

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/264081362>

# NITROCELLULOSE IN PROPELLANTS: CHARACTERISTICS AND THERMAL PROPERTIES

Chapter · January 2012

CITATIONS

11

READS

21,684

3 authors:



**Maria Angeles Fernandez de la Ossa**

21 PUBLICATIONS 387 CITATIONS

[SEE PROFILE](#)



**Mercedes Torre**

University of Alcalá

49 PUBLICATIONS 1,346 CITATIONS

[SEE PROFILE](#)



**Carmen García-Ruiz**

University of Alcalá

141 PUBLICATIONS 2,670 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Silica based materials for encapsulation of enzymes [View project](#)



EVALUACIÓN E INTERVENCIÓN EDUCATIVA PARA PREVENIR EL CONSUMO DE DROGAS Y VIOLENCIA SEXUAL EN CONTEXTOS DE OCIO JUVENIL [View project](#)

The exclusive license for this PDF is limited to personal website use only. No part of this digital document may be reproduced, stored in a retrieval system or transmitted commercially in any form or by any means. The publisher has taken reasonable care in the preparation of this digital document, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained herein. This digital document is sold with the clear understanding that the publisher is not engaged in rendering legal, medical or any other professional services.

## Chapter 4

# NITROCELLULOSE IN PROPELLANTS: CHARACTERISTICS AND THERMAL PROPERTIES

*M<sup>a</sup> Ángeles Fernández de la Ossa<sup>1,2</sup>, Mercedes Torre<sup>1,2</sup>  
and Carmen García-Ruiz<sup>1,2</sup>*

<sup>1</sup>Department of Analytical Chemistry, Faculty of Chemistry, University of Alcalá,  
Ctra. Madrid-Barcelona km. 33.600, 28871 Alcalá de Henares (Madrid), Spain

<sup>2</sup>University Institute of Research in Police Sciences (IUICP), Pilot Plant of Fine  
Chemistry, University of Alcalá, Ctra. Madrid-Barcelona km. 33.600, 28871  
Alcalá de Henares (Madrid), Spain

## ABSTRACT

Nitrocellulose was discovered, by the German-Swiss chemist C.F. Schönbein, in the first half of the nineteenth century but remains to have a great interest today. Nitrocellulose has a similar aspect to cotton (white and fibrous texture). It is a nitrate cellulose ester polymer with  $\beta$  (1 $\rightarrow$ 4) bonds between monomers, produced from the nitration of cellulose. Its chemical formula is  $[C_6H_7O_2(OH)_{3-x}(ONO_2)_x]_n$ , where  $x$  indicates the hydroxyl groups exchanged by nitro groups. This macromolecule has different applications depending on their degree of nitration. Nitrocellulose with a low degree of nitration is applied in paints, lacquers, varnishes, inks, etc., while nitrocellulose with a high degree of nitration (>12.5%) is used in explosives. Within the nitrocellulose-containing explosives are included dynamites and propellants. Propellants containing nitrocellulose are smokeless gunpowders, which are widely used by the international military community for propelling projectiles. Depending on gunpowder's composition (active components), they can be classified as: i) single-base gunpowders, which contain mainly nitrocellulose, ii) double-base gunpowders, which contain nitrocellulose and other explosive substance (nitroglycerin, dinitroethylenglycol or dinitrotoluene), and iii) triple-base gunpowders, which are composed by nitrocellulose and two other explosive substances (nitroglycerin or dinitroethylenglycol and nitroguanidine).

Nitrocellulose characteristics, i.e., its high molar mass, complex structure, and unusual chemical behavior, make difficult to perform ordinary studies of this polymer. For these reasons, most works on the characterization of nitrocellulose in propellants have been based on measurements of physico-chemical properties such as molar mass

distributions, viscosity, and specific refractive index of nitrocellulose by Size Exclusion Chromatography (SEC) with different types of detectors.

The thermal properties of nitrocellulose are important since it must be burned for its use as propellant. These properties have mainly been studied by determining, using spectrometric techniques (mainly infrared and mass spectrometry), the by-products released during the thermal degradation of nitrocellulose by means of pyrolysis or incineration processes. The most important kinetics parameters of thermal decomposition of nitrocellulose (activation energy, enthalpy, critical explosion and decomposition temperature, etc.) have been studied by typical thermal analytical techniques such as Differential Scanning Calorimetry (DSC) and ThermoGravimetry (TG) or Differential Thermal Analysis (DTA).

The aim of this book chapter is to provide an updated overview (from 1999 until nowadays) of the characteristics and thermal properties of nitrocellulose of high nitrogen content used in propellants.

## 1. INTRODUCTION

Nitrocellulose has a similar aspect to cotton, is white and has a fibrous texture. It is produced from cellulose. Cellulose is a polysaccharide formed of hundred to over ten thousand D-glucopyranose units linked by  $\beta$  (1 $\rightarrow$ 4) bonds [1]. This molecule is a natural polymer that reacts with nitric acid to give the nitrated cellulose ester polymer called nitrocellulose or cellulose nitrated. The general reaction is an esterification  $R-OH + HONO_2 \rightarrow R-ONO_2 + H_2O$ , which is reversible and highly exothermic [2].

The precursor (cellulose) and the final product (nitrocellulose) present a similar structure but some hydroxyl groups have been changed by nitro groups. This replacement occurs in carbons C2, C3 and C6, which are the unique available places for nitro groups, being the rate for nitration  $C6 \gg C2 \approx C3$  [2, 3]. Thus, in these positions nitro groups can be joined, giving a compound with the chemical formula of  $[C_6H_7O_2(OH)_{3-x}(ONO_2)_x]_n$ , where x indicates the hydroxyl groups exchanged by nitro groups. The degree of substitution (DS) designates the quantity of hydroxyl groups exchanged and can be calculated by the equation [4]:

$$\text{Degree of substitution (DS)} = \frac{3.6 \times \text{nitrogen content [\%]}}{31.13 - \text{nitrogen content [\%]}}$$

DS is one of the most important properties of nitrocellulose since it affects other properties such as solubility and viscosity and determines the applications of nitrocellulose. The lowest DS value is one, which means a nitrogen content of 6.76% in the nitrocellulose monomer. The highest DS value is 3; it means that all the hydroxyl groups are replaced with nitro groups producing a theoretical nitrogen content of 14.14% (Figure 1).

However, the maximum DS synthesized is usually lower than the maximum theoretically achievable, being reported a maximum DS of 2.9 ( $\approx$ 13.9% of nitrogen content) [3, 4, 5], because to achieve higher DS values is expensive and led to an unstable product.

Nitrocellulose solubility is inversely proportional to DS and to the degree of polymerization (DP, defined as the numbers of repeated units along the chain). In fact, while nitrocellulose is not dissolved by aliphatic and aromatic hydrocarbons, it can be dissolved by alcohols, esters or ketones, depending on its nitrogen content; for example, nitrocellulose with

a nitrogen content from 10 to 12.6% is soluble in ether-alcohol mixtures. In nitrocellulose solutions, the polymer is swelled and viscosity increases but it does not form a saturated solution like ionic or molecular compounds, because it is a macromolecular substance that forms colloidal solutions. On the other hand, there is a directly proportional relationship between viscosity of nitrocellulose solutions and the nitrogen content of this macromolecule, which is also influenced by DP [2 -4].

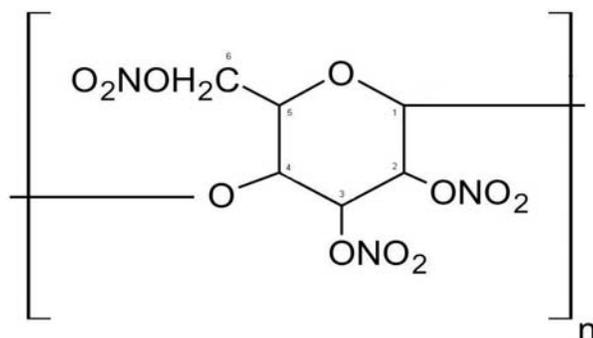


Figure 1. Theoretical chemical structure of a nitrocellulose polymer completely nitrated (degree of substitution, DS = 3, 14.14% of nitrogen content).

The first nitrocellulose was synthesized by the French chemist and pharmacist H. Braconnot, in 1832. He prepared an inflammable and unstable solid by the treatment of cotton or wood pulp (crude cellulose) with concentrated nitric acid (85%, v/v). This method produced a heterogeneous and unstable substance, called xyloidine, which was characterized by being a low nitrated cellulose (nitrogen content of 4-5% as maximum). Braconnot discovered the forerunner of nitrocellulose but it was C.F. Schönbein that created, 14 years later, nitrocellulose as a stable product. This German-Swiss chemist achieved it by the reaction between cotton and a mixture of nitric acid and sulfuric acid and patented it. At present, this method, with few variations, is used to generate commercial nitrocellulose [2, 5].

Nitrocellulose formulation did not suffer marked changes for over forty years until, 1884, when P. Vieille developed his famous “B gunpowder”. It was the first smokeless gunpowder. He discovered how to suspend nitrocellulose as a colloid into alcohol-ether solutions allowing to the nitrocellulose to be the main component in gunpowders [6].

With respect to the way by which nitrocellulose is obtained, as it has been stated above, when using concentrated nitric alone, a heterogeneous and unstable nitrocellulose with a low nitrogen content was achieved [3]. The synthesis process was improved adding nitric acid vapors as pretreatment, previously to the addition of 98% nitric acid. In this case, the vapor phase helped to the generation of stable and homogeneous nitrocellulose with a higher nitration degree (nitrogen content  $\approx$ 13.6%) [3]. The reaction of cellulose with a mixture of nitric and sulfuric acid allowed to achieve a stable product with a high nitration degree (nitrogen content of 13.9% as maximum) [3]. The best proportion of these two acids was demonstrated to be 1:1 to 1:3 (nitric acid:sulfuric acid). However, it is important to take into account that sulfuric acid generates unstable sulfuric esters of cellulose.

A mixture of nitric and phosphoric acid in a ratio of 1:1 to 1:3 (nitric acid:phosphoric acid) produced nitrocellulose with a nitrogen content up to 13.7% [3]. By this way, the final

product was a highly stable nitrocellulose, but phosphoric acid corrodes iron and steel, being a problem for nitrocellulose manufacture [2, 5].

Nitrocellulose with nitrogen content as high as 14% may be produced by mixing nitric and acetic acids [2]. The main disadvantage of this reaction was the appearance of acetyl nitrate in the reaction medium, which is a very unstable substance at high temperatures.

Another way to manufacture nitrocellulose consisted in the use of nitric acid and organic solvents, such as carbon tetrachloride, methyl nitrate or chloroform, which produced nitrocellulose with a high nitration degree (nitrogen content up to 13.4%) and large yields [3].

Nitrocellulose obtained by the above-mentioned methods is an acid and unstable substance that requires to be neutralized in order to stabilize it. The neutralization process is based on numerous washes with water at room temperature and at 100 °C, followed with washes at basic pH. Then, the trapped sulfuric acid on nitrocellulose fibers is released by broken of the fibers in a mill up to lengths from 0.2 to 0.5 mm. Finally, washes with water (1:10, nitrocellulose: water) at 140 °C under 3-4 atm of pressure are made. In conclusion, to obtain a stable product, long, expensive and complex stabilization procedures are needed [2].

Nowadays, nitrocellulose is usually prepared by the batch-type mechanical dipper process or by a continuous nitration processing method. Both procedures are based on the etherification reaction between the hydroxyl groups of cellulose and the nitric acid, in a mixture of nitric: sulfuric acids. Nitration and separation processes have changed little since the firsts nitrocellulose manufactures, about 100 years ago. However, the manufacture process has evolved in terms of the materials of manufacture equipments (changing lead and iron by stainless steel, to avoid corrosion and break down), transports of raw materials (from manual to automatic), experimental variables (flow, temperature, revolutions, etc.) and the quality control of the whole production process (from raw materials to final product). Dry nitrocellulose is very unstable, being necessary suspending it in water or other appropriate solvents for transport or storage [2]. Moreover, nitrocellulose decomposes for three mechanisms in ambient conditions: hydrolytic, thermal, and photochemical [7].

The nitrogen content of nitrocellulose defines the uses or applications of this polymer. Thus, films, inks, lacquers, and paints are manufactured using nitrocellulose with low nitrogen content (<12%). However, explosives are made with high nitrogen content nitrocellulose (>12%). Highly nitrated nitrocellulose, characterized by average molar masses from 20 to 250 kDa [2, 4, 7], takes part of the composition of some explosives such as dynamites and propellants. Dynamites, which are strong explosives mainly used for civil purposes, are composed by explosive components (ammonium nitrate and nitroglycol), combustible components (butyl phthalate, flour or sawdust, and nitrocellulose) and inert components (such as calcium carbonate). Propellants or gunpowders, which are used to move rapidly projectiles, are classified, according to their composition, as black gunpowders, homogeneous gunpowders, composed gunpowders, and high-explosive gunpowders [2, 5]. Black gunpowders contain mixtures of inorganic compounds such as potassium nitrate, sulfur, and coal [5]. Homogeneous gunpowders, also known as colloidal or nitrocellulose-based gunpowders, have nitrocellulose as common active component. Depending on the number of active components three types of homogeneous gunpowders can be distinguished: i) single-base gunpowders, which contain mainly nitrocellulose, ii) double-base gunpowders, which contain nitrocellulose and one more explosive substance (nitroglycerin, dinitroethylenglycol or dinitrotoluene), and iii) triple-base gunpowders, which are composed by nitrocellulose and two other explosive substances (nitroglycerin or dinitroethylenglycol

and nitroguanidine) [5, 8]. Composed gunpowders are plastic matrices with inorganic oxidants that do not contain nitrocellulose [5]. High-explosive gunpowders contain a high explosive, energetic and non-energetic binding materials, a plasticizer agent, and a stabilizer. As example, low-vulnerability-ammunitions (LOVA) are high-explosive gunpowders mainly composed by hexogen and a cellulose derivative [2, 9].

Nowadays, the research on explosives is of great interest in forensic science. This situation is, in part, due to the terrorist attacks committed in the last years towards civil and military people. Then, studies on the characterization and the sensitive determination of explosive substances to identify the explosive used and to obtain information that could lead to the criminals are needed nowadays. In this sense, Forensic Analytical Chemistry, defined as a discipline to analyze proofs of all of kind crime-scenes, choosing the better chemical analysis in each case, depending on the sample and the future use of the analytical information [10], may be very helpful.

In the explosive field, the characterization and determination of nitrocellulose is, still nowadays, a challenge goal for forensic analytical chemistry due to the difficulties in its analysis, inherent to the polymeric nature of this energetic material. As a consequence, the aim of this book chapter is to provide an updated overview from 1999 until nowadays of the characteristics and thermal properties of nitrocellulose of high nitrogen content used in propellants.

## 2. CHARACTERIZATION OF NITROCELLULOSE

Nitrocellulose characteristics, such as its high molar mass, complex structure, and unusual chemical behavior, make difficult to perform ordinary studies of this polymer. In addition, this macromolecule is generally inside a complex matrix, mixed with other components that should be removed before its analysis. For these reasons, most studies on nitrocellulose are aimed to the characterization of nitrocellulose as polymer.

In this section, recent studies developed to evaluate the physico-chemical, thermal, mechanical and morphological properties of nitrocellulose of high nitrogen content are presented.

### 2.1. Physico-Chemical Properties of Nitrocellulose

Molar mass, viscosity and specific refractive index of nitrocellulose are determined by Size Exclusion Chromatography (SEC), with different types of detectors.

G. Heinemann [11] reported the advantages of using a triple detection system (combining refractive index, viscosity, and light-scattering detectors) in SEC. This set up allowed to obtain information about molar mass (as conventional SEC with refractive index or ultraviolet detector) and polymeric structures. SEC with triple detection was appropriate to obtain accurate results on the mass average molar mass ( $M_w$ , average value of the distribution of the different molar mass taking part of the polymer) and the number average molar mass ( $M_n$ , total mass of all molecules in a polymer sample divided by the total number of molecules present) without the need of external standards required in conventional SEC. However, a

comparison between polystyrene standards and nitrocellulose was required to study the nitrocellulose structural properties by a Mark-Houwink-Plot (MHP), where the logarithm of the intrinsic viscosity is plotted versus the logarithm of the  $M_w$ . Due to a higher slope was obtained in the MHP plot for nitrocellulose than for polystyrene standards, a more open and stretched structure was attributed to nitrocellulose. In addition, for nitrocellulose samples of 240 and 440 kDa, values of  $M_w/M_n$  of 238.5/112 kDa and 443.8/102.2 kDa were obtained, respectively.

SEC with triple detection and simple detection using a calibration with standard polymers was also employed by A.F. Macdonald [12] to characterize nitrocellulose. Conventional standards, like polystyrene, polymethylmethacrylate, and polytetrahydrofuran were used to obtain the  $M_w$  of nitrocellulose by calibration. Well-characterized monodispersed standards of the same polymer of interest are necessary to obtain true values of  $M_w$ . However, this is not possible in the case of nitrocellulose and different values for  $M_w$  and  $M_n$  were obtained by calibrating with the above-mentioned standard polymers or by using SEC with triple detection. In addition, different  $M_w$  values were obtained depending on the standards employed, which confirmed the dependence of this determination from the standard used. In fact, polytetrahydrofuran standards presented the most similar values to those obtained by SEC with triple detection. In this work, a MHP comparison between nitrocellulose and polystyrene showed a similar trend to the work previously cited [11]. That is, a higher stiffness and a less coiled structure in nitrocellulose than in polystyrene standard were confirmed. This was attributed to the high intrinsic viscosity present in the different nitrocellulose samples studied (from cotton and wood).

In 2008, P. Deacon et al. [13] studied the reproducibility of SEC data obtained for nitrocellulose samples with different nitrogen content. It was demonstrated that different analysts presented low reproducible results ( $M_w$  and  $M_n$  data) while the same analyst gave an excellent reproducibility when the analysis was repeated over three months. It was also shown that  $M_w$  measurements were influenced by the moisture content of nitrocellulose, because lower  $M_w$  values were obtained for the driest samples. A more complete reproducibility study was performed later [14]. The assessment of the reproducibility obtained among nine laboratories from eight different countries using the same method (STANAG 4178 Ed.2) by SEC with different detectors (viscosity, refraction index, UV/Vis and/or light-scattering) was carried out for nitrocellulose samples having nitrogen contents ranging from 11.6 to 13.5%. Results obtained for these samples presented low reproducibility in  $M_w$  and  $M_n$  values. This was mainly attributed to the different drying methods used because dried samples led to low  $M_w$  and *vice versa*. Another factor leading to a lack of reproducibility was attributed to the non-definition of similar and good baseline in the chromatograms obtained, since the area measured affects the  $M_w$  determination. In conclusion, this work highlights how complicate is to generate data of quality for nitrocellulose by SEC, mainly among different analysts.

P.R. Deacon et al. [15] tackled the problem of the nitrocellulose behavior in solution. In this work, SEC with triple detection was used to study two types of samples: one with high nitrogen content nitrocellulose (propellant-grade) and, the other, with low nitrogen content nitrocellulose (lacquer-grade). Changes in  $M_w$ , viscosity, and refraction index of nitrocellulose samples were observed during the dissolution process until the sample dissolved completely, at which time, these parameters remained constant. Differences in  $M_w$  were also observed due to changes in the nitrocellulose concentration in solution. It was demonstrated that, when the concentration of nitrocellulose in solution was increased, the  $M_w$

was reduced, which allowed the authors to conclude that true Mw values only could be obtained at low polymer concentrations, except for nitrocellulose with low Mw values. This behavior was explained considering that, when the concentration of nitrocellulose in solution was increased, a reduction in the hydrodynamic volumes was produced, driving to a reduction in the Mw. Besides, these authors determined the dissolution time of nitrocellulose, by means of the refractive index detector, whose measurement is directly proportional to Mw. Interestingly, the dissolution time of nitrocellulose was also influenced by the nitrogen content of this polymer. Thus, high nitrogen content nitrocellulose required less dissolution time to achieve its complete dissolution. For example, the highly nitrated nitrocellulose (propellant-grade, nitrogen content of 12.6%) needed 72 hours for its dissolution in contrast with the lacquer-grade nitrocellulose sample (nitrogen content of 11.8%) that needed 168 hours.

The behavior of nitrocellulose in solution was also studied by J.M. Bellerby et al. [16]. These authors proved that the dissolution of nitrocellulose was not a reversible process since this polymer suffered a permanent change in its structure. Moreover, under stirring, the dissolution time decreased markedly and lower Mw were measured in comparison with non-stirred solutions ( $\approx 10\%$  lower values). This was explained by a change in the nitrocellulose structure, by breaking of polymer chains, with stirring. These authors also emphasized, in accordance with the studies of Deacon et al. [15], the influence of percentage nitrogen of nitrocellulose on its solubility, owing to possible internal associations, as hydrogen bonds, that create larger molecules.

High-quality analyses on the degradation process of nitrocellulose are very interesting in the explosive field to understand the behavior of this polymer and to obtain valuable information for the safe production, manipulation, transport, and storage of nitrocellulose-based explosives. In 2001, P.R. Deacon et al. [17] carried out an accelerating ageing experiment by using a thermal treatment for nitrocellulose (with a nitrogen content ranging between 11.7% and 12.2%) extracted from a Polymer Bonded Explosive (PBX). SEC with a triple detection system was used to study changes in molar mass, intrinsic viscosity, and refractive index, in order to investigate the kinetics of the degradation process. Nitrocellulose under ageing process reduced extremely its intrinsic viscosity (from 4.575 to 1.147 dL g<sup>-1</sup>), as well as its Mw (from 875.1 to 122.4 kDa). Moreover, an activation energy value of  $101 \pm 11$  kJ mol<sup>-1</sup> for the degradation process of nitrocellulose was reported. This value was consistent with those obtained for similar degradation processes such as acid catalyzed hydrolysis of cellulose and nitrocellulose and thermolysis of nitrocellulose.

A.F. Macdonald et al. [12] also investigated the ageing process of nitrocellulose extracted from PBX made from two different sources (wood pulp and cotton) through the variation of the molar mass of this polymer during this process. The investigation proved that the more extreme were the conditions of ageing (higher temperatures and more time under thermal treatment), the greater was the change in Mw values. Thus, Mw values in the cotton derived nitrocellulose sample were reduced from 378.166 to 87.433 kDa after 783 days. Intrinsic viscosity also was reduced, changing the values for the same sample from 3.555 to 0.360 dL g<sup>-1</sup>. These results were consistent with a random chain scission process that is one of the accepted models for the nitrocellulose degradation.

## 2.2. Thermal, Morphological, and Mechanical Properties of Nitrocellulose

G. Herder et al. [18] utilized Differential Scanning Calorimetry (DSC), Thermal Mechanical Analysis (TMA), and Dynamic Mechanical Analysis (DMA) to study the relaxation transitions values of nitrocellulose in a generic propellant (mainly consisted of pure nitrocellulose). Three small relaxation steps, designated as  $\alpha$ ,  $\beta$  and  $\gamma$ , at 40, -35, and -80 °C, respectively, were investigated. However, due to the dispersion of the data obtained by the three techniques, this study did not reveal the existence of relaxation transitions at these particular temperatures investigated.

A complete surface study of nitrocellulose contained in three nitrocellulose-based propellants was reported by using Scanning Electron Microscopy (SEM), Fourier Transform InfraRed Photoacoustic Spectroscopy (FTIR-PAS) and surface abrasion and posterior FTIR MicroReflectance Spectroscopy (FTIR-MR) analysis [19]. SEM images of burned samples showed that the region affected by the combustion process in these propellants was only a thin external layer of 5-10  $\mu\text{m}$  (Figure 2), remaining the major part of the internal surface without any modification. FTIR-MR spectroscopy was applied to burned samples at different depths made by surface abrasion procedures that were carried out with an abrasive blaster. The depth of the material removed was calculated from the changes in the weight of the material, and knowing the density and diameter of the unburned material. By this technique it was also confirmed that at a depth greater than 10  $\mu\text{m}$ , the material was not affected by burning.

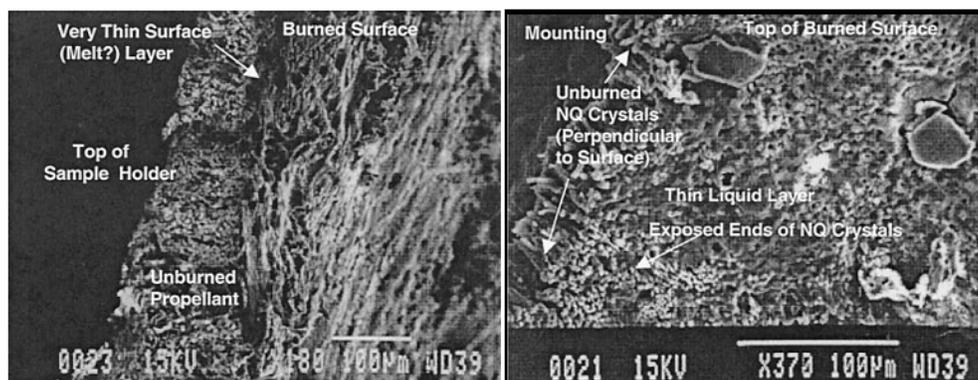


Figure 2. SEM photographs of burned surfaces (burned with a massive copper stub and quenched later) of nitrocellulose-based propellants. (Left) SEM photograph (x180) of cross-section of a propellant (59.5% of nitrocellulose with 13.04% of nitrogen content) burned in air at 0.5 MPa. (Right) SEM photograph (x370) of cross-section of a propellant (28% of nitrocellulose with 12.68% of nitrogen content) burned in air at 2.0 MPa. SEM conditions: JEOL Model JSM-820 instrument. Reprinted from [19]. Copyright (2001), with permission of Elsevier.

From FTIR-PAS and FTIR-MR spectra it was difficult to investigate the modifications in the structure of propellant samples because they also contained many other compounds that generated a great quantity of signals. The main information obtained for nitrocellulose analysis was related with the material affected by the burning process where a weak signal at  $1730\text{ cm}^{-1}$  appeared, which was assigned to the carbonyl groups formed in burned nitrocellulose.

The surface characterization of a propellant sample containing 59.5% of nitrocellulose with a nitrogen content of 13.04% was performed by J. Newberry et al. [20] using Macro-ATR, Micro-ATR, and FTIR Specular Reflectance Spectroscopy. Ignition of the sample was carried out by a plasma source. In spectra obtained by Macro-ATR and Specular Reflectance FTIR (not shown) one band about  $1700\text{ cm}^{-1}$  was observed, which was characteristic of carbonyl groups produced by the oxidation of the nitrate esters of nitrocellulose. However a higher signal-to-noise was observed by Macro-ATR FTIR, which allowed a better study of the nitrocellulose degradation in the propellant ignited by plasma.

Porosity (pore size and pore size distribution) of nitrocellulose was studied by thermoporometry using Differential Scanning Calorimetry (DSC) [21]. Nitrocellulose presented the typical difficulties of hydrophobic substances to achieve a complete penetration of water in its porous, for this reason nitrocellulose in water was stirred or boiled to help the water penetration. Nitrocellulose containing different nitrogen content (12.4 and 13.2%) was studied, being the sample of the highest nitrogen content in granular form. Pore size of nitrocellulose containing 12.4% of nitrogen was of  $6.8 \pm 0.9\text{ nm}$  while granular nitrocellulose with a nitrogen content of 13.2% was of  $15.4 \pm 2.0\text{ nm}$ . Since cellulose presented a pore size of  $6\text{ nm}$ , the pore size value for the lowest nitrogen content nitrocellulose suggested that the structure after cellulose nitration was not modified. The highest pore size for granular nitrocellulose was justified for the increase in the nitrogen content; nevertheless the different forms of nitrocellulose also may contribute to such changes. Moreover, values of  $29.0 \pm 0.6\text{ nm}$  (multiple value of pore size) for both nitrocellulose samples were obtained and were attributed to a layer structure of this polymer. A similar behavior was also obtained with benzene as solvent.

Finally, the characterization of nitrocellulose contained in triple base propellants used in tank gun ammunition attending its mechanical properties was made by R.R. Sanghavi et al. [22]. In propellants dissolved in a mixture of acetone and alcohol, the mechanical parameters of compression strength and percentage compression were measured. These properties decreased with the nitrogen content of nitrocellulose contained in propellants. For example, the compression strength for a sample containing nitrocellulose with a nitrogen content of 12.2% was  $395\text{ kg cm}^{-2}$ , while for a sample containing nitrocellulose with a nitrogen content of 12.6% it was  $316\text{ kg cm}^{-2}$ . The same trend was observed with the percentage compression, which decreased from 35 to 31%.

### 3. DEGRADATION OF NITROCELLULOSE CONTAINED IN EXPLOSIVES

There are also studies on different properties of nitrocellulose which are important for its use as explosive: the stability and the decomposition processes of nitrocellulose. Processes of decomposition of nitrocellulose contained in explosive formulations are of particular interest from the point of view of safety in the manufacture, storage, manipulation, and use of explosives. In this context, studies on kinetics and thermochemical processes involved in the degradation of explosives are quite important. In fact, several investigations on thermal, biological, and mechanical degradation have been developed for nitrocellulose-based explosives.

### 3.1. Thermal Decomposition of Nitrocellulose

Thermal analyses of nitrocellulose are the most widely performed since it must be burnt for its use. Some of these analyses deal with the study of by-products released in the thermal degradation of nitrocellulose by pyrolysis or incineration processes. The effect of nitrogen content on thermal stability and decomposition of nitrocellulose in explosives was investigated by DSC and ThermoGravimetry-Differential Thermal Analysis (TG-DTA) in four nitrocellulose samples (nitrogen content ranging from 12.5 to 13.9%) in solid state [23]. Critical explosion temperature and half-life were the thermal parameters obtained in this work. Also kinetics parameters like activation energy and frequency factor of thermal decomposition were acquired. The study of DSC curves proved that thermal stability of nitrocellulose decreased at higher nitrogen content and lower heating rate. Kinetics parameters were calculated in this work assuming that the nitrocellulose decomposition process followed a first-order kinetics. Activation energy about  $155 \text{ kJ mol}^{-1}$ , critical explosion temperature of  $196 \text{ }^\circ\text{C}$ , and half-life about five years at  $50 \text{ }^\circ\text{C}$  were determined for the nitrocellulose sample containing the highest nitrogen content (13.9%), which was the most unstable one. For this sample, a temperature of  $192 \text{ }^\circ\text{C}$  was defined, from TG-DTA curve data, as the starting temperature for its thermal decomposition.

The thermal decomposition of nitrocellulose fibers with a nitrogen content of 13.9% and possessing micro- and nano-particle sizes was studied by M.R. Sovizi et al. [24]. First, two different particle sizes images for the nitrocellulose fibers were confirmed by SEM (see Figure 3).

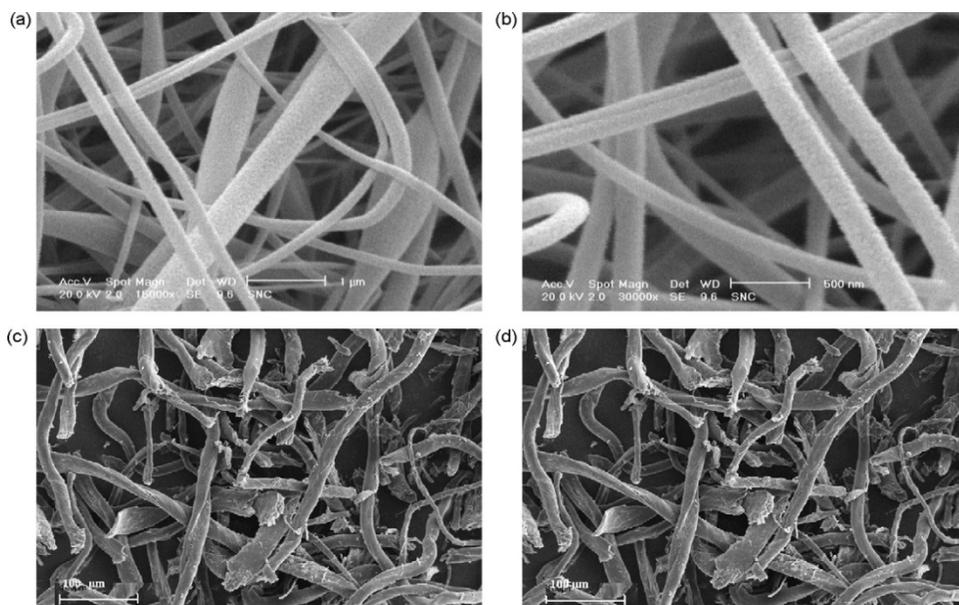


Figure 3. SEM images of nitrocellulose fibers. (a) nano-fibers sample ( $\times 1.5 \times 10^4$ ), (b) nano-fibers sample ( $\times 3.0 \times 10^4$ ) and (c and d) microfibers sample. SEM conditions: Philips XL30 series instrument using a gold film for loading the dried particles. Gold films were prepared by a Sputter Coater model SCD005 made by BAL-TEC. Reprinted from [24]. Copyright (2009), with permission of Elsevier.

Dependence between the thermal decomposition, studied by DSC and TG-DTA, and the nitrocellulose particle size was found. In addition, nitrocellulose micro-fibers presented higher thermal stability than nitrocellulose nano-fibers, due to their higher activation energy, enthalpy, decomposition temperature, and critical explosion temperature values, determined for the micro-fibers in comparison with the nano-fibers. First-order kinetics was also assumed in this work for the determination of the above-mentioned kinetics parameters. Thus, nitrocellulose nano-fibers were proposed for more exigent devices due to their higher heat sensitivity.

The thermal decomposition process of nitrocellulose was also studied by Accelerating Rate Calorimetry (ARC) and simultaneous TG-DTA, coupled to FTIR and Mass Spectrometry (TG-DTA-FTIR-MS) to study the thermal degradation of nitrocellulose samples (nitrogen content of 13.15%) in different environments [25]. TG-DTA curves showed usual mass loss while in FTIR spectra signals due to gasses release during the thermal decomposition of nitrocellulose were observed. For air and helium environments, similar activation energy values were obtained by DTA ( $170 \pm 4 \text{ kJ mol}^{-1}$  in air and  $169 \pm 6 \text{ kJ mol}^{-1}$  in He) and TG ( $166 \pm 2 \text{ kJ mol}^{-1}$  in air and  $174 \pm 2 \text{ kJ mol}^{-1}$  in He), which indicated an independence between the activation energy and the gas atmosphere. However, the activation energy values obtained by isothermal ARC measurements at different temperatures were lower than those previously reported ( $86 \pm 4 \text{ kJ mol}^{-1}$  for argon and  $122 \pm 8 \text{ kJ mol}^{-1}$  in air). In addition, a significant dependence on gas environment was observed for the parameter measured. The authors justified these results by a previous oxidation process of nitrocellulose in air that does not exist in an argon atmosphere. In air, an increase of pressure from 0.1 to 1.8 MPa generated a decrease in the onset temperature (decrease in the thermal stability of nitrocellulose), whereas a later increase in pressure did not changed significantly the onset temperature and thermal stability of nitrocellulose. Nevertheless, in argon atmosphere the opposite behavior was observed: a raise in pressure from 0.27 to 1.91 MPa improved the thermal stability of nitrocellulose but also a later increment in pressure did not modify strongly this behavior. Also kinetics parameters of thermal decomposition of nitrocellulose such as the activation energy ( $E_a$ ) and the pre-exponential factor ( $A$ ) was obtained in this study and were compared with those given in previous works. Three different kinetic processes were suggested: first-order, autocatalytic, and second-order. While first-order and autocatalytic processes were proposed in previous works, most measurements obtained in this study were included in a second-order line. It is important to remark that kinetic data compared were obtained by different reaction models, being not comparable and making difficult the establishment of the real process occurring in the thermal degradation of nitrocellulose.

Thermal decomposition of nitrocellulose was proposed by R.K. Campbell et al. [26] as a strategy to decrease the nitrogen content of nitrocellulose with the aim to transform it into a non hazardous material. Waste fines of nitrocellulose generated during the manufacturing process of this compound have explosive properties, being difficult their treatment or their application in alternative uses. In this work, two types of nitrocellulose (pulp and lint, with a nitrogen content of 13.5% and 13.1%, respectively) were heated at 130, 140, and 150 °C. The faster decrease in nitrogen was observed at the highest temperature, although at this temperature increased the explosion risks from nitrocellulose samples. Contrary to previous works, the application of an air flow (which implies the presence of an  $\text{O}_2$  atmosphere) and the water content of samples did not modify significantly the nitrocellulose decomposition

rate. However, the plot of mass loss against the nitrocellulose nitrogen content was of special interest because the value measured for this magnitude exceeded the limits corresponding to removal of all nitro groups of nitrocellulose, which led to the idea that the degradation of the polymer structure by other mechanisms was also produced. This fact was confirmed by Gas Chromatography (GC), where CO<sub>2</sub> was detected and there were not sources of carbon other than nitrocellulose in the analyzed environment. Thermal stability tests were carried out to confirm the non explosive characteristics of samples after their thermal degradation.

The nitrocellulose melting process was studied by Modulated Differential Scanning Calorimetry (MDSC) because from sixties/seventies years there was not agreement about the real process. N. Binke et al. [27] obtained various photographs of nitrocellulose during heating processes and proved that the melting and decomposition processes coexisted. For high nitrogen content nitrocellulose molecules (from 11.9 to 14.1%) the decomposition temperature was lower than the melting temperature, which indicated that the melting process was produced on a mixture of nitrocellulose and its decomposition products. This fact was confirmed by FTIR spectra, since nitrocellulose suffered a decrease in O-NO<sub>2</sub> peak by heating at 20 K min<sup>-1</sup>, which proved that nitrocellulose was decomposed partly before melting (see Figure 4).

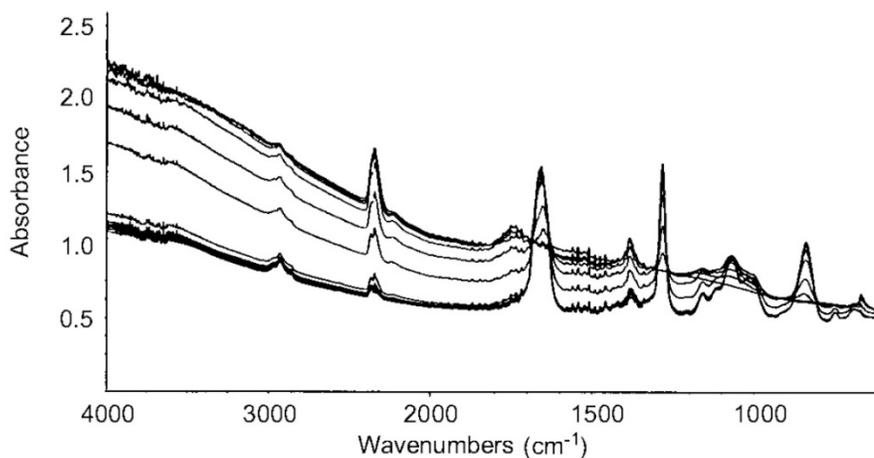


Figure 4. FTIR spectra obtained from the thermal decomposition process of nitrocellulose (12.97% of nitrogen content) at a heating rate of 20 K min<sup>-1</sup>. Collecting time spectra from bottom to top is 5.36, 5.93, 6.50, 6.78, 7.06, 7.35, 7.63, 7.94, 8.19, 8.48, 8.76, 9.33, 12.67 minutes, respectively. FTIR conditions: Nicolet Spectrometer (60SXR) with a deuterated triglycine sulfate (DTGS) detector using 4 cm<sup>-1</sup> of resolution (8 scans/file). Reprinted from [27]. Copyright (1999), with permission of Springer.

Another two interesting papers studying the kinetic of the melting process of highly nitrated nitrocellulose were published by the same research group [28, 29]. The TG curve obtained for the initial 50% of mass-loss of highly nitrated nitrocellulose was described by a first order autocatalytic equation, whereas for the latter 50% mass-loss two other mechanisms were suggested [28]. In addition, the critical temperature, measured by non-isothermal DSC and two different methods, was about 182 °C [29]. This value is consistent with the value of 192 °C previously reported for a nitrocellulose containing a nitrogen content of 13.9% and with the affirmation that, at higher nitrogen content lower thermal stability [23].

The ignition mechanism of nitrocellulose during isothermal storage at 393 K was studied by K. Katoh et al. [30]. In this work, nitrocellulose with a nitrogen content of 12% was stored at 393 K up to 35 hours in 4.7% (v/v) NO<sub>2</sub>/air, or an O<sub>2</sub>/N<sub>2</sub> mixture (dry air), at different O<sub>2</sub> partial pressures, to study its thermal behavior. After storage, gases released during this treatment were analyzed by GC. During nitrocellulose storage under dry air, a decrease in the O<sub>2</sub> pressure and a heat generation was observed, suggesting an autoxidation mechanism by a first-order reaction with respect to the O<sub>2</sub> decrease. During nitrocellulose storage in a NO<sub>2</sub>/air atmosphere, similar values of heat reaction were obtained (450 J g<sup>-1</sup>) in comparison with those obtained under dry air atmosphere (460 J g<sup>-1</sup>). Moreover, the heat conversion presented a linear relationship with the storage time in both atmospheres, which led to the fitting of these systems to a first-order reaction when O<sub>2</sub> decreased. Rate constant and induction period calculated by this way showed significant differences: in a NO<sub>2</sub>/air ambient the calculated rate constant was 1.5x10<sup>-4</sup> s<sup>-1</sup> while in dry air this constant was 7.7x10<sup>-5</sup> s<sup>-1</sup>, observing a lower induction period in NO<sub>2</sub> atmosphere (from 9.2 to 3.4 hours). According to these data, the authors proposed a spontaneous ignition mechanism where NO<sub>2</sub> had a strong influence in the initiation process but a low effect in the autoxidation reaction. This proposal was reinforced by the fact that an increase in the amount of nitrocellulose, which supposed an increment in the NO<sub>2</sub> content, generated a decrease in the induction time without modifying the heat released.

R.I. Hiyoshi et al. [31] studied the thermal degradation of nitrocellulose films (13% of nitrogen content) by pyrolysis (300 °C under 0.1 MPa) in air and Ar atmospheres using T-Jump/FTIR spectroscopy. The air atmosphere was created by combining 80% N<sub>2</sub> and 20% O<sub>2</sub>, to avoid interferences provided by the strong IR absorption of CO<sub>2</sub> present in natural air. The samples were analyzed by FTIR spectroscopy under both atmospheres. Products of decomposition in air and Ar were identified as CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, H<sub>2</sub>O, HCN, and CH<sub>2</sub>O, being CO the most widely produced. According to these results, it was obvious that the atmosphere did not interfere in the measurements. The authors attributed these results to the low vapor pressure of nitrocellulose (not measurable), which implied that nitrocellulose decomposed primarily in the condensed phase on the T-Jump filament and the products thus formed were relatively independent of the surrounding atmosphere. Moreover, higher vapor pressure explosives as pentaerythritol tetranitrate (1.1x10<sup>-7</sup> MPa at 100 °C) and nitroglycerin (3.1x10<sup>-5</sup> MPa at 90 °C) were studied in this work, showing a dependence with atmosphere. In this case, a vaporization-decomposition process occurred due to the higher vapor pressure of these compounds. Hence greater mixing of the gases during decomposition process was exhibit, modifying the gases in each environment.

The analysis of pyrolysates of nitrocellulose by T-Jump/Time-Of-Flight Mass Spectrometry (T-Jump/TOF-MS) with an electron ionization (EI) source [32] was carried out by mixing nitrocellulose with diethyl ether or acetone and coating on a T-Jump filament. Later it was heated at  $\approx 1.3 \times 10^5$  K s<sup>-1</sup>, during about 9 ms, and time-resolved spectra were recorded at different times and temperatures. In these spectra, above m/z 100 no signals appeared while the main signals were observed between 15 and 60 m/z values. Peaks were assigned to OH, H<sub>2</sub>O, N<sub>2</sub>, NO, NO<sub>2</sub>, CO, HCN, HNO, HCO<sub>2</sub>, and hydrocarbons (characteristic of nitrocellulose pyrolysis) were also detected (Figure 5). In addition, it was observed that the decomposition process started at 575 K (301.85 °C), because signals different to blank runs appeared.

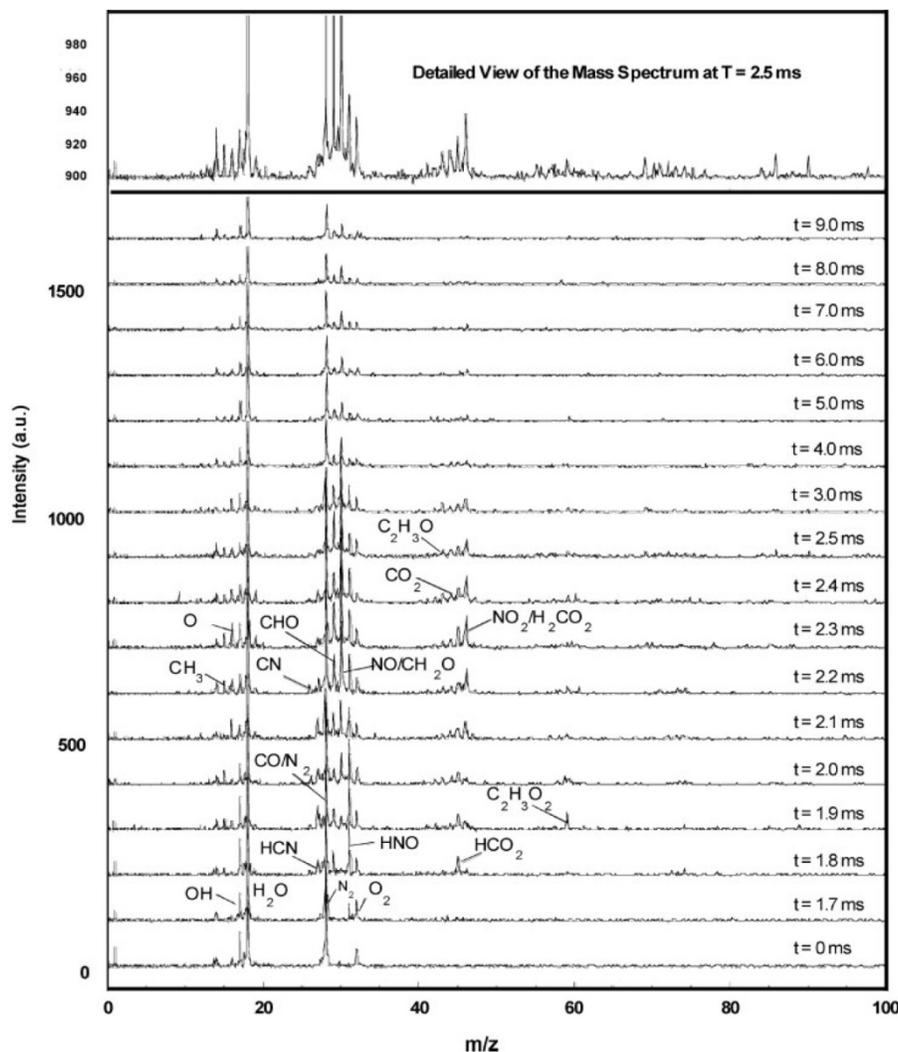


Figure 5. Time-resolved mass spectra of nitrocellulose. Heating rate  $1.3 \times 10^5 \text{ K s}^{-1}$ . EI/TOFMS conditions: Electron beam was nominally operating at 70 eV and 1 mA, with the background pressure in the TOF chamber at  $\approx 10^{-7}$  Torr. 95 spectra were sampled with a temporal resolution of 100  $\mu\text{s}$  per spectra ( $1.0 \times 10^4$  Hz), only 17 were plotted in this figure. A more detailed view of spectra at 2.5 ms (top of figure) is also showed. Reprinted from [32]. Copyright (2008), with permission of Wiley.

D.M. Cropek et al. [33] analyzed the pyrolysates of a double-base propellant composed by nitrocellulose (with a nitrogen content of 13.4%) and nitroglycerin using GC coupled with mass spectrometry (GC-MS). In addition to nitrocellulose, the other components of the propellant were investigated independently, to evaluate their contribution to the propellant behavior. Owing to the diverse mass of by-products obtained by pyrolysis, two different GC configurations were used, one for light molar mass (LMW) gases and another for heavy molar mass (HMW) gases. Main signals of the pyrogram obtained for the propellant in the LMW configuration corresponded to CO, NO, CO<sub>2</sub>, and H<sub>2</sub>O ( $\approx 70\%$  of the total peak area), while in the HMW configuration main signals were observed for not identified light gases ( $\approx 90\%$  of the total peak area) (see Figure 6).

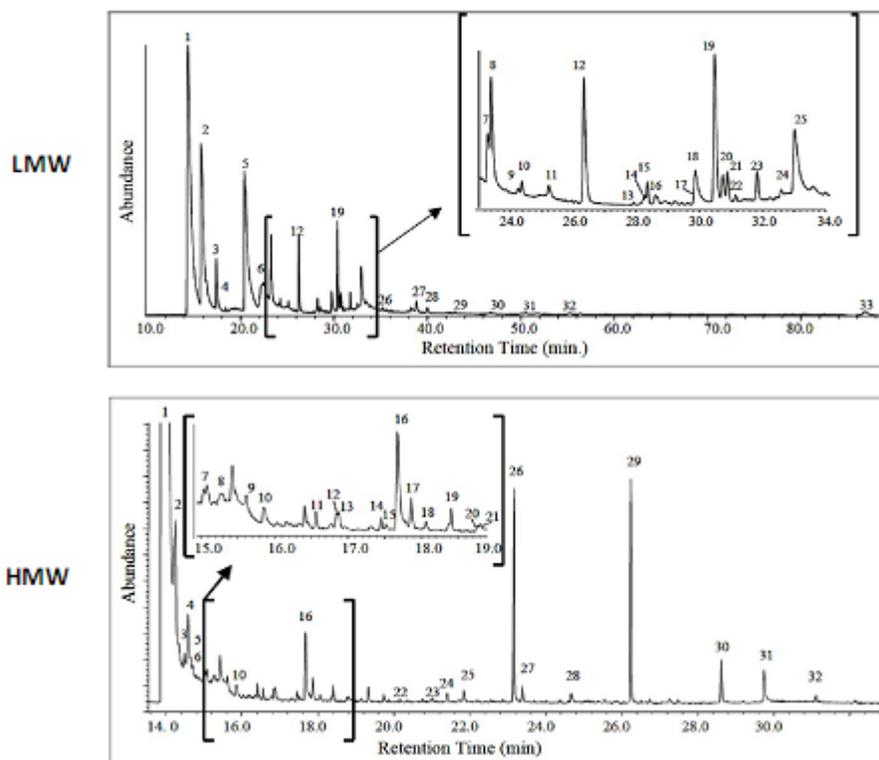


Figure 6. Pyrograms for (top) light molar mass (LMW) gases and (bottom) heavy molar mass (HMW) gases from a double-base propellant (mainly composed by nitrocellulose and nitroglycerin). GC and MS conditions: GC column of 50 m x 0.32 mm i.d. x 10  $\mu\text{m}$  film thickness. GC oven began at 40  $^{\circ}\text{C}$  for 13 minutes, ramped to 200  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C min}^{-1}$ , and stayed at 200  $^{\circ}\text{C}$  for 60 minutes. Injector port was held at 200  $^{\circ}\text{C}$  and used in the splitless mode. Detector port was held at 280  $^{\circ}\text{C}$ . Mass detector scanned from 10 to 400 amu. Identification of the pyrolysate peaks was accomplished by comparing mass spectral data to library standards. Peaks identification: (top) Peak 1: CO, NO (34.3% total peak area); peak 2:  $\text{CO}_2$  (18.7% total peak area) and peak 5:  $\text{H}_2\text{O}$  (16.1% total peak area). (bottom) Peak 1: non identified light gases (89.9% total peak area) Reprinted from [33]. Copyright (2001), with permission of US Army Corp. of Engineers.

Comparing the double-base propellant and the nitrocellulose pyrograms (not shown), it was observed that nitrocellulose was the main by-products source generated by the propellant pyrolysis. Approximately, the 50% of products proceeded from nitrocellulose, since 25 products were common in propellant and nitrocellulose. It is remarkable that the only two compounds appearing in the nitrocellulose pyrogram ( $\text{C}_2\text{H}_4\text{O}_2$  and  $\text{C}_5\text{H}_4\text{O}_2$ , for LMW and HMW analysis, respectively), were presented in propellant pyrograms, which indicated that they were produced only during the nitrocellulose pyrolysis. In addition, these comparative studies were useful to investigate which products were obtained by the decomposition of the propellant and which were obtained by later reactions produced by the generated gases.

The same authors [34] collected and characterized the incinerator emissions released during the incineration treatment of the above-mentioned double-base propellant and nitrocellulose wastes. Owing to the different emissions produced, they were sampled in four fractions: volatile organic compounds (VOC), semivolatile organic compounds (SVOC), hydrogen cyanide (HCN), and continuous emission monitors (CEM). VOC and SVOS

fractions were analyzed by GC-MS under different conditions. CEM fraction, which was constituted by total hydrocarbons (THC), NO<sub>x</sub>, O<sub>2</sub>, CO<sub>2</sub>, and CO gases, was characterized by various EPA methods (based on nondispersive infrared spectroscopy, chemiluminescence, paramagnetic properties, and heated flame ionization) and measured continuously over an entire incineration run. Main compounds analyzed in VOC fraction of both samples were toluene and benzene. Most abundant components in the SVOC fraction were unknown hydrocarbons, 2-fluorobiphenyl (in nitrocellulose samples) and di-n-propyladipate and 2-nitrodiphenylamine, which are two minor components acting as additives in the propellant. No significant amounts of HCN were detected in neither of samples. About the CEM fraction, levels of NO<sub>x</sub>, CO, and CO<sub>2</sub> increased during the incineration of the double-base propellant, and then these gases were assigned as the incineration by-products. As it was expected, O<sub>2</sub> was consumed during the process. It was also observed that nitrocellulose generated different compounds than the propellant analyzed, which was attributed to the important role of the additives in the incineration process of gunpowders.

D.M. Cropeck et al. [35], compared pyrolysis and incineration results obtained in previous works [33, 34] and concluded that pyrolysis analysis gave information about the remaining components in the incineration process, the products coming from the incomplete combustion of each component separately or in combination with other species, as well as those components that contribute to the most troublesome emissions. For example, in the case of SVOC emissions, 2-nitrodiphenylamine (unwanted by-product) was one of the principal released compounds despite being a minority component. Hence additives dominated the pyrolysis behavior in this case.

### 3.2. Biological and Mechanical Degradation of Nitrocellulose

Biological decomposition processes are focused to remove nitro groups of nitrocellulose and to transform waste nitrocellulose into a non hazardous material. Biotransformation under denitrifying and sulfidogenic conditions using an activated sludge inoculum was performed by D.L. Freedman et al. [36] to turn into a non hazardous material the waste nitrocellulose. The variation of the nitrogen content in nitrocellulose was followed by a digestion/titration method. Nitrocellulose reduced in such conditions presented, approximately, 1% of nitrogen less than virgin nitrocellulose (the exact decrease in nitrogen content was from 13.1-13.2% to 12.2-12.4%). According to these results, it is necessary the presence of electron donors to achieve the reduction of nitrocellulose (methanol in denitrifying treatment and lactate in sulfidogenic conditions) because, without them, there were not changes in the nitrogen content of samples. In addition, a study of possible changes in the structure of nitrocellulose subjected to these treatments was made by FTIR spectroscopy. After the denitrifying treatment (Figure 7) monomeric alcohol signals about 3400-3500 cm<sup>-1</sup> were detected in the FTIR spectra, may be due to the presence of hydroxyl groups, which were generated by the loss of nitro groups in the nitrocellulose.

Nevertheless, under the sulfidogenic conditions the FTIR spectra of samples were not different to those of virgin samples. About explosive properties of nitrocellulose treated, neither of the two conditions applied were able to transform the explosive samples into non-hazardous materials, in spite of a decrease of flammable and explosive properties were observed.

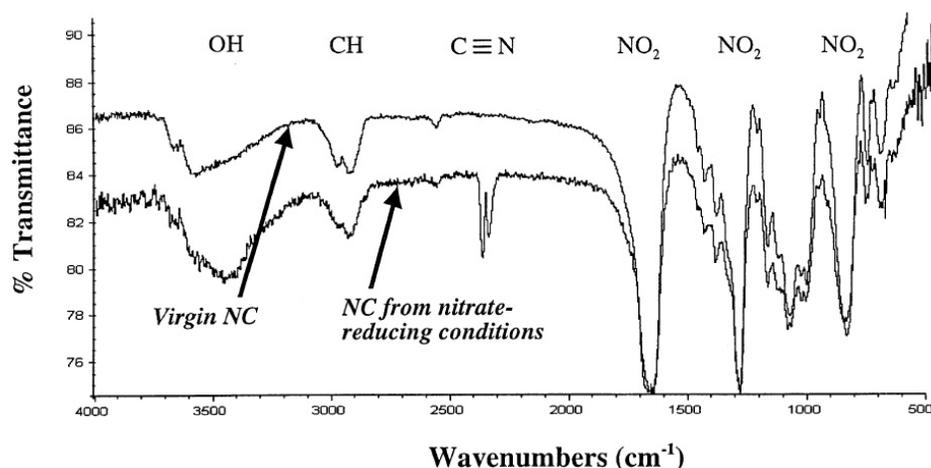


Figure 7. FTIR spectra of virgin nitrocellulose and nitrocellulose from nitrate-reducing conditions. FTIR conditions: Nicolet Spectrometer (Impact 410 IR). Reprinted from [36]. Copyright (2002), with permission of Elsevier.

Mechanochemical processes are made to assess the effect of mild stress on the nitrocellulose degradation, in order to evaluate its mechanochemical stability. S. Vyazovkin et al. [37] used a pioneer set-up based on Dynamic Mechanical Analysis (DMA) combined with Mass Spectrometry (MS) to study the degradation suffered by a film made from a nitrocellulose fiber sample with a nitrogen content of 12.4%. Experiments were carried out at 150 and 160 °C and frequencies from 100 to 600 Hz, increased manually in 100 units during 30 minutes. Temperatures above 150 °C were necessary to begin the degradation process since at lower temperature values more time was necessary to observe some degradation products by MS spectra. Nevertheless, the study of blank runs proved that there were not signals corresponding to degradation products when temperature increased, being possible to consider that only a mechanochemical degradation was present. From the different temperatures tested, nitrocellulose degradation needed more time at 150 °C. The decomposition of nitrocellulose was followed through MS peaks appearing at  $m/z$  30 ( $\text{NO}^+$  and  $\text{CH}_2\text{O}^+$  ions), because they were the most intense MS peaks of the spectra and corresponded to well known products formed during the thermal degradation of nitrocellulose. Both ions were detected in the all the experiments performed. Finally, reflected light micrographs were obtained by a polarized light microscope to take pictures of fractured films. Curiously, the examination showed that the fracture front looked similar to that of a broken window glass with a few cracks running under an angle to the front.

#### 4. CONCLUSION

Although the discovery of nitrocellulose was carried out two hundred years ago, today there are still no analytical methodologies to enable its determination with good accuracy and precision in explosive samples. In fact, main difficulties in the analysis of this polymeric compound are its high molar mass, structural complexity and unusual behavior in solution. Of

special interest is the analysis of nitrocellulose of high nitrogen content ( $\geq 12\%$ ), used in the manufacture of explosives, particularly in nitrocellulose-based gunpowders.

Most studies on high nitrogen content nitrocellulose deal with their characterization as a polymer. Regarding this subject, Size Exclusion Chromatography (SEC) is the main separation technique used for the physicochemical characterization of this polymer without previous treatment. This technique provides mainly information on molar mass, viscosity and specific refractive index of nitrocellulose.

In addition, due to the explosive nature of nitrocellulose, several studies found in the literature are focus on the determination of thermal properties of this macromolecule. Techniques such as ThermoGravimetry (TG), Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) are the most commonly used with this purpose, while Scanning Electron Microscopy (SEM) and Fourier-transform InfraRed Spectroscopy (FTIR) are employed for the morphological study of nitrocellulose.

Other important aspect of nitrocellulose contained in gunpowders is its stability and the possibility of decomposition by means of thermal, mechanical or biological processes. Most studies dealt with thermal decomposition of nitrocellulose, which is carried out mainly by means of thermal analytical techniques: TG, DSC, ThermoGravimetry-Differential Thermal Analysis (TG-DTA), Accelerating Rate Calorimetry (ARC), Modulated Differential Scanning Calorimetry (MDSC), and Pyrolysis. This degradation process was followed through the formation of by-products of reaction and the release of gases, utilizing with this aim, the analysis by FTIR, Gas Chromatography (GC), Mass Spectrometry (MS) and coupled techniques (FTIR-MS and GC-MS).

## ACKNOWLEDGMENTS

Authors thank to the Ministry of Science and Innovation the project CTQ2008-00633-E. M<sup>a</sup> Ángeles Fernández de la Ossa thanks to University of Alcalá her pre-doctoral grant.

## REFERENCES

- [1] Nelson, D.L.; Cox, M.M. *Lehninger Principios de bioquímica*; ISBN: 9788428214865; Omega: Barcelona, Spain, 2009; pp 235-270.
- [2] Monforte, M. *Las Pólvoras y sus aplicaciones. Vol. 1*; UEE Explosivos: Madrid, Spain, 1992; pp 304-360.
- [3] Saunders, C.W.; Taylor L.T. *J. Energ. Mater.* 1990, 8, 149-203.
- [4] Dow Wolff Cellulosics. (2008). Nitrocellulose. [http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh\\_014c/0901b8038014c3b9.pdf?filepath=dowwolff/pdfs/noreg/822-00007.pdf&fromPage=GetDoc](http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_014c/0901b8038014c3b9.pdf?filepath=dowwolff/pdfs/noreg/822-00007.pdf&fromPage=GetDoc).
- [5] Rasines, R.; López, M.; Torre, M.; García, C. *An. Quím.* 2009, 4, 265-270.
- [6] Helmenstine, T. Paul Vieille Biography. <http://chemistry.about.com/od/famouschemists/p/paul-vieille-bio.htm>.
- [7] Selwitz, C. *Cellulose nitrate in conservation*; ISBN: 0-89236-098-4; The Getty Conservation Institute: USA, 1998; pp 1-67.

- [8] López-López, M.; Fernández de la Ossa, M.A.; Sáiz Galindo, J.; Ferrando, J.L.; Vega, A.; Torre, M.; García-Ruiz, C. *Talanta*. 2010, *81*, 1742-1749.
- [9] Ouellet, N.; Brochu, S.; Lussier, L. *Appl. Spectrosc.* 2002, *56*, 125-133.
- [10] Cruces-Blanco, C.; Gamiz-Gracia, L.; Garcia-Campana, A.M. *Trends Anal. Chem.* 2007, *26*, 215-226.
- [11] Heinzmann, G. *Int. Annu. Conf. ICT. 33<sup>rd</sup>*. 2002, *58*, 1-5.
- [12] Macdonald, A.F. *Int. Annu. Conf. ICT. 34<sup>th</sup>*. 2003, *126*, 1-10.
- [13] Deacon, P.; Macdonald, A.; Gill, P.; Mai, N.; Bohn, M.; Pontius, H. *Int. Annu. Conf. ICT. 39<sup>th</sup>*. 2008, *68*, 1-12.
- [14] Deacon, P.; Macdonald, A.; Gill, P.; Mai, N.; Bohn, M.A.; Pontius, H.; van Hulst, M.; de Klerk, W.; Baker, C. *Int. Annu. Conf. ICT. 40<sup>th</sup>*. 2009, *81*, 1-14.
- [15] Deacon, P.R.; Garman, R.N.; Macdonald, A.F.; Baker, C.A. *Int. Annu. Conf. ICT. 37<sup>th</sup>*. 2006, *151*, 1-7.
- [16] Bellerby, J.M.; Deacon, P.R.; Gill, P.P. *Int. Annu. Conf. ICT. 37<sup>th</sup>*. 2006, *71*, 1-11.
- [17] Deacon, P.R.; Kennedy, G.R.A.; Lewis, A.L.; Macdonald, A.F. *Symp. Chem. Probl. Connected Stab. Explos. 12<sup>th</sup>*. 2004, 195-204.
- [18] Herder, G.; de Klerk, W.P.C. *J. Therm. Anal. Calorim.* 2006, *85*, 169-172.
- [19] Schroeder, M.A.; Fifer, R.A.; Miller, M.S.; Pesce-Rodriguez, R.A.; McNesby, C.J.S.; Singh, G. *Combust. Flame*. 2001, *126*, 1569-1576.
- [20] Newberry, J.; Kaste, P.J. *IEEE Trans. Magn.* 2003, *39*, 253-256.
- [21] Ksiazczak, A.; Radomski, A.; Zielenkiewicz, T. *J. Therm. Anal. Calorim.* 2003, *74*, 559-568.
- [22] Sanghavi, R.R.; Pillai, A.G.S.; Velapure, S.P.; Singh, A. *J. Energ. Mater.* 2003, *21*, 87-95.
- [23] Pourmortazavi, S.M.; Hosseini, S.G.; Rahimi-Nasrabadi, M.; Hajimirsadeghi, S.S.; Momenian, H. *J. Hazard. Mater.* 2009, *162*, 1141-1144.
- [24] Sovizi, M.R.; Hajimirsadeghi, S.S.; Naderizadeh, B. *J. Hazard. Mater.* 2009, *168*, 1134-1139.
- [25] Turcotte, R.; Acheson, B.; Armstrong, K.; Kwok, Q.S.M.; Jones, D.E.G.; Paquet, M. *Proc. Int. Pyrotech. Semin. 33<sup>rd</sup>*. 2006, 351-361.
- [26] Campbell, R.K.; Freedman, D.L.; Kim, B.J. *Environ. Eng. 1999 Proc. ASCE-CSCE Natl. Conf.* 1999, 246-253.
- [27] Binke, N.; Rong, L.; Xianqi, C.; Yuan, W.; Rongzu, H.; Qingsen, Y. *J. Therm. Anal. Calorim.* 1999, *58*, 249-256.
- [28] Binke, N.; Rong, L.; Zhengquan, Y.; Yuan, W.; Pu, Y.; Rongzu, H.; Qingsen, Y. *J. Therm. Anal. Calorim.* 1999, *58*, 403-411.
- [29] Rong, L.; Binke, N.; Yuan, W.; Zhengquan, Y.; Rongzu, H. *J. Therm. Anal. Calorim.* 1999, *58*, 369-373.
- [30] Katoh, K.; Le, L.; Kumasaki, M.; Wada, Y.; Arai, M.; Tamura, M. *Thermochim. Acta*. 2005, *431*, 161-167.
- [31] Hiyoshi, R.I.; Brill, T.B. *Propellants, Explos., Pyrotech.* 2002, *27*, 23-30.
- [32] Zhou, L.; Piekiet, N.; Chowdhury, S.; Zachariah, M.R. *Rapid Commun. Mass Spectrom.* 2009, *23*, 194-202.
- [33] Cropek, D.M.; Kemme, P.A.; Day, J.M. (2001). Pyrolytic decomposition studies of AA2, a double-base propellant. [http://owww.cecer.army.mil/techreports/Cropek\\_Pyrolysis\\_Decomposition/Cropek\\_Pyrolysis\\_decomposition.pdf](http://owww.cecer.army.mil/techreports/Cropek_Pyrolysis_Decomposition/Cropek_Pyrolysis_decomposition.pdf).

- [34] Cropek, D.M.; Day, J.M.; Kemme, P.A. (2001). Incineration by-products of AA2. NC fines, and NG slums. [http://owwww.cecer.army.mil/techreports/cropek\\_incineration/cropek\\_incineration.pdf](http://owwww.cecer.army.mil/techreports/cropek_incineration/cropek_incineration.pdf).
- [35] Cropek, D.M.; Kemme, P.A.; Day, J.M.; Cochran, J. *Environ. Sci. Technol.* 2002, 36, 4346-4351.
- [36] Freedman, D.L.; Cashwell, J.M.; Kim, B.J. *Waste Manage.* 2002, 22, 283-292.
- [37] Vyazovkin, S.; Dranca, I.; Lang, A.J. *Thermochim. Acta.* 2005, 437, 75-81.