} \text{ and } \log A = 16.8 \text{ s}^{-1}. \]

Research of thermal decomposition of nitrate esters is limited primarily by the experimental techniques used to monitor the decomposition resulting from various primary and consecutive reactions. A very interesting contribution is the recently published work of Kimura [25] who utilizes a chemiluminiscence technique for the study of the thermal decomposition processes in nitro-cellulose and diethyleneglycol dinitrate. Wallace has also discussed this method [26, 27] The results of the work are that the primary nitrate esters decomposition, Eq. 1, is followed by auto-oxidation of an alcoxyradical by the released nitrogen dioxide under formation of a peroxyradical and nitrogen oxide (2). Dependent on decomposition conditions either formation of hydroperoxides occurs (3) or formation of a peroxyradicals termination by their disproportionation (4). The released oxygen thereafter oxidizes nitrogen oxide to nitrogen dioxide (5).

\[
\begin{align*}
RCH_2O-NO_2 & \rightarrow RCH_2O^* + NO_2 \rightarrow RCH_2OO^* + NO \uparrow \\
RCH_2OO^* & \xrightarrow{h\nu} RCH_2OOH \rightarrow RCHO^* + H_2O \\
2 RCH_2OO^* & \rightarrow RCHO^* + RCH_2OH + O_2 \\
2NO + O_2 & \rightarrow 2NO_2 \uparrow
\end{align*}
\]
Nucleophilic reactions of nitrate esters are discussed by Lurie [23]. The main nucleophilic agents in propellants are considered to be water, hydroxyl anion or RNHR (stabilizer). Presence of carbonyl or carboxyl groups in the nitrate ester molecule brings about a vigorous increase in base catalysed hydrolysis (in case of nitro-glycerine derivatives it is a matter of acceleration by 3 to 5 orders).

Reactions with electrophilic agents are widely extended secondary processes accompanying nitrate esters decomposition including the thermal decomposition. This is a matter of reaction with acids and agents of (NO' A')-type like N₂O₄, N₂O₃, HNO₂. These are the main reasons for the rapid acceleration in the course of thermal decomposition.

The schematic scheme Fig. 1 (modified here) was presented in paper III.

---

**Figure 1. Schematic picture of NC decomposition (from paper III)**
4.2 Chemical stabilizers and their behaviour in a propellant

As said earlier the decomposition processes in propellants are very complex. Besides the primary decomposition a whole series of consecutive reactions occurs, the products of which may be accumulated in the propellant to assist accelerating its decomposition, see Fig. 1. The primary decomposition processes are not possible to stop but it is possible to delay the accelerated process by adding chemical stabilizers to the propellant. These compounds preferably react with the decomposition products released during propellants ageing - primarily nitrogen oxides, nitrous and nitric acid.

Although stabilizers have been used in propellants for more than one hundred years, and thus been subjected to several scientific studies, the chemical processes are, even today, not known in all details. The cause for this is the complexity both of nitrate esters decomposition and stabilizers reactions. Along with the development of modern instrumental methods, especially the HPLC technique, introduced in the middle of the seventies [28], this research was significantly accelerated. Similar improvements in other experimental techniques, such as microcalorimetry and chemiluminiscence have further contributed to the elucidation of propellant degradation.

The stabilizer used in single base propellants is primarily DPA. Urea based stabilizers, sometimes in combination with diphenylamine, are frequently used for double base and nitro guanidine propellants. Typical representatives of this type of stabilizers are Centralite I (N,N'-diethyl-N,N'-diphenylurea), Centralite II (N,N'-dimethyl-N,N'-diphenylurea), Akardite I (N,N'-diphenylurea) and Akardite II (N,N'-diphenyl-N'-methylurea, AII). In case of homogeneous solid rocket propellants inorganic stabilizers (magnesium oxide) are also used together with Centralites, 2-nitro-diphenylamine, 4-nitro-N-methylaniline (PNMA) or resorcinol or combinations of these [29].

Comparison of some stabilizers’ reactivity with nitrogen dioxide is given in [27]. Comparison of stabilizers from the viewpoint of their ability to delay accelerated decomposition of propellants and to decrease their weight loss rate is given in [13]. Comparison of the abilities of CI, DPA and AII to prevent the decrease of nitro-cellulose molecular weight in single base and double base propellants is given in [30]. In [24] the depletion rate of some stabilizers in pure nitro-glycerine are compared.

When DPA reacts with liberated nitrogen oxides, it is converted into a number of different nitro and nitroso derivatives. The analytical procedure in
order to identify/ quantify these derivatives must therefore include a separation step. The DPA reaction products formed during storage of a propellant have been characterized with thin layer chromatography by Volk [31]. Due to the low thermal stability of some of the nitro diphenylamine derivatives (nitroso compounds), the dominating chromatographic technique used is liquid chromatography (HPLC) (paper I) [28, 32]. The HPLC separation of nitro diphenylamines can however be difficult since many derivatives have similar properties concerning polarity and affinity to commonly used reversed phase packings such as C8 or C18. With the right type of column (paper II and V) base line separation of the compounds of interest can be obtained. Gas chromatographic (GC) methods have also been published but are in general not suited for stabilizer analysis due to decomposition of heat sensitive derivatives like nitroso compounds.

An attempt to clarify the reaction paths of the degradation of DPA was made in 1949 by Schroeder et. al. [33]. Their proposed reaction pathways (Fig. 2) are now commonly accepted for the decomposition mechanism of DPA.

![Figure 2. Schematic reaction routes for the degradation of DPA in an aging propellant. From [33]](image)

From Fig. 2, it is seen that the reaction scheme contains both nitroso and nitro derivatives of DPA. It is noteworthy that DPA is capable to trap six
nitrogen oxide molecules before it decomposes to picric acid. Apart from DPA itself, the mono nitro and nitroso diphenylamines are the most important derivatives for maintaining the stability of NC 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. The study of the DPA decomposition is therefore focused on DPA, 2-nitro-DPA (2NDPA), 4-nitro-DPA (4NDPA) and N-nitroso-DPA (NNODPA). At normal storage temperatures the formation of higher derivatives is effectively hindered by the nitro groups already present in the aromatic ring [28].

4.2.1 Diphenylamine and its derivatives

Diphenylamine is the stabilizer that has been used for the longest time for smokeless propellants. However, DPA derivatives, primarily 2NDPA but also 4NDPA, are also used as stabilizers. During propellant ageing DPA is subject to a series of consecutive chemical reactions that give rise to various nitro and nitroso derivatives - the so-called daughter products - to which also 2NDPA and 4NDPA belong. Determination of DPA reaction products in the propellant is the scope for many works [13, 32, 34, 35, 36]. It is also mentioned that the course of the chemical reactions of DPA and its derivatives in the propellant is significantly affected by ageing conditions - primarily exposure of the propellant to air and to gases released from the propellant. Except for DPA, nitro- and nitroso derivatives, also unknown compounds are formed that have not been identified by HPLC. The same result is obtained from the measurement of weight increase rate [37] and change in chemical composition of pure DPA derivatives (DPA, NNODPA, 2NDPA, 4NDPA) in nitrogen dioxide flow at room temperature and various pressures. Schroeder et al [33] found that only 55-65% of DPA and its derivatives could be recovered. (The same result is presented in paper V). They conducted experiments aimed to exclude as possible error sources e.g. evaporation of DPA from the sample, its incomplete extraction, possible precipitation of some DPA derivatives during sample preparation for analysing, and also the possibility that some unknown compound would not have been detected in the extract. No plausible explanation has so far been presented, but an hypothesis considers the possibility of a DPA-nitrocellulose interaction leading to a non-extractable product. The mechanism of this transformation could be a radical reaction Ph2N• or Ph2N•• with nitrocellulose according to Bergens [35].

Works by Curtis [32, 34] and Bellerby [38, 39] also deal with chemical mechanisms of DPA reactions in a propellant.

Studies of radicals in a single base propellant have been performed by Mrzewinski [40, 41]. By measuring electron spin resonance (ESR) spectra, formation of EDA complex [DPA]• [NC]•• has been proven and the author
assume the other sources of ESR signal to be Ph₂N⁺, Ph₂N-O⁺ and the compounds with -N⁺-N⁻ bonds.

In unheated NC the radical spectrum is a superposition of at least two signals: one of high intensity, and one weaker with three components. The former may be attributed to a charge transfer (CT) complex of NC and DPA with the amine as a donor and the nitrate ester as an electron acceptor. The proposed charge transfer complex of NC and DPA is shown below.

\[
\begin{align*}
\text{NH}_2 & \cdot \\
\text{NC} & \cdot
\end{align*}
\]

A possible derivative of DPA, which could account for the ESR signals is:

\[
\begin{align*}
\text{Ph} & \text{Ph} \\
\text{N} & \text{N} \\
\text{NO} & \text{O}
\end{align*}
\]

The ESR signal intensity increases strongly with propellant conditioning time, followed by a rapid drop after the maximum value has been reached. The maximum value is directly proportional to the starting quantity of DPA in the sample. Experimental samples in which DPA derivatives such as NNODPA, 2NDPA, 4NDPA or NNO-4-NDPA have been used instead of DPA have shown significantly lower ESR signal values than the samples with DPA. The results of ESR signal measurement during conditioning of DPA solution in nitro-glycerine are given in [42]. The signal intensity curve reaches its maximum at a time corresponding to about 60 % of DPA being consumed.

DPA, however, does not only act as a stabilizer in propellants but also as a compound that accelerates nitrate ester decomposition relative to the thermal decomposition or neutral hydrolysis [24, 42].
4.3 Nitrogen oxide compounds

One of the complications in the interpretation of the NC degradation is the variety of nitrogen oxides participating in the reactions. Very well known is the equilibrium \( \text{N}_2\text{O}_4 \leftrightarrow 2\ \text{NO}_2 \), where 83.9% is present as \( \text{N}_2\text{O}_4 \) at 21,15°C and 1 atm. A compilation of nitrogen oxide compounds is made by Jolly [43].

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Nitric oxide</td>
<td>-164</td>
<td>-152</td>
<td>Moderately reactive, blue in liquid and solid state, eleven valance electrons, bond order of 21/2, one unpaired electron, odd molecule.</td>
</tr>
<tr>
<td>HNO</td>
<td>Nitroxyl</td>
<td></td>
<td></td>
<td>Unknown except as kinetic intermediates and salts</td>
</tr>
<tr>
<td>HNO(_2)</td>
<td>Nitrous acid</td>
<td></td>
<td></td>
<td>Unstable, but salts stable</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}_4)</td>
<td>Dinitrogen tetroxide</td>
<td>-11</td>
<td>21</td>
<td>Colourless; largely dissociated to brown NO(_2)</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}_5)</td>
<td>Dinitrogen pentoxide</td>
<td>-</td>
<td>-</td>
<td>Sublimes at 32,4°C, unstable vapour</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>Nitric acid</td>
<td>-42</td>
<td>83</td>
<td>Strong acid</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>Nitrous oxide</td>
<td>-91</td>
<td>-89</td>
<td>Relatively unreactive, linear molecule, NNO</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>Nitrogen dioxide, nitric peroxide</td>
<td>-111</td>
<td>2</td>
<td>Brown, reactive gas</td>
</tr>
<tr>
<td>NO(_3)</td>
<td>Unstable intermediate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{N}_2\text{O}_3)</td>
<td>Dinitrogen trioxide</td>
<td>-111</td>
<td>2</td>
<td>Largely dissociated to NO and NO(_2)</td>
</tr>
<tr>
<td>HNO(_4)</td>
<td>Peroxy/nitric acid</td>
<td></td>
<td></td>
<td>Unstable</td>
</tr>
<tr>
<td>H(_2)NO(_2)</td>
<td>Hydronitrous acid</td>
<td></td>
<td></td>
<td>Explosive sodium salt known</td>
</tr>
<tr>
<td>H(_2)N(_2)O(_3)</td>
<td>Unstable, known in solution and as salts</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH(_2)NO(_2)</td>
<td>Nitramide</td>
<td></td>
<td></td>
<td>Unstable, weak acid</td>
</tr>
<tr>
<td>H(_2)N(_2)O(_2)</td>
<td>Hyponitrous acid</td>
<td></td>
<td></td>
<td>Unstable, weak acid</td>
</tr>
<tr>
<td>H(_2)OONO</td>
<td>Peroxonitrous acid</td>
<td></td>
<td></td>
<td>Unstable, but anion stable</td>
</tr>
</tbody>
</table>

**Comments:**

1) NO reacts rapidly with oxygen to form brown NO\(_2\).

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

For this reason, it is often mistakenly concluded that NO\(_2\) is formed in reactions that are carried out in open vessels and that actually involve the initial evolution of only NO. The rate constant for this reaction is very unusual in having a negative temperature coefficient.

2) It is often assumed that two-electron reducing agents such as stannous iron react with nitrous acid to form an unstable intermediate called nitroxyl, HNO. The molecule is not planar with an H-N-O angle of 110°.
3) A solution of HNO₂ decomposes reversibly and is believed to proceed by the following mechanism.

\[
\begin{align*}
4\text{HNO}_2 & \rightarrow \text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O} \\
(\text{rapid, reversible}) \\
\text{N}_2\text{O}_4 & \rightarrow \text{NO}^+ + \text{NO}_3^- \\
(\text{rate-determining}) \\
\text{NO}^+ + \text{H}_2\text{O} & \rightarrow \text{HNO}_2 + \text{H}^+ \\
(\text{rapid, reversible})
\end{align*}
\]

Secondary amines (e.g. DPA) react with HNO₂ to form a stable N-nitroso-amine:

\[
\begin{align*}
\text{H} & \quad \text{R} - \text{N} - \text{R'} + \text{HNO}_2 \\ & \quad \quad \quad \quad \rightarrow \\ & \quad \text{NO} \quad \text{R} - \text{N} - \text{R'} + \text{H}_2\text{O}
\end{align*}
\]

4) In gaseous and liquid state NO₂ and N₂O₄ always exist in the presence of one another. The reaction

\[
\begin{align*}
2\text{NO}_2(\text{g,l}) & \rightleftharpoons \text{N}_2\text{O}_4(\text{g,l})
\end{align*}
\]

rapidly achieves equilibrium. The NO₂ molecule is V-shaped with the O-N-O bond angle of 134°. The N₂O₄ molecule is planar with the same O-N-O bond angles as in NO₂.

5) N₂O₅ is the anhydride of nitric acid. It is deliquescent and reacts with water as follows:

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3
\]

The gaseous molecule probably has the structure O₂N-O-NO₂, but the solid consists of an ionic lattice of nitryl ions, NO₂⁺, and nitrate ions, NO₃⁻.

6) HNO₃ is an oxidising agent, but both the rate of its reactions and its reduction products are strongly influenced by concentration. At low concentrations the principal reduction product of HNO₃ is NO, whereas at higher concentrations considerable amounts of NO₂ are evolved.
5 Analytical methods used to monitor the decomposition of nitro-cellulose

5.1 General
Ageing and decomposition of propellants are accompanied by a series of phenomena such as gas release, reduction of nitro-cellulose molecular weight, decrease of primary stabilizer concentration or heat generation. These accompanying phenomena can be utilised in propellant stability judgment, and for study of its decomposition kinetics or estimation of its storage life. Considering the fact that the above-mentioned processes proceed under common conditions very slowly (propellant storage life is normally longer than 20 years) it is impossible to conduct some tests under room temperature. Therefore long time ageing of propellant is performed at increased temperature to reduce the ageing time. Considering the complex mechanism of a great number of chemical and physical processes taking place it is, however, desirable that the temperature of the test is kept as close as possible to the common temperature of propellant storage. Too high a temperature may result in changes in propellant ageing mechanisms during the test in comparison with the course under normal conditions. The results of such tests are then not capable to predict propellant behaviour under common conditions. Earlier test were almost exclusively so-called heat tests performed at temperatures up to 132°C.

However, the decomposition of NC proceeds even at normal storage conditions and various methods have been developed over the years for stability monitoring of propellants both immediately after production and under storage. The most frequently used methods can be divided into the following classes:

- Basic test based on gas emission is vacuum test. Measurements of the time until visible amounts of nitrogen oxides appear over heat stored propellant samples (time-to-fume). By measuring the time-to-fume at different temperatures, the time-to-fume at normal storage
temperatures can be estimated. This is an old high temperature test, used some times also today.

- Monitoring the **weight loss** while storing the propellant at elevated temperatures.
- Determinations of stabilizer and degradation products by HPLC. By monitoring the **stabilizer consumption** at different temperatures, the time for stabilizer consumption at normal storage temperatures can be estimated. The values can be used in kinetic models [35, 36, 45-46] for evaluation of measured stabilizer concentrations vs. conditioning time dependencies at a given temperature.
- Monitoring the change in **molecular weight** distribution of the NC by size exclusion chromatography or determine the **viscosity** of nitro-cellulose [47-49].
- Measurements of the **heat flow** from the exothermal decomposition reactions by microcalorimetry (MC) (paper I, III), [2, 17].
- Chemiluminescence is a method capable of monitoring the **emitted light quanta** during the proceeding chemical reactions.

The choice of method is governed by the purpose of the investigation. For quality control during production, simplicity, speed and high sample throughput is desired. Weight loss or time-to-fume measurements are therefore preferably used. Methods like for example determinations of nitrogen oxides by chemiluminescence or FTIR spectroscopy can be used in special cases like, for example, production failures or suspected unstable propellant batches.

For the analysis of nitro-cellulose methods like High Performance Liquid Chromatography (HPLC), Fourier Transform Infrared spectroscopy (FTIR) and MicroCalorimetry (MC) are used on a regular basis at the CMK laboratory.

### 5.2 HPLC

To analyse the stabilizer in a propellant, in order to determine the amount of stabilizer and its different derivatives, Liquid Chromatography is used. This method has since long outdated Thin Layer Chromatography (TLC). Both straight phase and reverse phase methods are used (paper II and V). With the proper combination of column and mobile phase no gradient system has to be used to obtain base line separation of the peaks of interest. With a gradient system the analysis normally is more time consuming as one has to equilibrate the column after each run.
HPLC was used at Bofors as early as 1975 and an analytical system was developed where almost all of the derivatives could be analysed in an isocratic run on a straight phase column, Fig. 3 [from 28].

On a straight phase column only organic solvents are used for the elution and the least polar component leaves the column first. The higher and more polar components that are eluted much later and thus become more difficult to observe as they tend to give very flat peaks when the component is present in low concentration. Thus they might be overlooked. Using a more polar solvent like isopropanol to modify the mobile phase will shorten the retention times but will give a poorer resolution.

Figure 3 Isocratic analysis with HPLC of DPA and derivatives up to penta nitroDPA

Figure 4 Chromatogram of DPA and derivatives on a reverse phase column
Later when the column technique had been evolved also a reversed phase system was developed. In such a system, where a mixture of water and e.g. acetonitrile is used, the most polar component in the injected sample is eluted first. With both techniques the components of interest were eluted with base line resolution. A typical chromatogram of a reverse phase run is shown below Fig. 4 (from paper V).

When analysing derivatives of DPA normally only the stabilizer and the first three derivatives, NNODPA, 2NDPA and 4NDPA, are quantified as no di-derivatives are supposed to be present in a propellant used in ammunition. The lowest acceptable level of DPA in an aged propellant, according to [50], is 0.2%.

Today the HPLC method is used on a regular basis to control the stability of propellants in store in a so-called ammunition surveillance testing.

However, there might be problems if this lower limit is accepted without critical considerations.

When a propellant has more than 0.2% stabilizer it is considered safe until the next inspection. Normally this is also the case but there have been some deviations from this rule resulting in fires in ammo depots or worse explosion [51]. The reason for these accidents was a sudden increase in stabilizer consumption. (The reason for this acceleration is still one of the unanswered questions in nitro-cellulose chemistry). To be sure that the propellant is safe one has to compare several analyses made after different storage time e.g. 5, 10 and 12 years and check if the consumption is constant over the whole storage time. A sudden change in the slope \( \frac{dC_{\text{DPA}}}{dt} \) will indicate there might be problems with the propellant.

On the other hand a value lower than 0.2% shouldn’t be of any concern from safety reasons as there is a factor 16.6 [11] in time until autocatalysis occurs when DPA is reduced to 50% of its initial value. (The performance of the propellant will however be influenced. Thus it might not fulfil its tactical purpose.

When too low a value is found another sample should be analysed. It happens that a low stabilizer value can be found in some propellant grains. This does not mean that there will be an autocatalysis in these grains as the stabilizer in the next grains will diffuse over and stabilize the grain. The stabilizer also acts via the gas phase [17], (paper II).

Before the analysis, the propellant has either to be extracted with e.g. DCM (dichloro methane) to get the stabilizer and its derivatives separated from the NC matrix, or dissolved in e.g. acetonitrile. When using this latter method adding a solution of 2% calcium chloride to the solution precipitates
the NC. In this latter case a reversed system with a mobile phase of water/acetonitrile is used.

To quantify the components an internal standard is added. The time for an analysis is less than 15 minutes as seen from Fig. 4.

One problem to be aware of when using HPLC is the condition of the column. Sometimes an irreversible absorption of DPA occurs on the column (paper II). This can severely affect the analysis and a too low value of DPA will be reported. Thus a whole lot of ammunition might be scrapped long before the end of its normal shelf life. (However, a control of the propellant using MC, described shortly, should reveal the true condition of the propellant.)

The best way to check the condition of the column for absorbing DPA is to analyse a calibration solution containing all the derivatives of interest plus the internal standard. When injecting a series containing e.g. 1, 2, 4, 8 and 16 μl of calibration solution one should always get the same result independently of the injected amount. If there is too little DPA found, when injecting small amounts, this is a sign that the column does not work properly. DPA is the compound mostly affected, due to its basicity. To avoid this problem, described in paper II, the active sites that absorb the DPA can be made inactive by adding a small amount of another amine to the mobile phase, or by using a so-called end capped column. Here the active sites in the column have been blocked by a neutral substituent.

During the decomposition of NC the NO2 released will form acids. Due to internal reaction also NO will be produced leading to the formation of both nitrite and nitrate. Using a modified HPLC method, based on a C18 column, using acetonitrile with a water solution containing a quaternary ammonium salt, the determination of nitrite and nitrate can be made in the same analysis as when determining the stabilizers [52]. Normally the nitrite and nitrate do not appear until the main stabilizer has been consumed.

A storage of a propellant at different temperatures e.g. 50°, 65° and 80°C, and analysing the extract after different storage time will give valuable information about reaction kinetics. It was found (paper I) that the activation energy, $E_a$, was 122.0 kJ/mol meaning an acceleration of 4.3 when raising the temperature by 10°C.

It was also found that the reaction order changed considerably with temperature.
<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Reaction order ( n )</th>
<th>Acc. faktor/10°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.46</td>
<td>4.1_{50-65°C}</td>
</tr>
<tr>
<td>80</td>
<td>0.35</td>
<td>3.6_{65-80°C}</td>
</tr>
</tbody>
</table>

Reaction order, \( n \), varies linearly with temperature:

\[
\begin{align*}
\text{n} &= -8.33 \cdot 10^{-3} t + 1.01 \\
(R=0.998)
\end{align*}
\]

meaning that \( n = 1 \) at \( \approx 0°C \) and \( n = 0 \) at \( \approx 120°C \). This probably indicates that a diffusion problem exists so that liberated NOx can’t reach the DPA and its derivatives as there is only one DPA on 50 NC-units [16] with the amount DPA normally added to the propellant. At lower temperature the diffusion plays a minor role as diffusion is not very sensitive to temperature. \( \text{E}_a \) for diffusion is about 50 kJ/mol. The diffusion problems might also be the reason for the change of acceleration factor. The higher the temperature the more NOx is liberated but all of it does not reach the DPA due to diffusion problems.

5.3 FTIR

This method has proved to be a very useful tool for analysis of most organic and inorganic compounds. This is a very fast method of analysis that can give valuable chemical information. Normally a result is obtained in a couple of minutes if the sample preparation has been done in the proper way. The use of the method is discussed in [53]. Here several examples are given, showing how the method can be used in the explosives industry e.g. for analysis of suspected lead azide, residues in a cannon barrel (turning out to be KCN), finding amount TNT in octol, find the penetration depth of dibutylphthalate in a propellant. Another interesting application shown in [53] is the determination of the amount of nitrogen in NC using FTIR in combination with chemometry. However, at that time the chemometric software was not fully developed. Thus the method was very cumbersome and time consuming to use. Despite of this a crude correlation between samples containing different amounts of nitrogen was obtained.

Gases produced in NC during ageing are easily analysed in a 10 cm gas cell. An analysis of gas from an aged propellant is shown below in Fig. 5.
An interesting thing with the example shown in Fig. 5 is that the storage was performed in a microcalorimeter flask, volume 3 ml, from which the gas is taken into the gas cell (paper III). Thus very little gas is needed to get a sufficiently good spectrum. The other peaks observed in Fig. 5 also belong to the gases mentioned.

5.3.1 FTIR with chemometry

Using a modern chemometric programme (like Sirius from “Pattern Recognition Systems A/S” in Norway) has made it possible to determine e.g. the content of stabilizer in a propellant, (paper IV).

Introduction to chemometry

Using FTIR together with a chemometric method has proved to be a very strong combination for the study of small chemical changes. Normally when studying dissimilarities between different samples it can be sufficient to compare spectra and visually note the changes that have taken place. One example, is the conversion of diphenyl nitramine into 4NDPA, Fig. 6 (from paper V).
This experimental observation is contradictory to the findings proposed by Hughes [54] according to which mainly a 2-nitro compound is to be expected. The spectrum of 2NDPA is shown at the bottom in Fig. 6. The difference compared to 4NDPA in Fig. 6 is quite obvious.

The formation of a nitramine and its subsequent transition into a nitro compound is discussed more in detail under 6.1 Reactions in Nitro-cellulose.

When the changes are subtler it might be very difficult to observe the differences between the spectra. If the two spectra from different samples are of good quality one might get a good result by subtracting the spectra. However, due to light scattering and the subsequent wavenumber shift, a distorted derivative looking spectrum is usually obtained with this method.

One way to overcome this problem, and at the same time improve the sensitivity quite considerably, is to use a chemometric method to enhance spectral differences. However, in order to get reliable results it is important to keep the time of analysis short, i.e. not using too many scans per analysis or too high resolution since this prolongs the time of analysis and hence the time the sample is exposed to water from the atmosphere. With higher resolution the spectra also contain more noise. A resolution of 8 cm⁻¹ is normally sufficient. Multiple scatter correction is a mathematical correction of the spectra that minimises spread due to background effects. It is recommended to apply this correction on spectra before multivariate analysis.

Figure 6  IR-spectra of diphenyl nitramine and references of 4NDPA and 2NDPA
The strength of chemometry is shown in the example below using acetone, 3 and 6%, in water.

To the left are the spectra of various amounts (0, 150, and 300 μl) of acetone in 5 ml of water. Note the small peaks from acetone around the 1640 cm⁻¹ peak from water.

To the left is the resulting chemometric spectrum (target coefficient plot). The target coefficient plot is explained in paper V. (The wave numbers given are only indicative.)

In Fig. 7 the IR spectrum of pure acetone is shown. In the chemometric spectrum an exact correlation is not obtained with the pure compound as the water gives a shift to the peaks from acetone. It is also seen that the concentration of water has decreased, as a negative water peak has been visible at “1640” cm⁻¹ in the target coefficient plot. As acetone concentration increases, water concentration is lowered.

No peaks are seen from the CH-stretch around 2900 cm⁻¹ because these peaks are lower than normal as the cell used for the analysis, the Circle...
Cell®, is an ATR-cell (Attenuated Total Reflection). With this method the beam penetration depth \(d_p\) increases with increasing wavelength. 

This can be mathematically corrected for. Most software packages offer ATR correction routines. The difference between a transmission spectrum (top) and a sample measured with ATR is shown in Fig. 8.

![Figure 8 Comparison of transmission spectrum and ATR spectrum (Polystyrene)](image)

How does the chemometric method work?

Chemometry is not chemical in its nature but should be looked upon as an application of mathematical statistics on a chemical problem. One of the applications is called Multivariate Analysis (MA). This method is not used only by chemists but also e.g. by demographers, economists and meteorologists. The main issue is that a large amount of data can be treated where it is normally difficult to distinguish relevant information. It is thereby possible to find significant variables which make it possible to systemise or predict properties of an unknown sample – in the case of propellants e.g. chemical changes or changes in amount of stabilizer (discussed in paper IV), [55].

There are several types of MA e.g. principal component analysis (PCA), fractional design, and partial least square regression (PLS). Using FTIR to analyse a propellant gives an IR spectrum where every wave length measured is a variable. Measuring between 4000 – 600 cm\(^{-1}\) thus gives 450 variables when using a resolution of 8 cm\(^{-1}\).
Using the PCA method no linear regression is made. Instead one tries to identify variables in a big population that are connected. Usually the PCA method is used at the beginning of a chemometric experiment to group or systemise data. An example of this is the case where a couple of unknown propellant samples shall be identified. After analysis with e.g. FTIR, a spectrum of each sample is obtained. Application of the PCA method to these samples gives a graphical display of how they are correlated to each other. This might look as in Fig. 9. If there are 450 wave lengths (variables) measured, each point in Fig. 9 represents a sample plotted in a 450 dimensional space.

![Figure 9 Illustration of a PCA analysis.](image)

From the diagram three types of propellant can be identified. The four samples that lie outside these groups could be mixtures of the three, however, with no linear assignment of the mixing ratio.

Real samples of a single base and a double base propellant – both have participated in a storage test at elevated temperature - looks according to Fig. 10.
The two propellants fall in different groups. The change caused by ageing is seen in the curved distribution of the samples.

Partial-Least Squares, PLS

PLS means a modelling of variables present to produce a series of responses (e.g. concentrations) by using a least square regression in matrix form. This can not be done by hand and thus has to be performed by a computer and a suitable computer programme.

Decomposition by means of the PLS method has so far been used mostly for calibration. For this purpose, PLS represents an alternative to established approaches to regression. The method aims at a decomposition of X-space into components, which better describe another block of variables (Y-space) than, e.g., principal components. In the X-space the variables might covariate (e.g. weight and height of a man covariate since they are strongly correlated). In the Y-space no such correlations exist.

Using PLS the programme creates a number of principal components (PC). To illustrate this Fig. 11 has only three variables X, Y and Z forming a coordinate system in three dimensions. Looking at the data swarm (left part...
of Fig. 11) one might intuitively fit a line through the swarm (middle part of Fig. 11) and that this line would describe the data swarm almost as well as the original 3 variables.

Mathematically one searches for the line that gives the best fit to all the points using the least square principle. We search for the line that minimizes \( \Sigma(e_i)^2 \). Fig. 11 right part.

Here a normal linear regression can be performed that only minimises the deviation in direction Y. This gives a representation in the form:

\[
y = kx + l \text{ (equation for a straight line)}
\]

If instead the deviation is to be minimized in both X- and Y-directions, according to a Pythagorean minimization (projection), a principal component (PC) is obtained. The projections of the points (objects) on the PC create "scores" (= t), coordinates on the line that represents the PC. The PC is a reduction of many variables to one "super variable".

The method with PC intends to give a description of a data table in terms of uncorrelated new variables, principal components.

Using the PCs we can describe the variables X, Y and Z (or better X₁, X₂ and X₃). If we look at X₁, X₂ and X₃ as a matrix \( X \), a simplification can be made:

\[
X = \text{direction} \times \text{scores} + \text{residuals} \text{ (compare with equation for the straight line)}
\]

Direction is what is called "weights" or "loading" (= w)

\[
X = w \ t \text{ (+ residuals/ noise )}
\]

where \( w \) and \( t \) can be looked upon as vectors (or matrixes).

\( t \) (scores) is a measure of variations between the samples ("score plot = map of samples").

---

Figure 11  Illustration of how PC1 is created

Data swarm  Data swarm with PC  Projections of points onto a PC
\( w \) (loadings) describes how the variables are connected. (“loading plot = map of variables”). (See Table 2, at the end, explaining the data matrix).

These vectors can in most chemometric softwares be plotted separately as a score or loading plot. Score or loading is plotted against the principal components (one at a time, preferably against PC1). The result looks similar to what is seen in Fig. 11. The different variables or samples are grouped in clusters or spread in a certain direction depending on their properties. If only statistical noise is present the points should be randomly spread in the diagram.

If a too large residual is obtained (determined by the software) another PC has to be calculated. This is orthogonal to PC1 and in the direction with the second largest variance. Here new \( t \) and \( w \) are obtained, (Fig. 12). With this operation all information has been processed and been described by two principal components, if the programme decides this. If a third PC has to be calculated it is orthogonal both to PC1 and PC2 and lies in the direction of the third largest variance.

All information available in the variables \( X_1, X_2 \) and \( X_3 \) has been explained with 2 PCs. If we only have noise in our measurements, no systematic information is present, and we get many PCs from our calculations - in the worst case as many PCs as there are variables or samples, depending on which is the smaller one.

With these two “super variables” the information from 450 variables in an IR-spectrum, mentioned earlier, have been explained. What we see is a projection from a 450 dimensional space down onto two dimensions.
Normally one strives for as few PCs as possible, preferably 3, as with more PCs problems arise with linearity and, because of this, inferior prediction of unknown samples.

Another fact to remember is that low quality measurements give corresponding bad chemometric results. One cannot save a bad laboratory job by using chemometric methods. Here the sentence “GIGO, Garbage In Garbage Out” is valid.

In the measurements made, IR spectra have been used to quantify unknown amounts by absorbance measurements. The absorbance for a compound is concentration dependent according to Lambert-Beers law:

\[ A = \varepsilon \cdot b \cdot c \]

where \( \varepsilon \) = extinction coefficient at the given wavelength, \( b \) = sample thickness and \( c \) = concentration. In an IR-spectrum the absorbance is measured at different wave-lengths. The absorbance thus can be considered as a vector \( A \).

Consequently \( \varepsilon \) will be an extinction matrix, and \( b \) can be set equal to 1 if the sample thickness is constant.

This gives:

\[ A = E \cdot C \]

where \( C \) is the concentration vector

\( A \) in our case is the same as the matrix \( X \) above. This gives the relation:

\[ E \cdot C = A = t \cdot w \]

With the chemometric programme \( t \) and \( w \) can be determined for the samples in the calibration set and be related to \( C \) (scores and loadings). From this operation the predicted values is obtained for the unknown concentrations with standard deviation and limits for “outliers” e.g. samples, which for some reason do not fit the model.

Finally the programme gives a correlation between measured and predicted values in the form of an xy-plot. In this model unknown propellant samples can be evaluated regarding the concentration of stabilizer (paper IV).

5.4 MICROCALORIMETRY

The microcalorimetric method is based on a heatflow calorimeter with a very high sensitivity. This implies that chemical reactions with very slow rate can be monitored. The micro calorimeter (MC) used (Thermometric “2277
Thermal Activity Monitor”) has a very high temperature constancy in the thermostating bath (10^{-4} °C or better), which explains the high sensitivity. (According to STANAG 4582 the method is also called HFC, Heat Flow microCalorimetry).

In practice a reaction heat around 1 μW/ g can be measured with acceptable accuracy. 1 μW/ g is typically the power given off continuously by a propellant at a decomposition rate of 1%/ year.

**About MC and Shelf Life Work**

MC is an important tool to use when determining the ageing behaviour of a propellant. This is due to the fact that MC measures the directly critical factor for the storage safety, namely the evolution of heat. Paper I demonstrates that the heat generation in NC precedes the weight decrease (caused by the heating). Using MC one can study the rate of propellant degradation at some elevated temperature for certain duration, e.g. 70°C for 10 days. This will give a window to look into the future to see how the propellant will behave during the coming ≈10 years at normal storage temperature.

The heat released is of vital importance especially when storing large amounts of propellants. This is because the heat generation for a certain volume of the stored propellant might exceed the heat loss, leading to a gradual increase in the temperature that eventually might cause an ignition. This can happen even when there is a certain amount of stabilizer in the propellant. MC data obtained can also be used as input for safety calculations.

The increased heat evolution when the stabilizer has been consumed can be seen with MC. This heat evolution might eventually lead to a run away reaction. When such a reaction takes place in an ammunition store a fire or an explosion will often occur [51]. When the stabilizer has been depleted a so-called autocatalysis will occur, (Fig. 15).

MC is thus a good method for surveillance testing of ammunition. The drawback is that it is rather time consuming with observation times of 1 week or more. This severely affects the sample throughput since normally many thousands of samples have to be analysed every year.

MC measurements on the propellant at three different temperatures (e.g. 80, 70, and 60°C), Fig. 13, give an experimental base for determining the activation energy, E_a, for the propellant degradation using the Arrhenius equation.
\[ k = A \cdot \exp \left( \frac{-E_a}{RT} \right) \quad \text{or} \quad \ln k = \frac{-E_a}{RT} + \ln A \quad (y = kx + 1) \]

where A is the pre-exponential factor and k is the rate constant.

According to this equation a plot of \( \ln k \) vs. \( 1/T \) should result in a straight line from which \( E_a \) can be calculated from the slope, Fig. 14, using the equation \( E_a = -R \cdot \text{slope} \).

Reaction rates (or the proportional heatflow data) obtained from microcalorimetric experiments can often be used as a substitute for the rate constant in the Arrhenius equation without introducing significant errors. This is due to the fact that reactant concentrations are normally changing extremely slowly, at the low heatflow levels used in microcalorimetric measurements, making the reaction rate and rate constant proportional quantities, and thus to equivalent quantities in Arrhenius plots.

\( E_a \) from the example above is 110 kJ/mole and the linearity is good with \( R^2 = 1 \).

In the shelf life work not only propellants are interesting. Also the stability of pyrotechnic compositions can be supervised. Since these are normally sensitive to moisture, it is very important to determine the rate of water ingress into a construction and how soon the pyrotechnic composition will be consumed to such a degree that it no longer works properly [56].

MC can be used to measure the permeability coefficient (K) of water through seals (e.g. o-rings, gaskets)
under realistic conditions. K is used as input data for the water vapour ingress calculating programme “HUMID” based on Flick’s laws. [56] The reaction rate between water and the pyrotechnic composition can also be determined by MC.

Another important MC application is compatibility studies where materials used together with e.g. explosives are tested for chemical and physical interaction. The technique allows rapid determination of the compatibility of new explosive/ material combinations. The experiment can be carried out either with direct surface contact between the components or with separated components, to make it possible to distinguish between surface and gas phase interactions [57].

MC was used to show (paper V) that an extracted green NC sample, stored 24 days at 70°C prior to extraction, could be stored 70 days at 70°C before autocatalysis occurred for the extracted sample.

![MC used to study time to autocatalysis for extracted NC samples](image)

Figure 15  MC used to study time to autocatalysis for extracted NC samples

MC measurements on other extracted samples (stored 1 – 8 days at 70°C before extraction) described in paper V resulted in the curves seen in Fig. 15, where the peaks represent the autocatalytic reaction. (See also Fig. 16.)

5.5 UV SPECTROSCOPY

UV spectroscopy is a useful analytical technique used as a standard detector in HPLC where normally only a single wavelength is used e.g. 225 nm. However, using a more complete UV-region between 200 – 500 nm will
greatly facilitate sample identification. An UV spectrum of a compound is sensitive to the chemical environment both in the molecule and around the molecule (solvent effect): Depending of the substituent and the environment some different shifts of the wavelength and the intensity will occur. This technique will be discussed in conjunction with the analysis of green NC.

Definitions

CHROMOPHORE
A covalently unsaturated group responsible for electronic absorption (for example C≡C, C=O, and NO₂).

AUXOCHROME
A saturated group which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption maximum (for example, OH, NH₂, and Cl).

BATHOCHROMIC SHIFT.
The shift of absorption to a longer wavelength due to substitution or solvent effect (a red shift).

HYPSOCHROMIC SHIFT.
The shift of absorption to a shorter wavelength due to substitution or solvent effect (a blue shift).

HYPERCHROMIC EFFECT.
An increase in absorption intensity.

HYPOCHROMIC EFFECT.
A decrease in absorption intensity.

5.6 NMR
Proton NMR (Nuclear Magnetic Resonance) was used to determine whether aged extracted nitro-cellulose contains any aromatic component. NC being a aliphatic compound should give peaks between 1 – 4.5 ppm. However, an aromatic compound will give peaks between 6.5 – 8 ppm.

In paper V lines of low intensity were observed for green NC in the aromatic region. These lines were not strong enough to allow an identification of the green substance but pointed towards the presence of an aromatic compound.
6 Reactions

6.1 Reactions in Nitro-cellulose

The mechanism normally agreed upon is mainly attributed to the unstable nitrate ester groups in the nitro-cellulose polymer. (Bonding energy 155 kJ/mole for –O-NO₂ in comparison with C-ONO₂, 238 kJ/mole [11]). The initial step of the degradation consists of a breakage of the nitrate ester group and the liberation of free NO₂ that is very reactive due to its unshared electron, with radical properties, and to generation of nitrating and nitrosating agents. The liberated NO₂ also forms acids with the water present that accelerates the degradation due to acid hydrolysis. The alcoxy radical (RO⁺) left in the polymer reacts further in a series of steps that eventually leads to chain fission [4, 5, 8]. The dominating products due to the decomposition of NC are carbon oxides, nitric and nitrous oxides, nitrogen, methane, formaldehyde and water. To take care of the liberated NO₂, a stabilizer is added to the propellant. The stabilizer (e.g. DPA) will react faster with NO₂ and its reaction products than NO₂ reacts with NC itself.

An extensive review on the decomposition of simple aliphatic mononitrates and a few of the dinitrates and polynitrates has been performed by Boshan [18].

The nitrate ester can be hydrolysed by a nucleophilic substitution reaction (predominates in neutral and alkaline media) or by elimination of α- or β-hydrogen. A suggested mechanism describing the general features of the thermal decomposition of a nitrate ester includes fission of O-NO₂ bonds and radical reactions between lower alkyl radicals and NO₂ with the formation of NO. The mechanism is supported by the observed lowering of the rate by addition of NO₂ that is explained by the fact that NO₂ accelerates the reverse of the initial –O- NO₂ fission reaction. Similarly, the inhibiting effect of O₂ on the rate involves oxidation of NO formed to give NO₂. This oxidation of NO or NNODPA explains the initial heat evolution frequently observed when studying a propellant in MC (paper III).

Fifer [10] made an extensive review on the Chemistry of Nitrate Ester and Nitramine Propellants.
A simple explanation for the unusual kinetic parameters of NC is proposed by the author:

The condensed-phase reaction is inhibited by NO₂ with the inhibition decreasing with increasing temperature. Mobility is severely limited for the newly formed NO₂ molecule in the solid propellant; most of the time it will recombine to regenerate the nitrate group. (This is supported by the results presented in paper I). This implies that the measured reaction rate is slower than the rate at which dissociation takes place. The inhibiting effect of the recombination reaction diminishes with increasing temperature. This is due to increased mobility following the temperature rise and/or the expected tendency for the NO₂ to undergo an oxidation-reduction reaction rather than a recombination reaction. (Recombination reactions have lower E_a than other types of reactions; in the gas phase they frequently have negative E_a). The net result is that the reaction has a large apparent activation energy, which in turn necessitates a high-frequency factor to account for the experimentally measured rate.

Hughes [54] also discusses the formation of nitramines. It has been found that phenyl nitramine, methylphenyl nitramine, and similar aryl nitramines undergo rearrangements upon treatment with aqueous strong acids, or with hydrogen chloride in organic solvents, to yield mainly o-nitroaniline or its derivatives, sometimes with a small amount of p-nitroaniline or its derivatives.

It was suggested [54] that the aromatic C-nitration with strongly acidic nitrating agents starts with a N-nitration followed by an acid catalysed intramolecular rearrangement of the N-nitro-compound to the C-nitro-compound (indirect nitration).

Some other hypotheses also supported by the experimental evidence are the following:
In terms of this scheme, instead of assuming 'indirect nitration', e.g. that reaction (3) really is (2+4), it is also possible to assume an 'intermolecular rearrangement', that is, that (4) is really (1+3). A third, alternative hypothesis is equally open, namely, that both the preceding assumptions are incorrect, and that reactions (3) and (4) both exist as independent processes.

It was found [54] that of the three suggested hypothesis the third one was the most probable one. That is, a nitrating agent can be produced under the conditions of rearrangement, but the rearrangement is not dependent on it.

It is of interest to consider why an intramolecular isomerisation plays the important role in the acid-catalysed nitramine rearrangement, in contrast to the chloramine, in the diazoamino-aminoazo, the Fischer-Hepp, the Hofmann-Martius, and the aryl-hydroxylamine rearrangements. It would seem that the nitramine rearrangement has an especially facile intramolecular route, denied to the other rearrangements. A possible scheme is:

\[
\begin{align*}
\text{R}^+ & + \text{N}_2\text{O}^{-} \rightarrow \text{R}^+ \text{N}^+ \text{N}^- \text{O}^- \\
\text{R}^+ \text{N}^+ \text{N}^- \text{O}^- & \rightarrow \text{R}^+ \text{N}^+ \text{O}^- \\
\text{R}^+ \text{N}^+ \text{O}^- & \rightarrow \text{R}^+ \text{N}^+ \text{H}^+ \\
\text{R}^+ \text{N}^+ \text{H}^+ & \rightarrow \text{R}^+ \text{N}^+ \text{O}^- \\
\text{R}^+ \text{N}^+ \text{O}^- & \rightarrow \text{R}^+ \text{N}^+ \text{H}^+
\end{align*}
\]
Schroeder [33] mentions oxidation of an N-nitrosamine to the N-nitramine with subsequent rearrangement, although he found no evidence for reactions of this nature.

Hollingworth [20] also mentions diphenyl nitramine as an intermediary compound, which is transformed into 2NDPA. Nitramine can be formed from nitrosamine and \( \text{N}_2\text{O}_5 \).

### 6.2 Reactions in stabilizer

Many different reactions take place in DPA.

Weil [58] studied the reaction of a stable organic free radical with \( \text{NO}_2 \) and found that the \( p \)-nitration occurred in two distinct steps.

The reaction between NO and primary and secondary amines was studied by Drago [59] and was found to result in ammonium salts with the NO acting as a Lewis acid. Some of the reactions were exothermic and resulted in violent explosions.

Mrzewinski [40, 41] has performed several ESR (Electron Spin Resonance)-experiments indicating that DPA and its derivatives form radical intermediates in the course of inhibiting radical oxidation processes of nitro-cellulose (NC). The formation of a charge-transfer complex of NC and DPA with the amine as a donor and the nitrate ester as an electron acceptor is suggested.

Alm [60] performed an extensive investigation of the reaction of DPA and some of its derivatives with NO and \( \text{NO}_2 \) during different experimental conditions. The reactivity with \( \text{NO}_2 \) appeared to be unaffected by the presence of oxygen but increased in the presence of water. It was generally suggested that differences in reaction mechanisms possibly could explain the results. In closed systems it was reported that the reactivity of \( \text{NNODPA} \) with \( \text{NO}_2 \) decreased in the presence of oxygen. However, the results appeared to be uncertain.

Curtis [34] studied the stabilization mechanisms of DPA derivatives. It was found that N-nitroso-DPA is a weak stabilizer but that direct nitration is insignificant in propellants containing DPA and its unnitrosated nitro derivatives, which are more reactive towards nitrogen oxides. As with other studies conducted at elevated temperatures (e.g. 80°C), it was claimed that the behaviour at ambient temperatures might be too different for meaningful comparisons or for prediction of service-life to be made. A general mechanism describing the stabilisation mechanism is presented.
Bergens [4] studied the stabilisation mechanisms of DPA in NC. Based on experimental data supplied by Curtis [34] of DPA and its derivatives a model was suggested including an unknown compound (possibly a complex between NC and DPA as suggested by Mrzewinski [40]). Considerations were taken to the importance of alcoxy radicals formed during degradation and the formation of NOx and their secondary reactions. The model was successful in describing the concentration of DPA and it’s derivatives versus ageing time.

Sammour and Bellamy [61] studied the reactions of stabilizer solutions in acetonitrile with NO2, HNO2, and HNO3 - the normal degradation products of nitrate esters - and found different reactivities between p-NMA, 2NDPA and 4NDPA. In real systems there is a possibility of several competitive reactions of the stabilizers with the complex range of potential reactants such as nitrogen oxides, nitrogen acids, radicals, and other species formed during the decomposition of propellants.

6.3 Reactions between NC and DPA

In paper V it was shown that 10% of the stabilizer added to NC had disappeared. An extended investigation was made to explain this apparent “loss” of stabilizer. A possible explanation was a reaction between NC and DPA or some type of physical bonding of DPA to the nitro-cellulose, which FTIR indicated. Only one sample was studied in paper V, a sample that had been stored for 24 days at 70°C before extraction. This extracted sample was subsequently stored at 70°C in a micro calorimeter ampoule. The sample showed a remarkable stability and did not reach auto-catalysis until 70 days after start of the storage, which means that the NC contains about 0.2% of bonded stabilizer. Other samples stored between 1 to 12 days at 70°C prior to extraction, were not analysed until after paper V was published. The results for these samples showed that the time to autocatalysis (T\text{autocat}) increases with the time the sample had been stored at 70°C before extraction.

The results from these extracted samples are summarised below in Fig. 16:

Time to autcatalysis raises linearly. Despite some uncertainty in T\text{autocat} due to the small amount of sample available, the correlation coefficient is high or \( \approx 0.98 \). When a small amount of NC sample is used, the time to autocatalysis gets longer as a certain concentration of NOx has to build up, which takes longer time in an ampoule only half full with sample.
6.4 Reactions according to paper III

The summary of some of the reactions in nitro-cellulose, presented in a modified form in paper III, is shown in Fig. 1.
7 Discussion

Methods used in the investigation
As previously mentioned the basic analytical methods used have been HPLC, FTIR and microcalorimetry. FTIR has been combined with chemometry and certain investigations have been made using also UV and NMR.

Results obtained compared to literature referenced
From HPLC investigations many interesting results are available. The most important information concerns the remaining amount of the stabilizer in the propellant. This is of vital interest for safety reasons [50]. If too little stabilizer is left the propellant might start to decompose rapidly eventually causing a fire or an explosion.

Also kinetic information concerning the reaction order can be gained (paper I).
From storage at different temperatures the temperature dependence and $E_a$ can be determined as described earlier.

However, a HPLC analysis should always have a reference to earlier analyses made on the same lot of the propellant. It is important to ascertain that the decomposition of the propellant proceeds at a rate that does not change with time: $d(DPA)/dt$ should be approximately constant down to a DPA concentration of 0.2% (Fig. 17).

Also, as pointed out in paper II, it is important to find out how long a propellant can be stored from a tactical point of view. Consumption of stabilizer means that the nitrogen content of the propellant is decreasing. This leads to a lowered initial velocity, $V_0$, of the projectile, as seen for the propellant analysed in paper II. Despite consumption of stabilizer it was found that the $V_0$-range valid for a new propellant is still fulfilled as long as all DPA has not been consumed. During the ageing there has been a continuous lowering of the $V_0$. From the literature cited it is obvious that there are many problems connected with the decomposition of NC. There are so many different paths the decomposition can take that a complete picture
of the decomposition probably can be obtained only under very specific conditions.

The mechanism for the transformation of DPA to NNODPA is still under debate. In paper V an approach was made to see if one of the paths for DPA to 2NDPA and 4NDPA could go via a nitramine, diphenyl nitramine. This compound has been mentioned by other investigators (Schroeder, Hughes, Hollingworth). In paper V different reaction paths were suggested:

One mechanism is the direct reaction between a NO₂ group in NC and DPA forming a nitramine. We suggest as a hypothesis that NO₂ will react as a radical not only at the 2- and 4-position of DPA, but also at the amine nitrogen, forming a nitramine (diphenyl nitramine, N-nitro-diphenylamine). This product is rather unstable and is further degraded to 2NDPA and 4NDPA and other derivatives. We also suggest that this nitramine could be formed from DPA and a nitrate ester:

\[
\begin{align*}
\text{DPA} + \text{NO}_2^+ & \longrightarrow \text{N-nitro-diphenylamine} \\
2\text{NDPA} + 4\text{NDPA}
\end{align*}
\]

The reaction above is in analogy with the reaction between an organic ester and ammonia where a primary amide is formed.[62]

\[
\begin{align*}
\text{H}_2\text{N} & \longrightarrow \text{CH}_3 \\
\text{H}_2\text{N} & \longrightarrow \text{CH}_3
\end{align*}
\]

A secondary amine should give a tertiary amide, and with nitro-cellulose, the ester of an inorganic acid, a nitramine could form.

\[
\begin{align*}
\text{O}_2\text{NOEt} + \text{HN}_2\text{O} & \rightleftharpoons \text{O}_2\text{N}-\text{N}_2\text{O} + \text{EtOH} \\
nitric\text{ acid ester} & \text{ diphenylamine} \text{ diphenyl nitramine} \text{ ethanol}
\end{align*}
\]

According to Welzel [63] the nitramine is unstable and transforms to 2NDPA and 4NDPA and also to DPA. This occurs through a homeolytic
split of the N-NO₂-bond whereby the NO₂-radical, through an intramolecular rearrangement, migrates to o- or p-position of the aromatic ring. The transformation of a nitrate ester to nitramine is a reversible process.

Another route to diphenyl nitramine could be the reaction between NNODPA and NO₂ (or N₂O₅) [20] according to:

\[
\text{NNODPA} + \text{NO}_2 \rightarrow \text{N(NO₂)DPA} + \text{NO}
\]

The NO, possibly formed, can, after oxidation to NO₂, react with DPA forming more NNODPA.

The search for N(NO₂)DPA has so far been negative. One possible reason for this is the low thermal stability of this compound. In an experiment it was shown that already after 4 days at 46°C it had been converted to 4NDPA according to IR-analysis, Fig 6.

From Fig. 6 it was clear that the main product formed from diphenyl nitramine is 4NDPA. The spectrum of 2NDPA looks quite different.

The finding of 4NDPA is surprising as another author [Hughes, 54] has found 2NDPA to be the main conversion product.

One fact, which has been neglected for a long time is: Using DPA as a stabilizer results in loss of stabilizer, Fig 17. About 40% of the stabilizer, including its derivatives cannot be recovered. More than 50 years ago Schroeder [33] addressed this problem and he says:

The greatest loss of DPA (and its derivatives) occurs during the period of depletion of DPA itself, and it might be concluded that all of the loss occurs by some reaction of DPA. However, experiments have shown that the less highly nitrosated and nitrated derivatives may also account for some of the loss.

From [33] is seen that the total recovered amount of stabilizer and its derivatives goes up after NNODPA has been depleted. No correlation of this fact to NNODPA was made. Schroeder continues:

Because the blue compounds contain the cation of diphenylamine blue, it is evident that three molecules of DPA have been combined with a carbon atom from some source, presumably NG or NC, to give the triphenylmethane.

Such a reaction would be expected to occur in steps so that the presence of intermediate compounds, which contain one or two diphenylamine molecules rests attached to a carbon atom, is to be anticipated. Although there is no evidence for the formation of such compounds, it is not unreasonable to assume that some reaction occurs between the DPA and the NG and/ or NC to produce the brown colour (in work described in paper V the propellant turned green) of the aged powder. It is suggested that some unknown compound capable of reconversion to simple nitro derivatives can be formed during initial conversion of DPA in order to explain the minor decrease of the total amount of DPA detected after severe ageing.
In our case there should not be any cation of diphenylamine blue as there are no chloride ions present. No blue compound can be extracted with methanol from the green NC used for the experiments in paper V. (This NC was manufactured by Bofors).

However, after further ageing of an extracted sample an unidentified yellow compound could be extracted (paper V). The results from the storage of extracted NC samples at 70°C clearly demonstrated that stabilizer is bonded to the NC. The longer the sample had been stored with DPA before the extraction the longer the time to autocatalysis was. In fact a linear correlation with R=0.98 was obtained, see Fig. 16.

Bergens suggested an intermediary compound [4]. Bohn [44-46] showed this was not necessary using a better kinetic model. If the intermediary compound exists could it be the green compound in NC?

The question remains: What is the non-extractable green compound giving stability to extracted NC? Has it something to do with the compounds suggested by Welzel [63]?

\[
\begin{align*}
\text{H} & \quad \text{C}_6\text{H}_5 \\
\text{p-(C}_6\text{H}_5\text{)}_2\text{N-C}_6\text{H}_4\text{-N-C}_6\text{H}_5 & \quad \text{p-(C}_6\text{H}_5\text{)}_2\text{N-C}_6\text{H}_4\text{-N-C}_6\text{H}_4\text{-NHC}_6\text{H}_5 - (\text{p})
\end{align*}
\]

Extended interpretation of results from paper V

The information in paper V is path breaking new information, with the help of FTIR and chemometry, about the nature of the compound giving the green
colour to the NC. However, more information can be obtained from the analyses performed in paper V e.g.:
- Which chemical compound is bonded to the NC backbone.
- Confirmation of this by UV spectroscopy.

In paper V a resulting IR spectrum in the form of a “Target coefficient plot” Fig. 18, was shown. The only spectral interpretation made was to point out that this is the spectrum (referring to the positive peaks) of an aromatic compound.

![Figure 18](image.png)

The peak seen at 1490 cm\(^{-1}\) belongs to the asymmetrical NO\(_2\)-stretch in a nitro compound. Normal absorption range is 1550 –1500 cm\(^{-1}\) for an aromatic nitro compound. The asymmetrical NO\(_2\)-stretch in NC (a nitrate) is at a higher wavenumber, or 1650 cm\(^{-1}\) and gives a negative peak here, meaning disappearance of nitro-groups in NC.

The symmetric NO\(_2\)-stretch in a nitro compound at 1360-1290 cm\(^{-1}\) is hidden by the negative NO\(_2\)-peak from NC at 1280 cm\(^{-1}\) as they happen to be at the same wavenumber. However, the height of the negative peak observed is lower than normally observed when compared to the asymmetric NO\(_2\)-stretch in NC, indicating that a probable positive peak might be hidden here. A comparison of the spectrum in Fig. 18 in the range 1700 - 650 cm\(^{-1}\) with IR spectra from DPA and its three first derivatives (NNODPA, 2NDPA and 4NDPA) is shown in Fig. 19.

From these spectra, by comparing peaks present and absent, it can be confirmed that neither DPA nor NNODPA are present in the chemometric IR spectrum, Fig. 19.
The most likely compounds are 2NDPA and 4NDPA.

Creating a mixture in the ratio 1:1 of 2NDPA and 4NDPA gives a spectrum, Fig. 20, which is very similar to the result from the chemometric spectrum. Certainly there must be other compounds in minor amounts present. These can’t be identified here.
Most of the peaks in this mixed spectrum are found also in the chemometric spectrum.

The two peaks in Fig. 18 at 750 and 710 cm\(^{-1}\) represent the \(-\text{C-H out-of-plane bending bands.}\) As it happens the 1,2-disubstituted ring has a C-H band at 770-735 cm\(^{-1}\) and a 1,4 disubstituted ring has a C-H band at 860-800 cm\(^{-1}\). The latter band cannot be seen as the negative peak from the N-O stretch in NC hides it. 1,3 disubstituted or 1,2,3 trisubstituted compounds are also probable candidates but these compounds should also have a carbon-carbon out-of-plane bending mode around 690 cm\(^{-1}\). It is possible this band is absent or hidden.

The 1:1 mixture of 2NDPA and 4NDPA can also be interpreted as if 2,4’-dinitroDPA is present. A comparison between this compound and the chemometric spectrum yields an even better resemblance, Fig. 21, than for the 2NDPA-4NDPA mixture. This will be further discussed when analyzing the UV spectrum of green NC (Fig. 23).

![Figure 21 Comparison of chemometric IR-spectrum and an IR-spectrum of 2,4’-dinitroDPA](image)

The chemometric IR-spectrum obtained is a low resolution one and also a very limited spectral area (about 300 wavenumbers or 10% of a normal IR-spectrum) is covered. Thus only limited spectral information can be obtained. The only functional groups that can be identified are the nitro-
group and an amine band. However, a surprisingly good resemblance is seen between the two spectra in Fig. 21. An interesting piece of information is:

The fact that we get a spectrum of 2,4′-dinitroDPA shows that no bonding to the NC occurs via the aromatic rings of the stabilizer but rather via the nitrogen creating a tertiary amine. These compounds have a strong C-N stretch between 1360-1310 cm⁻¹. The absorption at 1341 cm⁻¹ could thus point to a tertiary amine. Unfortunately a secondary amine like 2NDPA, should also have a C-N stretching band in the same region (1350-1280 cm⁻¹). The “poly-DPA” compounds suggested by Welzel [63] are probably not involved according to the IR-results.

**Conclusion:**

The substance bonded to the NC can be a mixture of 2NDPA and 4NDPA in the ratio 1:1, or 2,4′-dinitroDPA. The last one is more probable. This should also explain the low yield of 2NDPA and 4NDPA in Fig. 17.

The green NC analysed by UV (paper V)

According to HPLC with a UV diode-array-detector we find the following absorption bands for 2NDPA, 4NDPA and 2,4′-dinitroDPA, Fig. 22:

In the UV-spectrum Fig. 23 (from paper V) of green NC two extra peaks (marked in Fig. 22) are found: one at 276.5 nm and one at ~430 nm.

If the peak at 430 nm (see Fig. 23) stems from 2NDPA, one would expect a peak 2-3 times higher from 4NDPA if we had a mixture 1:1 of these compounds. This is because when auxochromic groups (e.g. –NO₂) appear on the same ring as the chromophore (-NHR), both groups influence the absorption. The influence is most pronounced when an electron-donating group and an electron-attracting group are para to one other (complementary substitution). See the following examples: [64]
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-NO₂ Phenol</td>
<td>279</td>
<td>6.500</td>
</tr>
<tr>
<td>p-NO₂ Phenol</td>
<td>318</td>
<td>10.000</td>
</tr>
<tr>
<td>o-NO₂ Aniline</td>
<td>283</td>
<td>5.400</td>
</tr>
<tr>
<td>p-NO₂ Aniline</td>
<td>381</td>
<td>13.500</td>
</tr>
</tbody>
</table>

The expected absorption from 4NDPA should therefore be 2-3 times that from 2NDPA [64] and the resulting peak 2-3 times higher, when they are present in the ratio 1:1.

**Conclusion:** According to the UV-spectrum, Fig. 23, the compound causing the green colour of NC is not a mixture 1:1 of 2NDPA and 4NDPA.

A logical alternative is the compound 2,4´-dinitroDPA.

Further facts: Nothing in the extract from a sample being stored at 70°C after the first extraction absorbs at 276 or 430 nm according to HPLC with a diode-array-UV detector (paper V). Thus the compound in the green UV is bonded to NC and is not extractable.

The peak at 276.5 nm has not been identified so far, but an attempt is made below.

Figure 23  UV spectrum of green NC. From paper V.
The UV-spectra of 2N-, 4N- and 2,4´-dinitroDPA (Fig. 22) give interesting information. UV spectrum of the last compound is not just a sum of 2N- and 4NDPA. The general appearance is that 2,4´-dinitroDPA contains 3 peaks compared to two peaks each for 2NDPA and 4NDPA. The peaks at 261 and 263 nm have shifted down to 248 nm forming a single peak, which now is the most intense in the spectrum (Hyperchromic effect). As can be seen in Fig. 22 the 2NDPA peak at 438 nm has a blue shift from 438 nm down to 358 nm (Hypsochromic shift) and the 4NDPA peak at 400 nm has a red shift upwards (Bathochromic shift) to 417 nm. From reasons given above this, the most intense of the NO2-peaks, should be from the 4NDPA.

Compared to the UV spectrum obtained from green NC (Fig. 23), the spectrum of 2,4´-dinitroDPA in Fig. 22 has a better agreement with that result.

Thus in Fig. 22 the peak at 248 nm must have had a bathochromic shift to 276.5 nm and also undergone a hyperchromic effect since the intensity is much higher (effect from the chromophore -NO2 in NC?).

The small peak at 358 is not seen in Fig. 23 as it could be hidden in the tailing from 276.5 nm.

The peak at 417 nm might have undergone a bathochromic shift to 430 nm, Fig. 22.

Is the green compound chemically bonded to NC?

One drawback of the experiments described above is that no information has been obtained whether the green substance really is chemically bonded to NC. A way to find this out could be to dissolve the green NC and then precipitate the NC. If the precipitated NC still has the green colour and still has a long time to autocatalysis at 70°C then the green substance is likely to be chemically bonded to the NC.

A repetition of the storage of NC with 10% of DPA, for 10 days at 70° was thus initiated. Only one storage time was chosen as this was judged to give sufficient information. Additional samples with 10% 2NDPA and 10% NNODPA respectively were also prepared. The NC used for this experiment was not from Bofors (called NC Type I) but from a foreign source. This nitro-cellulose is called NC Type II.
However, after extraction of aged NC Type II with DCM, the NC/ DPA was no longer green but blue. This is different from the results described in paper V and indicates the formation of a compound different from 2,4’-dinitroDPA. Extracting the blue sample with methanol gave a blue solution and a faint green residue. (Photo 1). After evaporation of MeOH the blue solution gave a film that turned out to be NC. See IR-spectrum in Fig. 24.

This is not surprising as about 32% of the blue sample dissolved in methanol. In methanol only low molecular and/ or low-nitrated NC dissolves.

NC/ 2NDPA was red after storage and turned white upon extraction with DCM (Photo 1).

NC/ NNODPA turned brown-green after storage and was green after extraction with DCM. With methanol only a light yellow component (which contains NC according to FTIR) could be extracted. Dissolution in acetonitrile (ACN) gave upon precipitation a light green residue.

The blue solution from NC/ DPA/ methanol turned colourless or faint yellow upon addition of NaOH. A slightly more intense blue colour was obtained when HCl was added.

From the green NNODPA sample photo 1 left: NC with 10% DPA before extraction (green) after extraction with DCM (blue) and after extraction with MeOH (faint green).

middle: NC with 10% 2NDPA before extraction (red), after extraction (white).

right: NC with 10% NNODPA before (brown green) and after extraction (green) and after dissolution in ACN and precipitation with 2% CaCl₂ in water (light green).

However, after extraction of aged NC Type II with DCM, the NC/ DPA was no longer green but blue. This is different from the results described in paper V and indicates the formation of a compound different from 2,4’-dinitroDPA. Extracting the blue sample with methanol gave a blue solution and a faint green residue. (Photo 1). After evaporation of MeOH the blue solution gave a film that turned out to be NC. See IR-spectrum in Fig. 24.

This is not surprising as about 32% of the blue sample dissolved in methanol. In methanol only low molecular and/ or low-nitrated NC dissolves.

NC/ 2NDPA was red after storage and turned white upon extraction with DCM (Photo 1).

NC/ NNODPA turned brown-green after storage and was green after extraction with DCM. With methanol only a light yellow component (which contains NC according to FTIR) could be extracted. Dissolution in acetonitrile (ACN) gave upon precipitation a light green residue.

The blue solution from NC/ DPA/ methanol turned colourless or faint yellow upon addition of NaOH. A slightly more intense blue colour was obtained when HCl was added.

From the green NNODPA sample...
only a yellow component could be extracted with methanol. NC remained green. The extraction residues, blue from DPA/DCM, and faint green after wash with MeOH, green from NNODPA/DCM and white from 2NDPA/DCM were stored in MC at 70°C until autocatalysis occurred.

Results from the storage in the MC at 70°C are shown in Fig. 25.

![Figure 25](image)

**Autocatalysis occurred after:**

- DPA light blue sample (dissolved/precipitated) \(~4\) days
- DPA blue sample washed with MeOH (turned faint green) \(17.3\) days
- DPA blue sample \(26.7\) days
- DPA green sample (from paper V. Ref. value NC Type I) \(37.0\) days
- 2NDPA white sample \(8.3\) days
- NNODPA green sample dissolved/precipitated \(11\) days
- NNODPA deep green sample (storage aborted) \(>90\) days

**DPA.** Time to autocatalysis in MC at 70°C for extracted, dissolved and precipitated NC, with initially 10% DPA, was about 4 days, a marginally increase compared to 2.7 days for pure NC. Probably no extensive chemical bonding. See discussion below.

**NNODPA.** Time to autocatalysis in MC at 70°C for dissolved and precipitated NC with initially 10% NNODPA was 11 days. Probably some chemical bonding. See discussion below.

The different chronological treatments of the samples and the results obtained are summarised in Table 1.
Table 1  Compilation of results from experiments with NC + DPA/ NNODPA/ 2NDPA

<table>
<thead>
<tr>
<th>Sample NC + stab</th>
<th>Time (d) at 70° before extraction</th>
<th>Colour of NC after extraction</th>
<th>Time to AC (d)</th>
<th>Extract MeOH</th>
<th>Solvation in ACN</th>
<th>Precipitated NC in 2% CaCl₂</th>
<th>Time to AC (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC (Bofors) Type I DPA</td>
<td>10</td>
<td>Green</td>
<td>Green</td>
<td>37</td>
<td>No colour</td>
<td>No test</td>
<td>No test</td>
</tr>
<tr>
<td>New NC of Type II DPA</td>
<td>10</td>
<td>Green. Gave yellow solvent</td>
<td>Blue. Gave yellow solvent. Faint blue residue with MeOH</td>
<td>27</td>
<td>Blue solution 32% NC dissolv, Light green residue</td>
<td>Yes</td>
<td>Faint blue NC 1&lt;sup&gt;st&lt;/sup&gt; Blue solution contains NC. 2&lt;sup&gt;nd&lt;/sup&gt; does not</td>
</tr>
<tr>
<td>New NC of Type II NNODPA</td>
<td>10</td>
<td>Brown-green</td>
<td>Dark green</td>
<td>&gt;90 (No AC)</td>
<td>Yellow solution Green residue</td>
<td>Yes</td>
<td>Light green NC. 1&lt;sup&gt;st&lt;/sup&gt; Green solution contains some NC. Also 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>New NC 2NDPA</td>
<td>10</td>
<td>Red</td>
<td>White</td>
<td>8</td>
<td>No test</td>
<td>No test</td>
<td>No test</td>
</tr>
<tr>
<td>Ref. pure NC (Bofors)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Time/ event axis**

**Comments:**
The extracted NC (Type I) studied in paper V is more stable (37 days to AC) compared to the one of Type II tested here (27 days to AC).

Extracted NC Type II which contained 10% NNODPA is very stable, >90 days to AC.

Extracted/ dissolved/ precipitated NC with DPA has low stability, 4.5 days to AC.

Extracted/dissolved/ precipitated NC with NNODPA has higher stability, 11 days to AC.

As mentioned the NC (Type II) used for the repetition test was not of the same type used previously. The first NC used (Type I) was manufactured by Bofors and had a N-content of 13.4%. The other NC was produced by another manufacturer and contains 13.25% N with 85% as high molecular NC.

Fully nitrated NC is 14.14% nitrogen per weight [10]. For NC containing an average of two nitrate groups per unit, the nitrogen content is about 11.1%. NC used in propellants commonly contains 12-13.2% nitrogen and
has therefore a significant number of unnitrated hydroxyl (-OH) groups randomly distributed along the polymer chain.

The results obtained show that general conclusions concerning the behaviour of NC cannot be drawn from a single batch of NC. This further complicates the understanding of NC chemistry.

The statement made earlier: “The sequence of reactions (in NC) is probably so complex that it is unlikely that the total mechanism leading to gaseous products will ever be completely understood” seems very true, indeed.

Chemical bonding of a stabilizing compound to NC

The results from the precipitated NC do not give a clear yes or no concerning chemical bonding to NC. A bonding seems to occur for NC stored with NNODPA.

Where in the transformation from DPA to NNODPA, 2NDPA and 4NDPA does this bonding occur?

From the test with 2NDPA it is clear that this molecule is not bonded to NC as a white NC is obtained when extracting an aged sample containing only 2NDPA. However, the time to AC has increased from 2.7 days (for pure NC) to 8 days indicating either bonding of a colourless substance or some 2NDPA not being extracted. About 0.01% should be sufficient to give the observed extra time to AC. It should also give the sample a faint orange/yellow colour.

No DPA, NNODPA, 2NDPA or 4NDPA was found with IR in the extracted NC Type I (Fig. 19). Also from the experiment above we know that neither DPA nor NNODPA bind to NC. Thus it seems like NNODPA should be the starting compound for bonding to NC and play a key role in the stabilization of NC.

In [33] was shown in a figure that the total recovered amount of stabilizer and its derivatives goes up after NNODPA has been depleted. No correlation of this fact to NNODPA was made. This is also confirmed from the test with pure NNODPA as a much more stable extracted NC is obtained compared to NC with DPA. Time to AC goes up by a factor 2.5 for extracted/ dissolved/ precipitated NC with NNODPA compared to DPA, Table 1.

The MC test on aged and extracted NC samples (Fig. 16) clearly shows that the longer the sample has been stored before extraction the longer the time to AC. The idea that dissolution of the extracted NC with subsequent precipitation with 2% CaCl₂-solution should give the answer to the question if there is a chemical bonding, doesn’t give a clean answer. The precipitated NC/ DPA or NNODPA, which loses some of its colour, has a longer time by a factor 2 - 4 to AC compared to pure NC. However the time to AC is shorter by a factor >6 compared to the extracted sample.
However, when the dissolved NC is precipitated not all NC is precipitated. A blue (from NC/ DPA) and a green solution (from NC/ NNODPA) remain. This solution contains NC pointing to the presence of low molecular NC.

The same was seen when trying to dissolve blue NC/ DPA in MeOH. 32% of the blue NC was dissolved and only a faint blue residue, with inferior stability (17 d compared to 27 d for the blue NC), was left. The blue compound thus acts as a stabilizer. The extra stabilizing effect is about a factor 3 compared to the faint blue NC.

The ability to be dissolved points to either a low molecular and/ or a low nitrogen containing NC. Thus it is natural that a shorter time to AC is obtained for extracted, dissolved and precipitated samples as most of the stabilizer bonded to low molecular NC is removed from the sample.

The conclusion drawn from these observations is that the bonding of 2,4´-dinitroDPA preferably occurs at the ends of the NC molecule. This is also the place where the degradation starts [23]. Since no chemical information has been obtained about the blue substance (from NC Type II/ DPA) and the green substance (from NC Type II/ NNODPA) it is not even sure these are of the same type as found with NC from Bofors with DPA.

This raises the question if the two different types of NC used have different chemistry and if the same type of stabilizer derivative is bonded to the NC backbone. This has not been possible to find out in this investigation.

Bonding to NC, mechanism

Since the bonding occurs after the NNODPA has been formed and the bonding is at the nitrogen in DPA the following mechanism is suggested:

The NO in NNODPA is oxidized to –NO₂, or a nitramine is formed from the direct reaction between NC and DPA. This unstable molecule soon will lose NO₂ leaving a free radical on N in DPA. This free radical then reacts with e.g. an alcoxyradical, formed in NC when a nitrate group is split off, thus forming a chemical bond to the NC-molecule. The reaction should be facilitated as the DPA is locked to the NC backbone as shown earlier.

If the bonding occurs at this stage in the reaction scheme of DPA, the intermediary compound, described by Bergens [4], should, if it exists, not be the compound giving the green/ blue colour to NC. This intermediary compound was introduced as something occurring in the reaction scheme between DPA and its transformation into NNODPA.
8 Conclusions

The methods described here provide good analytical tools to follow the degradation of nitro-cellulose. The degradation products formed from diphenylamine (DPA) during storage both at ambient temperature (safety control) and from accelerated ageing can be followed with HPLC. This is the standard method today. In paper IV the use of FTIR together with chemometry was shown to be a fast alternative method that gave the precision needed for safety control of propellants.

Study of aged NC (paper V) showed that nitro-cellulose with 10% DPA obtained a green colour already after 1 day storage at 70°C. HPLC analysis revealed that about 10% of the DPA, and its derivatives, added were not extractable. There was no proof that the non-extractable compound was a nitramine despite the fact that it could be transferred into 4-nitro-DPA when stored at slightly elevated temperature.

With the results presented here it is obvious that a green compound is also formed when using NNODPA as a stabilizer. The bonding to NC occurs after the formation of NNODPA and therefore should not be the substance Bergens suggested, as this compound [4] only existed only as long as DPA was present.

With UV, FTIR and chemometry it was shown that the aged and extracted NC samples contained a non-extractable nitro compound. The most likely compound is 2,4'-dinitroDPA as both the IR-spectrum and the UV-spectrum of the green NC give a better agreement with this compound.

This green, non-extractable, compound gave NC an prolonged time to autocatalysis, a time that was proportional to the storage time before extraction. Thus the time to autocatalysis could be extended up to 70 days at 70°C compared to about 3 days for non-stabilized NC as shown by MC. This is something not reported earlier. A new extraction of the extracted NC, after a new storage period at 70°C, showed that some of the bonded stabilizer now was given off in an unknown form.

NMR helped to establish that the compound bonded to the NC was an aromatic compound.

The IR-spectrum obtained from the chemometric study is of low resolution, and covered about 10% of a normal IR-spectrum. Thus no...
complete identification of the compound, except for the nitro groups found, has been possible to do. The best identification so far of the green compound in NC (from Bofors) is 2,4´-dinitroDPA, probably bonded to NC via the amine nitrogen. This is something not described before.

A chemical bonding most probably occurs also when using NNODPA as a stabilizer, indicating NNODPA plays a key role.

With DPA inconclusive results are obtained as low molecular NC, with high stability, was split off when NC from another source was used for these experiments. This NC gave with DPA a blue residue upon extraction, pointing to another type of compound, different from 2,4´-dinitroDPA, being formed.

The approach given in paper V is certainly a method to refine to get still more insight into the complex behaviour of NC and to find out more about the compound(s) being bonded to NC. The use of FTIR in combination with chemometry reveals that this is a method with a very promising future when small chemical changes in a system are to be studied.

To get a better understanding of the decomposition mechanism of NC the experiments, when repeated, should also include GPC analysis in order to determine molecular weight of the different coloured samples.
Table 2. The data matrix

<table>
<thead>
<tr>
<th>Objects</th>
<th>X-variables</th>
<th>p</th>
<th>Y-variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>q</td>
<td>X_{11} X_{12} ... X_{1p}</td>
<td></td>
<td>Y_{11} ... Y_{1q}</td>
</tr>
<tr>
<td>1</td>
<td>X_{21} X_{22} ...</td>
<td></td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>. . .</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td></td>
<td>. . .</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>n</td>
<td>X_{n1} ... X_{np}</td>
<td></td>
<td>Y_{n1} ... Y_{nq}</td>
</tr>
</tbody>
</table>

Object: Observations on one sample.
X-variables: Easily obtained observations on the same object, e.g. spectroscopic data.
Y-variables: “Expensive” observations on the same object.
n: Number of objects.
p: Number of X-variables.
q: Number of Y-variables.
9 Acknowledgements

This thesis would never have been possible without the supervision given by my mentor Prof. Bengt Nygård who continuously kept pushing me during the long time it took to accomplish this work. I’m also very thankful for valuable experimental suggestions aiming at enhancing the colour in aged nitro-cellulose.

This work has been going on for more than 10 years since Prof. Bengt Nygård and I first discussed the possibility to present the research results, obtained during my time at Bofors and Bodycote CMK, as a thesis. Due to a high workload in other areas and restricted funds for research in this special field, this thesis could be accomplished only after my retirement.

I’m grateful to the people at CMK for their friendly help after my retirement when they had me there “disturbing them”. Special thanks to managing director Lars Åberg at Bodycote CMK who allowed me to use the laboratory to finish the last experiments and to Mr. Lars Berndt and Dr. Hans Malmberg for experimental assistance.

Lars-Erik Paulsson, Lars-Gunnar Svensson and Hans Malmberg I also thank for inspiring discussions on nitro-cellulose stabilization.

I also thank Lars-Gunnar Svensson for the many hours he spent scrutinizing the manuscript and for the valuable linguistic improvements he suggested. Also special thanks to my English friends Mr. and Mrs. Clawly for checking my English.

For financial support I thank Mr. Nils-Erik “Lucas” Pettersson at FMV (Swedish Defence Material Administration). Also Mr. Lennart Hednert, managing director at former Celsius Invest, I thank for financial support.

Last, but not least, I thank my wife Kerstin, the joy of my life, for her patience during the many days I robbed her of my presence while writing this thesis.
10 Swedish Summary:
Kemiska reaktioner i systemet nitrocellulosa/difenylamin med speciell inriktning på bildandet av till nitrocellulosa kemiskt bundna stabiliserande föreningar

Torbjörn Lindblom

Bakgrund

I början av 1800-talet växte intresset för att behandla olika naturliga polymerer med salpetersyra. 1845 ägnade Schönbein ett speciellt intresse åt den produkt han erhöll då han behandlade bomull (cellulosa) med en blandning av salpetersyra och svavelsyra. Han kallade produkten “bomullskrut” och antydde därmed dess framtida användningsområde. Att skala upp denna produktion visa sig bjuda på betydande svårigheter, beroende på den kemiska instabiliteten hos NC.

Explosioner i NC-fabriker inträffade vid ett flertal tillfällen i England, Frankrike och Österrike varför användandet av bomullskrut begränsades under många år.

1868 gjorde Abel ett markant framsteg då han visade att olyckorna med NC berodde på att bomullskrutet ej var tillräckligt rent efter tillverkningsprocessen. Alfred Nobel gav 1889 ett ännu mer betydande bidrag genom att införa difenylamin (DPA) som en stabiliserande tillsats i NC-baserade explosivämnen. Denna NC-kvalitet, utvecklad av Nobel, hade en anmärkningsvärd stabilitet och kom att användas i både militära och
civila sprängämnen. 1894 köpte Nobel företaget Bofors, känt för sina kanoner, och byggde en fabrik för att producera nitrocellulosa/krut. Under min tid som anställd vid Bofors utfördes eller initierades flera av de forskningsresultat som presenteras här.

Kemiska åldringsreaktioner i nitrocellulosa

Den breda användningen och praktiska betydelsen av NC har lett till ett stort antal undersökningar beträffande nedbrytningsmekanismerna hos NC under olika betingelser [6-10]. Huvudorsak till nedbrytningen är den instabila nitraterestergruppen (-O-NO₂). Andra kemiska processer i NC är t.ex. stabilisatorreaktioner, reaktioner med luftens syre och fukt samt nedgången i nitrocellulosans molekylvikt.

Det är allmänt accepterat att det primära steget i nedbrytningen av NC är brytandet av O-NO₂ bindningen, varvid gasen NO₂ bildas. Denna bindning har den lägsta bindningsenergin, 155 kJ/mol, att jämföra med 238 kJ/mol för C-ONO₂ [11]. När NO₂, en radikal (skrivs ibland som *NO₂) p.g.a. sin udda elektron, spjälkas av (Fig. 1) lämnar den en alkoxyradikal (ROx) i NC-kedjan. Denna alkoxyradikal kan snabbt reagera i ett antal steg, via reaktioner som slutligen leder till brott av -C-C-bindningar i NC-kedjan [6, 10]. Detta kan man följa med GPC [13]. I [14] visar Phillips att ROx och *NO₂ kan rekombinera.

De dominerande produktarna som bildas vid nedbrytningen av NC är kolmonoxid, koldioxid, kväveoxider (inklusive lustgas, N₂O), metan, formaldehidy, vatten och kvävgas. Bildningen av NO och NO₂ orsakar de största problemen, då dessa går runt i en evig cirkel varvid syror bildas. Dessa påsynder nedbrytningen i ett accelererande förlopp, s.k. autokatalys. Detta framgår av Fig. 2.
Stabilisatorer
För att öka stabiliteten hos NC tillsätter man en stabilisator till krutet. En effektiv stabilisator måste kunna reagera med de frigjorda kväveoxiderna (NO och NO₂) liksom med syrorna (HNO₃) som bildas ur kväveoxiderna tillsammans med vatten. Stabilisatorn skall dessutom gärna vara en bra radikalfångare. De vanligaste stabilisatorerna som används idag är olika aromatiska aminer som difenylamin (DPA), 2-nitrodifenylamin (2NDPA), N,N´-dietyl-N,N´-difeny lurinämne (Centralit I eller CI) och N´-metyl-N,N- difeny lurinämne (Akardit II). En mängd andra substanser har också testats [3].

Analys av stabilisatorer och stabilitet

För analys av stabilisatorhalten i krut (säkerhetsTeknisk kontroll) använder man sig idag rutinmässigt av HPLC, vätskekromatografi. Före analysen
extraherar man ut stabilisatorn och dess reaktionsprodukter ur krutet. Dessa separerar man sedan med HPLC och detekterar dem vanligen med en UV-detektor. Den kvarvarande nitrocellulosan undersöker man normalt inte. Analys efter olika lång lagringstid ger kurvor enligt Fig. 3. Anmärkningsvärt är att all stabilisator ej kan återfinnas. Se summakurvan i Fig. 3.

För att studera stabiliteten hos krut kan man använda sig av olika högtemperaturtest. Bättre är att använda sig av mikrokalorimetri (MC) där man kontinuerligt följer värmeutvecklingen vid t.ex. 70°C. Måter man dessutom vid ytterligare 2 temperaturer kan aktiveringsenergin, $E_a$, beräknas ur Arrhenius ekvation.

$$k = A \cdot \exp \left( \frac{-E_a}{RT} \right)$$
eller
$$\ln k = \frac{-E_a}{RT} + \ln A \quad (y = kx + l)$$
Nyupptäckta reaktioner i NC

Då NC, innehållande DPA eller NNODPA, lagras finner man att den redan efter en dag vid 70°C antar en grön färg. Färgen blir intensivare ju längre tid provet lagras. Undersöker man stabiliteten vid 70°C hos extraherad NC finner man en avsevärd stabilitet, som ökar linjärt med ökande lagringstid vid 70°C före extraktionen. Detta har inte beskrivits tidigare. Se Fig. 4.

Kemisk inbindning av stabilisator i NC

Eftersom det finns ett stabiliserande icke extraherbart ämne i NC efter en tids lagring tyder detta på att stabilisatorn, eller ett derivat av densamma, binds till NC på något vis. Analys med FTIR av de extraherade NC-proverna ger ett antal IR-spektra som då de jämförs visuellt ser identiskt lika ut. Behandlar man spektra med kemometri (multivariat analys) finner man ett resulterande spektrum enligt Fig. 5. Med kemometri kan trender i stora datamängder urskiljas och kopplas till bestämda variabler.

Jämförelse med IR-spektra på DPA och de vanligaste stabilisator-derivaten visar att den förening som Fig. 5 visar (övre kurvan) bäst stämmer
överens med 2,4'-dinitroDPA (undre kurvan). Ev. bindning till NC bör ske via aminkvävet i stabilisatorderivatet enl. IR.

Detta resultat konfirmeras av UV-spektrum på grön extraherad NC. Detta har aldrig beskrivits tidigare.

Vid försök utförda för att säkrare fastställa om det handlar om kemisk inbindning erhölls inget säkert svar då det vid de nya försöken ej gick att erhålla samma nitrocellulosa som tidigare.

Denna nya NC färgades också grön vid lagringen men blev efter extraktion blå och uppvisade även den en förlängd tid till autokatalys. Tiden var dock kortare (27 dygn) än för motsvarande grönt prov (37 dygn). Den stabiliserande förmågan satt huvudsakligen i den blå delen, som kunde lösas ut, tillsammans med NC, med hjälp av metanol. Detta tyder på närvaro av lågmolekylar och/ eller lågnitrerad NC.

Prov innehållande NNODPA hade efter extraktion mer än 90 dygn till autokatalys och var kraftigt grön. Således en mycket stabil nitrocellulosa.

För att fastställa om det handlar om kemisk inbindning löstes NC upp i acetonitril och fälldes därefter med 2%-ig CaCl₂-lösning. Den blå nitrocellulosan hade endast obetydligt förlängd tid (4 dygn) till autokatalys medan NC innehållande NNODPA klarade 11 dygn vid 70°C. Detta senare tyder på kemisk bindning av stabilisatortill NC. Detta har aldrig beskrivits tidigare.

NNODPA tycks spela en nyckelroll när det gäller inbindningen i NC. En möjlig mekanism är: NO i NNODPA oxideras till –NO₂, varvid en nitramin (-N-NO₂) bildas. En dylik kan möjligens bildas även vid direkta reaktion mellan DPA och NC. Denna instabila molekyl förlorar snart NO₂ samtidigt som en fri radikal bildas på kvävet i DPA. Denna fria radikal rekombinerar därefter med t.ex. den alkoxyradikal som bildats då N₂O₅ i nitratgruppen i NC avspalts, Fig. 1. Härvid skapas en kemisk bindning till NC-molekylen. Denna reaktion bör underlåtts av att DPA, enligt IR, tycks läsas till nitrocellulosan.

**Slutsats**

De metoder som berörts, HPLC, mikrokalorimetri och FTIR tillsammans med kemometri, utgör goda analytiska metoder för att följa den kemiska nedbrytningen hos nitrocellulosa.

Nedbrytningsprodukterna från difenylamin (DPA), bildade vid lagring av krut, både vid normal temperatur eller vid accelererad åldring vid förhöjd temperatur, kan följas med HPLC.

FTIR tillsammans med kemometri ger även den nödvändig precision vid bestämning av stabilisatorhalter, för att kunna användas vid säkerhets teknisk kontroll av krut.
Åldrad NC med DPA eller NNODPA erhåller en grön färg redan efter 1 dags lagring vid 70°C. Omkring 10% av den tillsatta stabilisatorn, inklusive dess derivat, kan ej extraheras, och man finner en förlängd tid till autokatalys jämfört med ren NC. Denna tid är proportionell mot lagringstiden före extraktion. Tiden till autokatalys förlängdes således upp till 70 dygn vid 70°C jämfört med 3 dygn för icke stabiliserad NC. Detta har inte beskrivits tidigare.

UV, FTIR och kemometri visar att åldrade och därefter extraherade prover innehåller en icke extraherbar nitroförening. Den mest troliga föreningen är 2,4´-dinitroDPA, troligen bunden via aminkvävet till NC. Inbindningen sker efter det att NNODPA bildats (eller tillsatts). Detta har inte beskrivits tidigare.

Då försöken upprepades, med NC från en annan tillverkare, för att utröna om det verkligen handlade om en kemisk bindning till NC erhölls oklara resultat. Man erhöll med DPA en blå NC med en stor lågmolekylär andel med hög stabilitet. Troligtvis erhålls en kemisk bindning till NC då NNODPA används som stabilisator vilket visar att NNODPA spelar en nyckelroll.

De analysmetoder som använts här, och speciellt FTIR tillsammans med kemometri, bör kunna utvecklas ytterligare för att ge en bättre förståelse av det komplexa beteende nitrocellulosa uppvisar. Mer information om hur den stabiliserande föreningen binds till NC bör också kunna erhållas. Resultaten från användandet av FTIR ihop med kemometri visar att detta är en metod med lovande framtidsutsikter när det gäller att studera små kemiska förändringar i ett system.

För att ytterligare karaktärisera NC, vid de försök som beskrivits här, bör man även bestämma molekylviktsfördelningen på åldrad NC med hjälp av GPC.
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