
Project in Chemistry: 15p

# Chemical Characterisation of Nitrocellulose

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**Sammanfattning**
Nitrocellulosa är den viktigaste komponenten i många typer av ammunition, drivmedel och sprängämnen. Principerna för produktionen av nitrocellulosa har inte förändrats mycket sedan det började produceras industriellt för detta ändamål på 1800 talet. Karaktären av nitrocellulosa har en stor inverkan på slutproduktens egenskaper. Syftet med denna studie var att utveckla en metod som skulle kunna karaktärisera och skilja mellan nitrocellulosa från olika tillverkare för att kunna relatera karaktären av nitrocellulosa till egenskaperna hos ammunition, drivmedel och sprängämnen. Proverna löstes i aceton och analyserades med GC/MS och data analyserades med multivariabel statistik. FTIR användes också för att karakterisera nitrocellulosan. Resultaten för båda proverna visade mycket små skillnader när kromatogram och spektra analyserades. Denna studie visar att GC/MS och FTIR inte är lämpliga för denna typ av karaktärisering. Skillnaderna i data var inte tillräckliga för att kunna skilja proverna från varandra.

**Abstract**
Nitrocellulose is the main component in many types of ammunition, propellants and explosives. The principles of production for nitrocellulose have not changed much since the 19th century when it started being industrially produced for this purpose. The character of the nitrocellulose has a large effect on the end products abilities. The aim of this study was to develop a method that would be able to characterise and distinguish between nitrocellulose from different manufacturers to be able to relate the character of the nitrocellulose to the properties of ammunition, propellants and explosives. Samples were dissolved in acetone and analysed by GC/MS and data were then analysed by multivariable statistics. FTIR was also used to characterise the nitrocellulose. Results from both methods showed very small differences when chromatograms and spectra were analysed. This study shows that GC/MS and FTIR are not suitable for this type of characterisation. The differences between the data were not sufficient to be able to separate the samples from each other.

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# 1. Introduction

## 1.1. Nitrocellulose

Nitrocellulose, also known as cellulose nitrate, is a nitrated cellulose ester polymer that is used as the main compound in many types of ammunition, propellants and explosives as well as a wide range of other materials.

Braconnot discovered in 1833 that mixing nitric acid with carbohydrates yielded inflammable materials which he called "xyloidines" (Miles 1955). This material was of much lower purity, probably only containing 5-6% nitrogen compared to nitrocellulose that Schönbein later produced and called guncotton (Urbański 1965). Schönbein was the first one to see the potential in using nitrocellulose in explosive material (Miles 1955). In the beginning the application of nitrocellulose was limited and it took several years before its use as a reliable explosive.

Nitrocellulose has been industrially produced since the 19th century. Even if the process has changed to become more automatic the manufacturing principle has not changed much in the last hundred years. Mixing cellulose with a sulfonitric mixture of sulphuric acid, nitric acid and water is still the common way to produce nitrocellulose with high nitrogen content. Nitrocellulose is similar to the cellulose in structure. It is produced through nitrification of one, two or three of the hydroxyl groups that are connected to carbons C2, C3, and C6 of the cellulose (see Figure 1). Each cellulose monomer have three hydroxyl groups that can be substituted. This gives nitrocellulose the chemical formula $[C_6H_7O_2(OH)_{3-x}(ONO_2)_x]_n$, where $x$ is the number of hydroxyl groups substituted by nitro groups and $n$ is the number om monomers. The nitrogen level of nitrocellulose is often described/measured in degree of substitution (D.S.) which gives a number that represents the average number of hydroxyl groups that has been substituted. The following equation can be used to calculate D.S.

Equation 1.
$$D.S. = \frac{3.6 \times \text{nitrogencontent}(\%)}{31.13 - \text{nitrogencontent}(\%)}$$

The theoretical maximum substitution would yield a D.S. of 3 which equates to a nitrogen content of 14.1 %. The highest reported nitrification is a D.S. of 2.9 (≈13.9% of nitrogen content) (Miles 1955, Selwitz 1988).

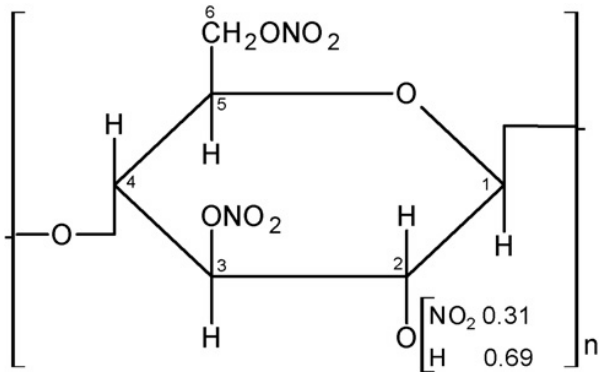


**Figure 1.** Chemical structure of nitrocellulose with nitrogen content of 12.2%. The figure also shows the distribution of hydroxyl and nitrogen on carbon C2 (López-López, de la Ossa et al. 2010).

The amount of nitrogen in the nitrocellulose affects the properties, such as solubility, viscosity and flammability. At low amounts of nitrogen the solubility in ether-alcohol increases when the nitrogen levels increases, peaking at 11 – 12% (see table 1). Higher amounts of nitrogen decreases in solubility and amounts nearing the theoretical maximum (14.1%) of nitrogen groups have a very low level of solubility in ether-alcohol. At these high amounts the nitrocellulose is commonly dissolved in acetone, etylacetate or ether-alcohol.

**Table 1.** Table showing the relationship between nitrogen content and solubility in ether-alcohol.

| D.S. | Amount of nitrogen | Solubility in ether-alcohol |
|---|---|---|
| 1.0 | 6.8% | <10% |
| 2.0 | 11.1% | 100% |
| 3.0 | 14.1% | <1% |

Different methods are used to achieve different degrees of substitution since different levels of nitrogen contents are used in the industries. Lower amount of nitrate nitrocellulose are used in a wide variants of products such as lacquer, plastic film and ink while higher percentage of nitrogen are used in propellants and explosive materials.

Especially the military applications requires a reliable product that behave as expected, and as such thorough quality controls are done. There are however two major difficulties in achieving this. The first is that cellulose, which nitrocellulose is produced from, is a natural product. Its characteristics are therefore affected by numerous variables, such as its geographical origin and the season of the year it is grown. The type of plant the cellulose is refined from also affects the characteristics of the end product. In table 2 is some examples of differences between different celluloses (table 2 is borrowed from Chemistry and technology of explosives Vol. II by Urbański, 1965). The characteristics of the nitrocellulose have large effect on the ballistic properties of ammunitions and propellants (Fernández de la Ossa et al. 2012, Johansson 2009).

**Table 2.** Different origin of celluloses molecular weight and degree of polymerization.

| Origin of cellulose | Molecular weight | Degree of polymerization |
|---|---|---|
| Unbleached cotton | 1,500,000 | 9200 |
| Purified linters | 1,500,000 – 500,000,000 | 10,000 - 3000 |
| Nettle fibre | 1,760,000 | 10,800 |
| Ramie fibre | 1,840,000 | 11,300 |
| Sulphite pulp | 400,000 | 2900 |

The second problem is the way nitrification of the cellulose is controlled. Nitrogen content of the nitrocellulose is monitored by taking out samples from the reaction chamber during production for measurements. Other characteristics, e.g. density and viscosity, are measured on the end product. Different batches often have to be mixed to achieve consistency in characteristics. The problem, that off-line measurements results in, has been approached by trying to develop a mathematical model to calculate the ideal batch time for the cellulose before nitrification (Barbosa, et al. 2005). The current standard method used to measure the nitrogen content of the nitrocellulose only measures the amount

of nitrogen per mass of nitrocellulose, it does not take in consideration how the nitrogen is distributed (MIL-DTL-244B 1996, MIL-STD-286C 1991).

### 1.2. Analytical techniques

The study of nitrocellulose is a complicated task given its high chemical and structural complexity. A wide range of techniques are being used for the analysis of this ester polymer. Here follows different techniques commonly used for characteristic studies of nitrocellulose.

#### 1.2.1. SEC

Size-exclusion chromatography (SEC) is an effective technique for analysing the polymeric characterisations of nitrocellulose. An effective set-up to use when analysing nitrocellulose is a SEC with triple detection (refractometry, viscometry and lightscattering) (Fernández de la Ossa, et al. 2011). SEC with simple detection system (refractometry) have been used to analyse the polymeric properties of nitrocellulose using polystyrene standards as a substitute (Fernández de la Ossa et al. 2011).

It has been demonstrated that the molecular weight reproducibility of data acquired by analysing nitrocellulose with SEC has a low reproducibility when comparing between different research teams (Fernández de la Ossa et al. 2012). In a study nine laboratories from eight different countries used the same SEC method to analyse nitrocellulose with nitrogen content of 11.6 – 13.5%. The result was that the main cause of the low reproducibility was differences in the drying process of the nitrocellulose and the lack of a definition of similar and good baseline in the obtained chromatograms (Fernández de la Ossa et al. 2012). This shows the complexity of generating reliable data when analysing nitrocellulose by SEC.

#### 1.2.2. FTIR

Fourier transform infrared spectroscopy (FTIR) is a common method for analysing nitrocellulose. It has been used to analyse the morphologic and thermal properties of nitrocellulose as well as the degradation of it (e.g., Kovalenko et al. 1994, Phillips et al. 1955, Schroeder et al 2001). By observing a decrease in the $NO_2$ signal and an increase in the $OH^-$ signal using FTIR and $^{13}C$-nuclear magnetic resonance (NMR) spectroscopy showed that highly nitrated nitrocellulose is not resistant to biodegradation (Tarasova et al. 2005). Using FTIR has also been proposed as a method to do quantitative analyses of nitrogen content in nitrocellulose (Gensh et al. 2011). A study of triple-bas gunpowder that used scanning electron microscope (SEM) and micro-reflectance FTIR was able to show among others that only 10µm of the top layer was affected in the ignition process (Schroeder et al. 2001).

#### 1.2.3. GC/MS

Gas chromatography (GC), alone or coupled to a mass spectrometer (MS), has commonly been used to analyse degradation of nitrocellulose that has been thermally treated (Fernández de la Ossa et al. 2011, Katoh et al. 2005). A study of fractions from pyrolysis of gunpowder by GC/MS showed that nitrocellulose was the main source of by-products. (Cropek et al. 2001b). The same study also showed that when thermally treated, nitrocellulose produced almost no heavy weight fractions. GC/MS has also been applied in characterising emissions of energetic material and energetic waste, there among analysing the incineration of nitrocellulose fines (Cropek et al. 2001a).

The common system used when studying the characteristics using GC/MS is to have a pyrolysis chamber installed to the injector (Fernández de la Ossa et al. 2011). This setup transports the gases produced from pyrolysis directly into the injector. This method is very effective to look at the characteristic of by-products and samples does not have to be dissolved but it does not give any data of the complete nitrocellulose molecule.

### 1.4. Objective
The objective is to establish a method that allows the characterisation of nitrocellulose and to be able to differentiate between nitrocellulose with different properties. That information could then be used to find correlations between the characteristics of nitrocellulose and properties of ammunition and explosives.

## 2. Method

### 2.1. Samples
The nitrocellulose samples were received from Eurenco Bofors AB. The nitrocellulose samples were from two different manufacturers, one from Finland and one from France.

### 2.2. GC/MS
Gas chromatograph was chosen for this project due to its high sensibility and reproducibility which are key qualities for this project. Samples were analysed with an Agilent HP 6890 Gas Chromatography System coupled to an Agilent HP 5973 Mass Spectrometer and an Agilent HP 7683 Injector tower with Agilent HP 7683 Autosampler. The separation was carried out using an Agilent DB-5MS (30m × 0.250mm, 0.25µm film thickness). The initial temperature was set to start at 90 ˚C because of the boiling point of the solvents and then raise to a final temperature of 350 ˚C which was the maximum of this GC system. The scan range of the mass detector was set to scan for 30.0-500.0 amu. For a more specific description of the temperature program and mass spectrometry parameters see appendix table A1. The tune profile (Figure A1) and tune scan (Figure A2) have been included in the appendix.

A series of solvents where tested to see if acetone could be avoided as solvent (see table 3). Unfortunately no other solvent then acetone was able to dissolve a satisfactory amount of nitrocellulose. Acetone was therefore used as the solvent for all analysis carried out with GC/MS. Chromatogram and mass spectrometry data were analysed using MassLynx V4.1 software. Peak areas were analysed statistically using SIMCA V13.0.3.

**Table 3.** Observed solubility of nitrocellulose in different solvents.

| Solvent | Observed solubility of nitrocellulose |
|---|---|
| Toluene | Did not dissolve and some slurry was produced |
| Propanol | Did not dissolve |
| Metanol | Did not dissolve |
| Acetone | Fully dissolved |
| Etanol | Did not dissolve and some slurry was produced |
| Methylene chloride | Did not dissolve and some slurry was produced |
| Hexane | Did not dissolve and a lot of slurry was produced |
| Acetonitrile | Most dissolved and some slurry was produced |
| Ethyl acetate | Fully dissolved but liquid became gelatinous |

Less than 1gm of each of the nitrocellulose samples were heated in a tin can until ignition. The cans were then swabbed with acetone which were then collected in glass vails. These samples were analysed with the same temperature program as the samples that were not thermally treated.

### 2.3. FTIR

Nitrocellulose samples were also analysed by comparing FTIR spectra. The spectra were acquired with a PerkinElmer Spectrum Two FTIR – UATR (Universal Attenuated Total Reflectance). A lithium tantalate detector was used with an applied scan range of 4000-450 $cm^{-1}$. PerkinElmer Spectrum V10.03.07.0112 software was used to analyse the spectra.

## 3. Results and analysis

### 3.1 Gas chromatography

The chromatogram from the Finish and French samples showed high similarity, as seen in figure 2. Higher concentrations of nitrocellulose would be needed to detect any possible differences between the Finish and the French nitrocellulose that could be used to characterise them. Unfortunately, because of the gelatinous effect of nitrocellulose it would not be possible to analyse such high concentrations with the GC/MS system used in this study (Miles 1955). Another option would be to further optimise the temperature program but further separation in the presence of the viscous nitrocellulose, was not expected to improve the results.

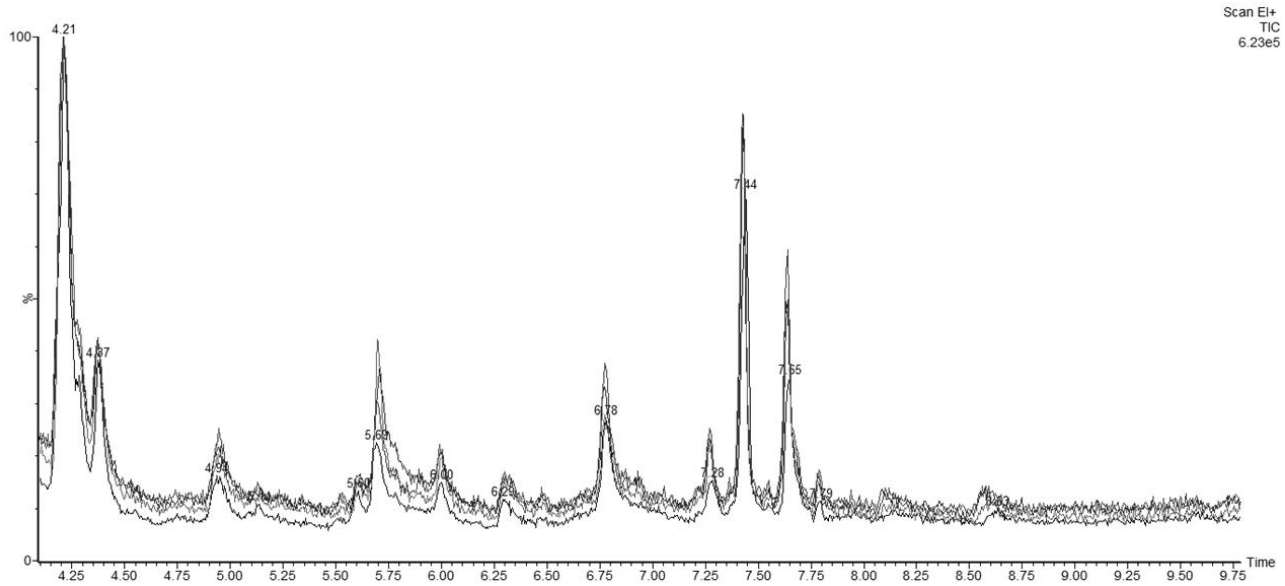


**Figure 2.** Total ion chromatogram showing the similarity of two samples of French and two samples of Finish nitrocellulose. The x-axis shows the retention time in minutes and on the y-axis the signal intensity is showed in percent of the highest peak. Full scan 50-500 at 3.09 scans/sec. GC conditions described in text.

The Finish and the French thermally treated samples also showed a very high similarity towards one and other. When the chromatograms of the thermally treated and untreated nitrocellulose samples are compared there are some differences but also a lot of similarities as seen in figure 3. Most of the difference are between retention times 4.10 – 6.50. The peak at 5.71 is not present in the thermally treated samples while the other peaks seem to have shifted slightly to a lower retention time.

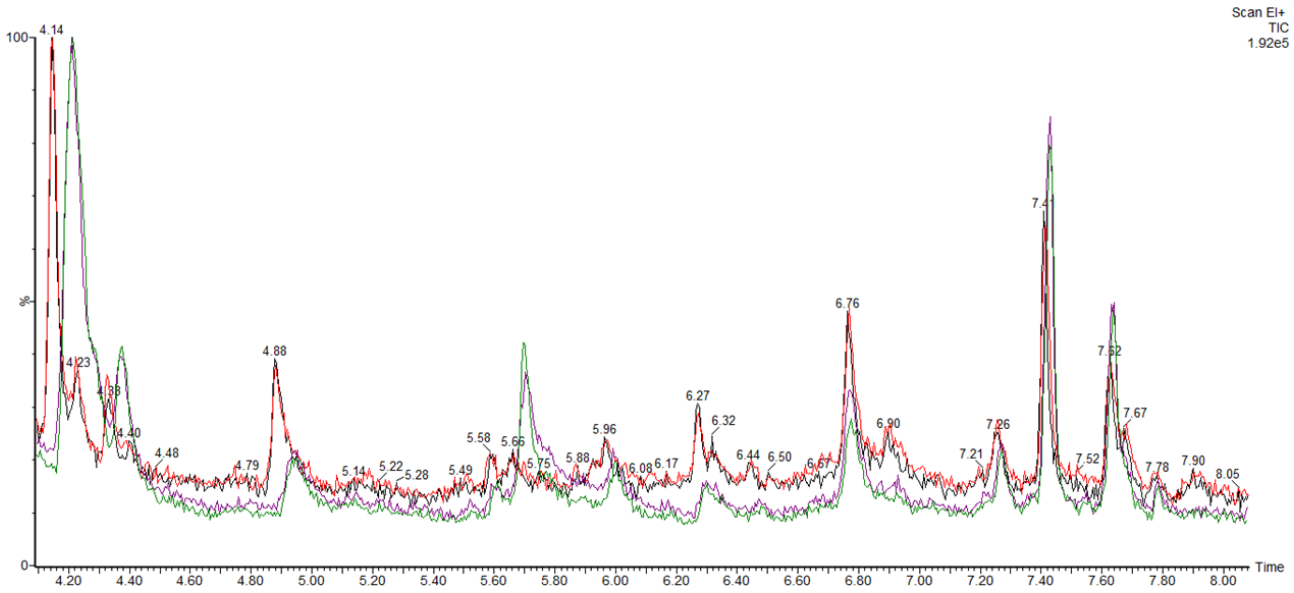


**Figure 3.** Total ion chromatogram of the Finish and French samples both thermally treated and not. The Finish sample that was not thermally treated is shown as the purple line and the thermally treated as the black line, the French sample that was not thermally treated is shown as the green line and the thermally treated as the red line. The x-axis is the retention time in minutes and on the y-axis the signal intensity is showed in percent of the highest peak which is set as 100%. Full scan 50-500 at 3.09 scan/sec. GC conditions described in text.

### 3.3 Multivariable statistical evaluation

When peak areas of selected peaks at different retention times were analysed by using multivariable statistics (SIMCA) no distinct difference could be observed between the Finish and the French nitrocellulose. Peak areas that had a shift in retention time, see figure 3, were interpreted as the same peaks. The score plot of the principle component analysis (PCA) is given in figure 7. The variation between the sample occasion (5, 6, B) is larger than the variation of between the Finish and French nitrocellulose. For a complete list of peaks and areas that were analysed see appendix table A2. All data was normalised in SIMCA by scaling to unit variance.

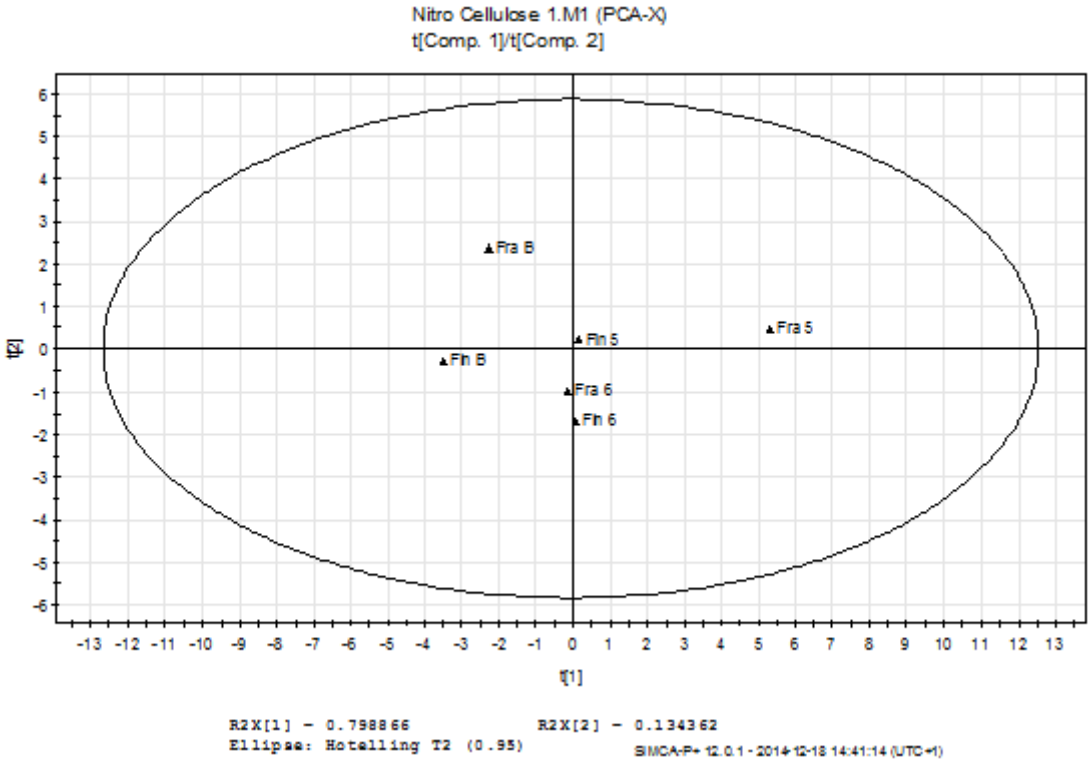


**Figure 4.** Score plot of peak areas of the thermally treated samples and samples that were not thermally treated. Samples of the Finish nitrocellulose are marked as *Fin* and samples of the French as *Fra*. The samples that were thermally treated before analysed are marked with a *B* at the end. Model statistics are given in table 4.

**Table 4**

| | R2VX | R2VX(cum) | Q2VX | Q2 limit | Q2VX(cum) |
|---|---|---|---|---|---|
| PC 1 | 0.798866 | 0.798866 | 0.573872 | 0.230769 | 0.573872 |
| PC 2 | 0.134362 | 0.933229 | 0.121646 | 0.266667 | 0.625709 |

The loading plot given in figure 8 clearly shows the configuration of all peaks except for the peak at 5.71 minutes (min). This peak indicates the difference between the thermally threated samples and the untreated nitrocellulose as can be seen in the corresponding score plot (figure 7). In PC2 a difference between the early (5-6 min.) and the later (>7 min.) elating compounds can be seen. And although the differences are minimal (13% PC2). Finish samples are always located below the French samples. Including more MS data might highlight this differences.

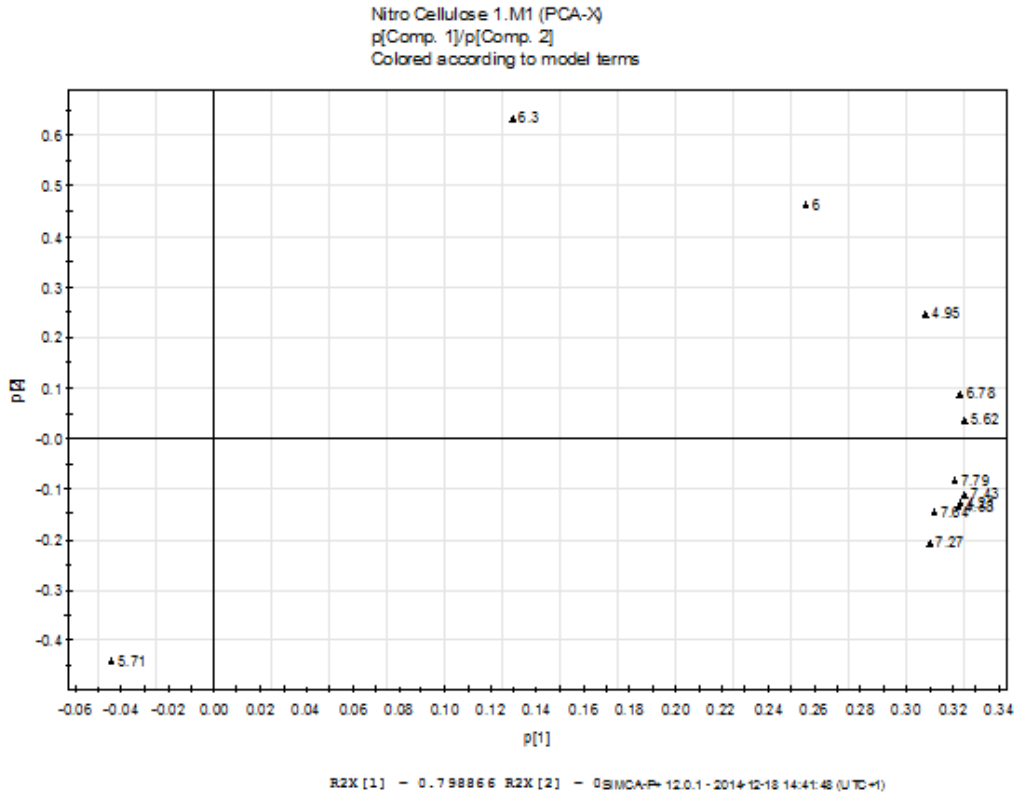


**Figure 5.** Loading plot of peak areas from the Finish and French samples. The number at each score point is the retention time of the peak. Showing different GC/MS peaks labeled with their retention times.

### 3.2. Mass spectrometry

The fraction patterns from the Finish and French nitrocellulose showed high similarity as seen in figure 4. This was to be expected since the chromatogram of the samples seen in figure 2 showed such similarity. The nitrocellulose were fractioned into light weight molecules. Fractions with an m/z over 100 was very scarce or very large, molecules with an m/z >500 could not be detected with the system used. The results were the same for the samples that were thermally treated. This was expected of the thermally treated samples since previous studies have shown that when nitrocellulose is ignited very small amounts of heavy weight species are produced (Cropek et al. 2001b).

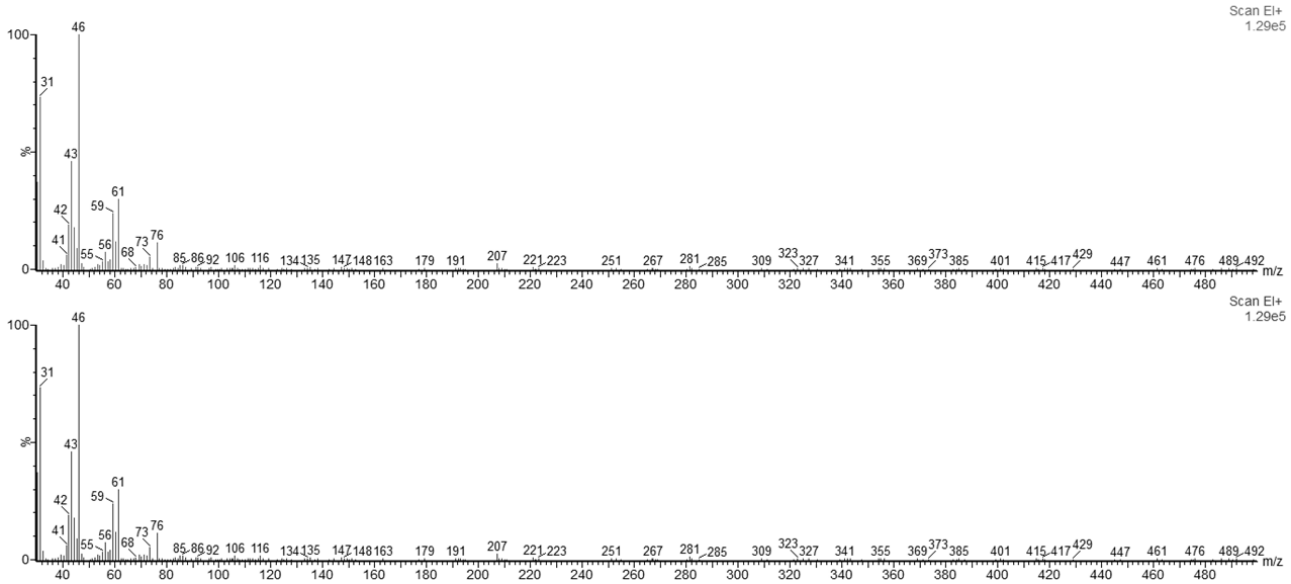


**Figure 6.** Mass spectra of peaks at 4.21 min elution time. Top spectrum is from a Finish sample and bottom spectrum is from a French sample. The fractions of the different nitrocellulose are very similar and shows no apparent differences in the mass ratios.

The mass spectra were identical when the peaks of the thermally treated samples were compared to the samples that were not thermally treated, for an example see figure 5. Which shows that there is a shift in retention times of the early peaks in the chromatogram between the samples. The reason for this shift of retention time is unknown. It could be speculated that in the samples that are not thermally treated the early peaks have a slightly longer retention time because of gelatinous effect and that the gelatinous effect does not occur when samples that are thermally treated are dissolved in acetone.

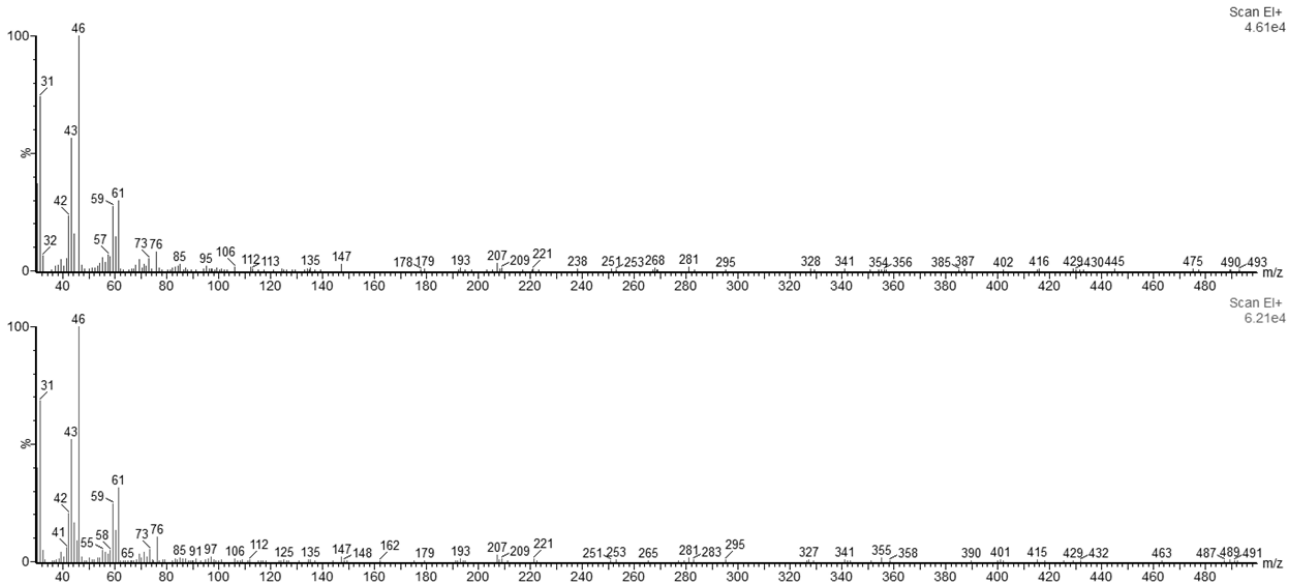


**Figure 7.** Mass spectra from French thermally treated sample with retention time 4.15 min (top spectrum) and sample not thermally treated with retention time 4.21 min (bottom spectrum). These retention times correspond to the largest peaks from each chromatogram, as seen in figure 3. The peaks seem to be the same species as the mass spectra are identical.

Mass spectrum of the untreated French nitrocellulose sample showed in figure 4 and 5 was compare to NIST mass spectra library. The results did not show nitrocellulose but showed the presences of nitro groups, the five top results are listed in table 4, all containing nitro groups. The resemblance of the nitrocellulose sample and 1,3-propanediol, 2-methyl-2-[(nitrooxy)metyl]-,dinitrate (ester) (the top result from table 4) are showed in figure 6. If this compound was to be subjected pyrolysis it would emit several of the gases seen in studies of pyrolysis of nitrocellulose, e.g. nitrous oxide, carbon dioxide and nitric oxide (Cropek et al. 2001b). Mass spectra of each peak of the same French was analysed and compared to NIST mass spectra library (see appendix figure A3 for a complete list of top hits).

**Table 4**

| Hit | Compound Name |
|---|---|
| 1 | 1,3-PROPANEDIOL, 2-METHYL-2-[(NITROOXY)METYL]-,DINITRATE (ESTER) |
| 2 | 1,3-PROPANEDIOL, DINITRATE |
| 3 | NITROGLYCERIN |
| 4 | 1,2-PROPANEDIOL, DINITRATE |
| 5 | 1,4-BUTANEDIOL, DINITRATE |

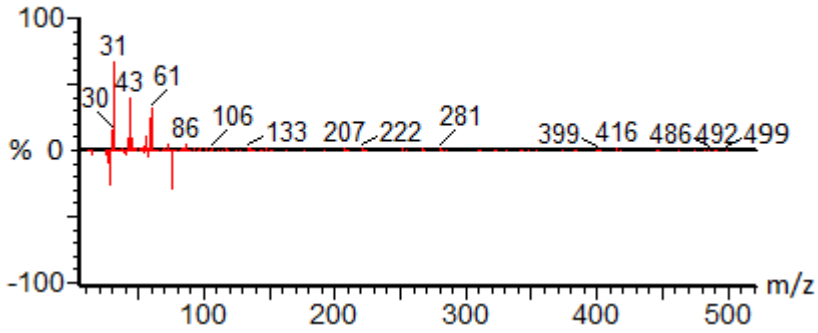


**Figure 8.** Delta spectrum of French spectrum from figure 4 and spectrum of top hit from table 4.

### 3.4. FTIR

While only small differences were seen using GC/MS, FTIR was used to characterise the nitrocellulose. The FTIR Spectra of the two nitrocellulose samples were very similar as seen in figure 9. Comparison showed a similarity >98% making it very difficult to characterise nitrocellulose from different manufacturers. Due to the high similarity of the two different nitrocellulose and time restraints no further attempts were made to characterise nitrocellulose with FTIR.

The spectra corresponds well with earlier studies on nitrocellulose using FTIR (López-López et al. 2010). The three most intense peaks (1660, 1280 and 840 $cm^{-1}$) are due to antisymmetric and symmetric stretching of $NO_2$ and valance stretching of NO. The small group of peaks with lower intensity in the range of 1200 – 950 $cm^{-1}$ are the effect of the different vibrations of the CO group (Kovalenko et al. 1994).

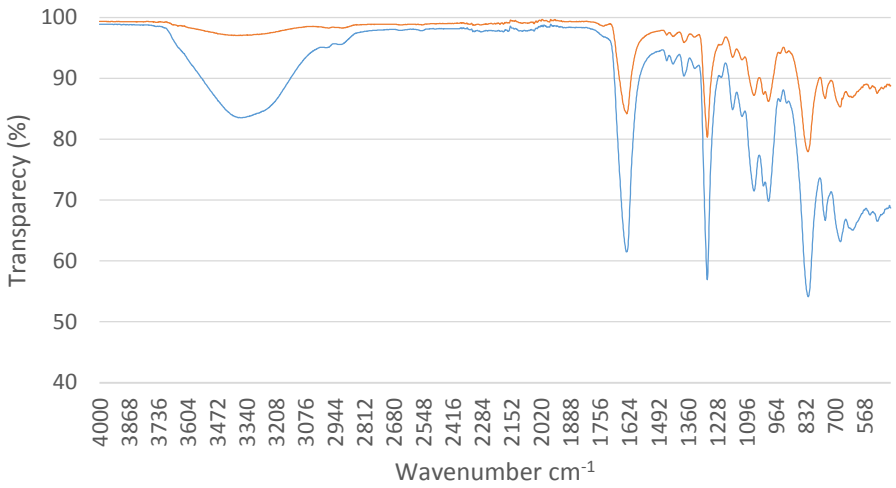


**Figure 9.** FTIR spectra of nitrocellulose from two different producers. The orange line is the result from the Finish manufacturer's nitrocellulose and the blue from the French.

## 4. Discussion

To date there are no published data of characterisation of nitrocellulose by GC/MS where nitrocellulose has not been thermally treated. Analysing nitrocellulose that has been subjected to pyrolysis gives much information of the by-products of nitrocellulose but very little of the complete nitrocellulose polymer. The results from the GC/MS method used in this study did unfortunately not show any complete monomers or polymers in the mass spectra generated by it. However, the results still show consistency with published data as many of the species that were identified when mass spectra where compared to NIST library would yield the same gases if ignited as found when analysing nitrocellulose by GC/MS coupled to a pyrolysis chamber (Cropek 2001b).

The reason that the nitrocellulose from the Finish and French manufacturers show such high similarity when analysed with both GC/MS and FTIR could be that there is a very small variation between nitrocellulose samples. However, it seems very unlikely that nitrocellulose produced at different places should end up almost identical. The manufactory procedure, environment, cellulose and other raw materials would have to be identical. For an ester polymer such as nitrocellulose this is highly improbable, especially considering how that batches often need to be mixed to achieve some consistency.

One explanation would be that there are polymerisation problem and other species than nitrocellulose present in the samples that hides the peaks of the nitrocellulose. Another explanation could be that the peaks that represents the difference are not intense enough and higher concentrations would be needed to observe differences using GC/MS.

### 4.1. Safety percussions

The nitrocellulose samples were stored in room temperature (RT) in a secured cabinet. Small amounts of water was added to each sample to prohibit spontaneous combustion. Fume hoods and safety apparels were used when samples and solvents were handled.

### 4.2. Problems during the project

Several technical problems were encountered with the GC/MS system which set the project back several weeks. The initial test-runs of the samples with acetone as solvent looked promising. When the first measured samples were run systematic contaminating peaks where obscuring the spectra of

the nitrocellulose. The origin of the peaks are not clear but appeared to be silica when analysed. The contaminating peaks disappeared after column, and liner model were changed.

It was also discovered that any sample dissolved in acetone could only be analysed ones. Contaminating peaks of what seemed to be silica when analysed would appear if the same sample was loaded to the GC/MC system multiple times. This was also observed in the blank acetone samples as seen in figure 10. The silica membrane on the caps to the vails could be the source of the contamination if a piece of silica membrane is pulled down into the acetone and dissolves every time the injector needle takes a sample. This is supported by the fact that the contaminating peaks area became larger for every time a sample was analysed, seen in figure 10.

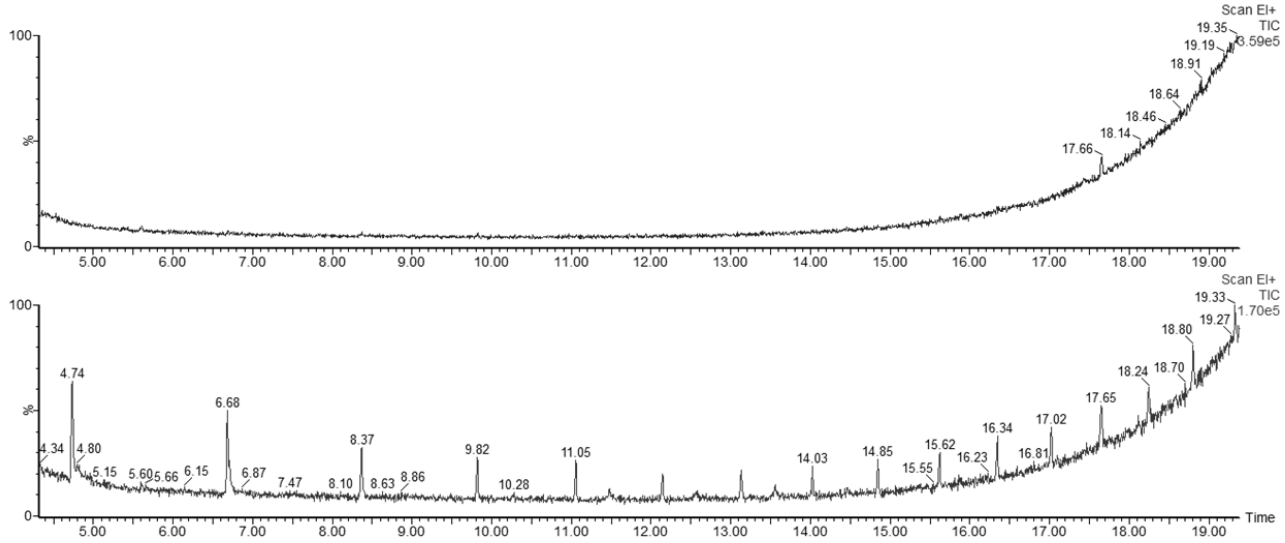


**Figure 10.** Gas chromatogram of acetone. Top chromatogram is from first time the acetone is analysed. The bottom chromatogram shows the same sample of acetone analysed for the second time two days later.

### 4.3. Further experiments

If the study were to be continued more replicates should be done to get better statistical significance. Another method that was speculated but not carried out due to time restraints was to do a solid phase microextraction (SPME) of the nitrocellulose and analyse by GC/MS. A factor that has to be addressed before performing this experiment would be the risk of thermal activation of the nitrocellulose when heated, which could cause an explosion when in a closed vessel.

It would be interesting to analyse the samples by LC/MS which is more compatible with macro molecules such as nitrocellulose.

## 5. Conclusion

It is the conclusion of this paper that it is not preferable to use GC/MS or FTIR to characterise nitrocellulose from different manufacturers. There are several aspects that lead to this conclusion. The chromatograms of the different nitrocellulose samples showed much similarity.

As mentioned before, due to time limitation and technical problems the sample group of this analysis is small. However, the high similarity between the samples strongly supports this conclusion.

## 6. Consideration

Nitrocellulose is a very stable pollutant and has a high resistance to biodegradation. The effect of nitrocellulose pollution and how to minimize the effects of it is a problem that is being researched (e.g., Ganev 2001, Kim et al. 1997, Liu 2003, Cropek et al. 2001a). A better understanding of the correlation between characteristics of nitrocellulose and the properties of ammunition, propellants and explosives manufactured from it could lead to the development of safer products. Not only safer ammunition, propellants and explosives but also better ignition yarn which is used in fire exits. Other products could also benefit from a better understanding of the characteristics of nitrocellulose, e.g., lacquers, glue and plastics. It would also help with the development of a more efficient manufacturing processes which would have environmental benefits.

The increase of terrorism in recent years demands new methods to investigate these types of crimes. Better characterisation of nitrocellulose would help in identification and tracking of ammunition and explosives. Qualitative analyses of nitrocellulose are not common, and have rarely been published to date. The only analytical tools used in qualitative studies of highly nitrated nitrocellulose are ion-mobility spectrometry (IMS), mass spectroscopy (MS), liquid chromatograph (LC) and vibrational spectroscopy (Fernández de la Ossa et al. 2011). There has been a large progress since the new millennium, making it possible to characterise and identify highly-nitrated nitrocellulose in explosives (Fernández de la Ossa et al. 2011).

## 7. Acknowledgment

I would like to take this opportunity to thank my advisor Bert van Bavel for all his help, advice and suggestions.

I would also like to thank everybody that works in the MTM laboratory for making me feel so welcomed.

## 8. References


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## 9. Apendix

**Table A1.** GC method

**OVEN**
Initial temp: 90 'C (On)
Initial time: 2.00 min
Ramps:

| # | Rate | Final temp | Final time |
|---|---|---|---|
| 1 | 15.00 | 350 | 11.00 |

Post temp: 0 'C
Post time: 0.00 min
Run time: 30.33 min
Maximum temp: 350 'C
Equilibration time: 0.00 min

CRYO (N2)
Cryo: Off
Cryo fault: Off
Cryo timeout: 120.00 min (Off)
Quick cryo cool: Off
Ambient temp: 25 'C

**INLET**
Mode: Splitless
Initial temp: 250 'C (On)
Pressure: 10.00 psi (On)
Purge flow: 15.0 mL/min
Purge time: 2.00 min
Total flow: 19.1 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 4.00 min
Gas type: Helium

**COLUMN**
Capillary Column
Model Number: J&W 122-5032
DB-5
Max temperature: 325 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant pressure
Pressure: 10.00 psi
Nominal initial flow: 1.0 mL/min
Average velocity: 37 cm/sec
Inlet: Back Inlet
Outlet: MSD
Outlet pressure: vacuum

**THERMAL AUX 2**
Use: MSD Transfer Line Heater
Description: MSD TL
Initial temp: 280 'C (On)

**GC INJECTOR**
Sample Washes 0
Sample Pumps 4
Injection Volume 1.00 microliters
Syringe Size 10.0 microliters
PreInj Solvent A Washes 8
PreInj Solvent B Washes 8
PostInj Solvent A Washes 0
PostInj Solvent B Washes 0
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

MS Information
Solvent Delay : 4.00 min

[Scan Parameters]
Low Mass : 30.0
High Mass : 500.0
Threshold : 150
[MSZones]
MS Quad : 106 C maximum 200 C
MS Source : 230 C maximum 250 C

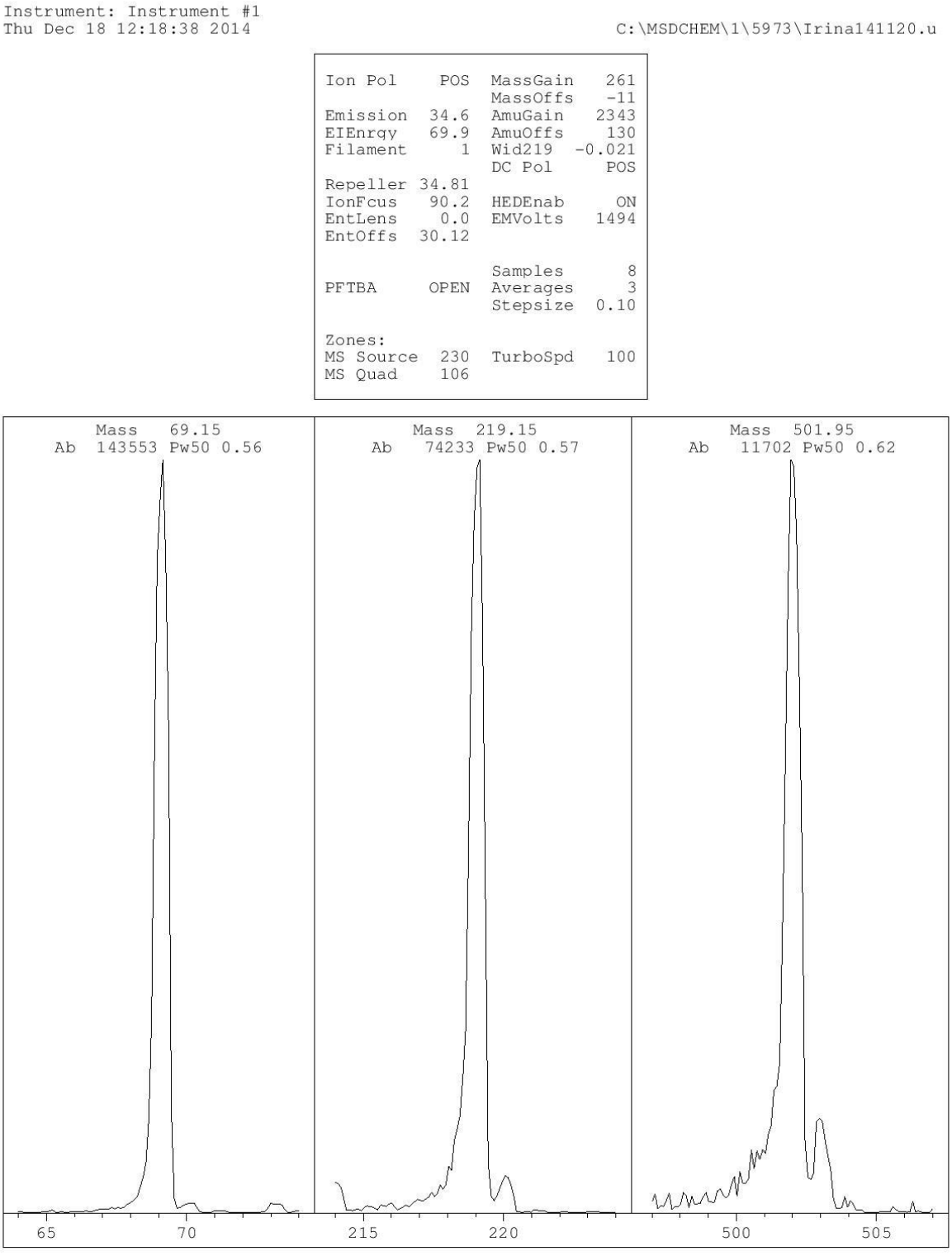
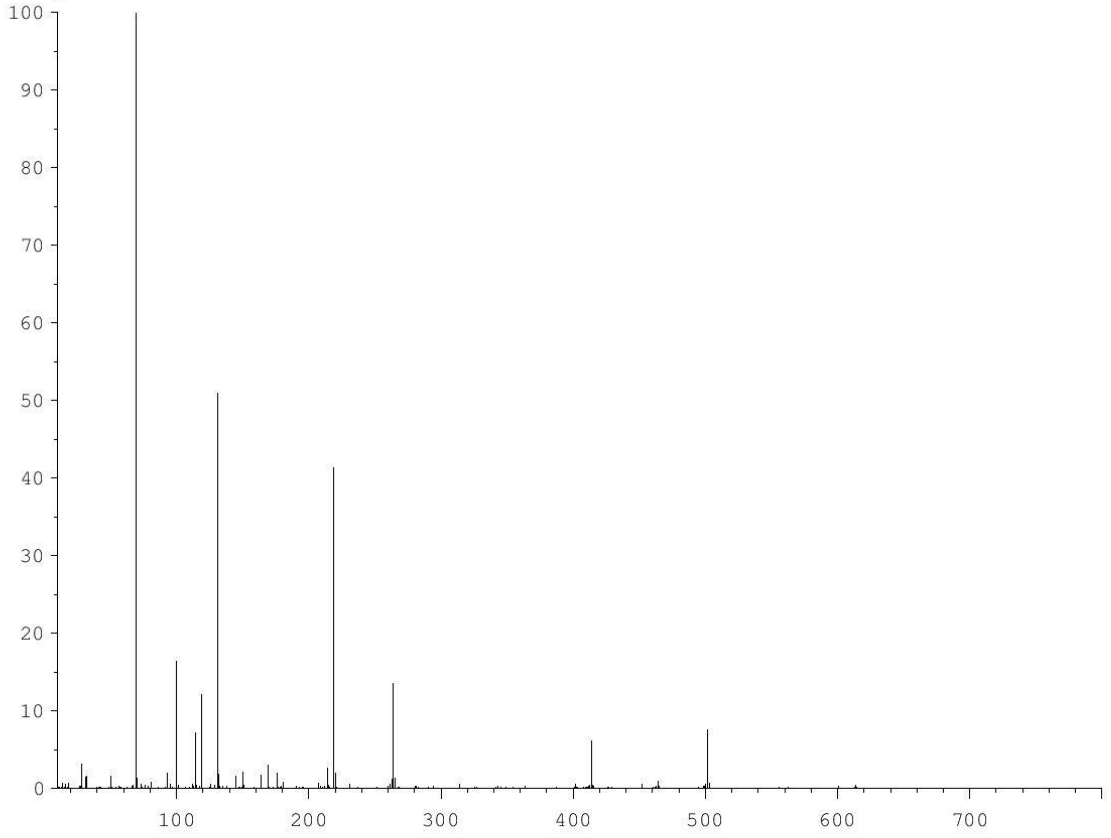



**Figure A1.** Tune profile of GC/MS

Instrument: Instrument #1
Thu Dec 18 12:19:23 2014 C:\MSDCHEM\1\5973\Irina141120.u

| | | | |
|---|---|---|---|
| Ion Pol | POS | MassGain | 261 |
| | | MassOffs | -11 |
| Emission | 34.6 | AmuGain | 2343 |
| EIEnrgy | 69.9 | AmuOffs | 130 |
| Filament | 1 | Wid219 | -0.021 |
| | | DC Pol | POS |
| Repeller | 34.81 | | |
| IonFcus | 90.2 | HEDEnab | ON |
| EntLens | 0.0 | EMVolts | 1494 |
| EntOffs | 30.12 | | |
| | | Samples | 8 |
| PFTBA | OPEN | Averages | 3 |
| | | Stepsize | 0.10 |
| Zones: | | | |
| MS Source | 230 | TurboSpd | 100 |
| MS Quad | 106 | | |

Scan: 10.00 - 800.00 Samples: 8 Thresh: 100 Step: 0.10
157 peaks Base: 69.15 Abundance: 73504




| Mass | Abund | Rel Abund | Iso Mass | Iso Abund | Iso Ratio |
|---|---|---|---|---|---|
| 69.15 | 73504 | 100.00 | 69.95 | 951 | 1.29 |
| 219.05 | 30400 | 41.36 | 220.05 | 1467 | 4.83 |
| 502.05 | 5599 | 7.62 | 502.85 | 548 | 9.79 |

**Figure A2.** Tune scan of GC/MS

**Table A2.** Table of intergraded peak area of nitrocellulose samples. Sample that were thermally treated ends with a *B*.

| | | Peak area | | | | | |
|---|---|---|---|---|---|---|---|
| Retention Time | Mass used for area | Finish 5 | Finish 6 | French 5 | French 5 | Finish B | French B |
| 4.21 | 31 | 2867 | 3683 | 6079 | 3019 | 920 | 1192 |
| 4.38 | 56 | 415 | 546 | 905 | 463 | 93 | 155 |
| 4.95 | 55 | 895 | 787 | 1364 | 862 | 620 | 873 |
| 5.62 | 46 | 357 | 393 | 954 | 397 | 143 | 229 |
| 5.71 | 91 | 1368 | 2830 | 2396 | 3657 | - | - |
| 6.00 | 43 | 205 | 148 | 301 | 199 | - | - |
| 6.30 | 55 | 98 | 78 | 134 | 93 | 88 | 135 |
| 6.78 | 46 | 637 | 513 | 1107 | 594 | 127 | 411 |
| 7.27 | 57 | 304 | 301 | 396 | 290 | 171 | 163 |
| 7.43 | 61 | 1062 | 1204 | 2151 | 1161 | 481 | 486 |
| 7.64 | 71 | 971 | 970 | 1315 | 809 | 335 | 446 |
| 7.79 | 71 | 156 | 189 | 277 | 149 | 104 | 109 |

**Table A3.** Table of top five hits when mass spectrum of a French sample was compared to NIST mass spectrum library.

| Retention Time | Hit | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| 4.21 | 1,3-PROPANEDIOL, 2-METHYL-2-[(NITROOXY)M | 1,3-PROPANEDIOL, DINITRATE | NITROGLYCERIN | 1,2-PROPANEDIOL, DINITRATE | 1,4-BUTANEDIOL, DINITRATE |
| 4.37 | PENTAERYTHRITOL TETRANITRATE | NITRIC ACID, OCTYL ESTER | 1,3-PROPANEDIOL, 2,2-DIMETHYL-, DINITRAT | NITRIC ACID, HEXYL ESTER | OXIRANE, (FLUOROMETHYL)- |
| 4.95 | CARBAZIC ACID, 3-PENTYLIDENE-, ETHYL EST | 4,7,9-TRIOXABICYCLO(4,2,0)NONANE | 1-ISO-PROPYL-3,6-DIAZAHOMOADAMANTAN-9-ON | 2,6-DODECADIEN-1-OL, 3,7,11-TRIMETHYL-, | CYCLOHEXANAMINE, N-CYCLOHEPTYLIDENE- |
| 5.62 | XANTHATIN, 8-[4-[[(TETRAHYDROPYRROL-2,5- | L-HOMOCYSTEINE | HISTIDINE, N-BOC-2-CYANO- | IMIDAZOLE, 2-TRIFLUOROMETHYL-5-NITRO- | N-[4-(DIMETHYLAMINO)PHENYL]-N'-(3-HYDROX |
| 5.71 | THIOCYANIC ACID, PHENYLMETHYL ESTER | 4-BENZYLOXYPHENYLACETONITRILE | 4-BENZYLOXYBROMOBENZENE | 2-BENZYLOXYPHENYLACETONITRILE | 4-BENZYLOXYIODOBENZENE |
| 6.00 | TETRAACETYL-D-XYLONIC NITRILE | D-LYXO-D-MANNO-NONONIC-1,4-LACTON | L-GALA-L-IDO-OCTONIC LACTONE | 1-.BETA.-D-RIBOFURANOSYL-1,2,4-TRIAZOLE- | CYCLOCYTIDINE HYDROCHLORIDE |
| 6.30 | NITRIC ACID, NONYL ESTER | HYDROXYLAMINE, O-(2-METHYLPROPYL)- | N-METHYL-N'-NITROGUANIDINE | CYCLOHEXANOL, 2-METHYL-, TRANS- | HYDROXYLAMINE, O-(3-METHYLBUTYL)- |
| 6.78 | D-ALTRONIC ACID | 5-KETOFRRUCTOSE | METHYL-.ALPHA.-D-RIBOFURANOSIDE | 2,3,4,5-TETRAHYDROXYPENTANAL | 1-NITRO-1-DEOXY-D-GLYCERO-L-MANNOHEPTITO |
| 7.27 | HEXANOIC ACID, 3-ETHYL-, METHYL ESTER | .ALPHA.-D-GLUCOPYRANOSIDE, METHYL | BUTANOIC ACID, 2-METHYL-, HEXYL ESTER | BUTANOIC ACID, 2-METHYL-, HEXYL ESTER | BUTANOIC ACID, 2-METHYL-, HEXYL ESTER |
| 7.43 | 5-KETOFRRUCTOSE | 1-NITRO-1-DEOXY-D-GLYCERO-L-MANNOHEPTITO | L-ARABINOSE | D-GLYCERO-D-IDO-HEPTOSE | D-ALTRONIC ACID |
| 7.65 | 1,2,4-BUTANETRIOL, TRINITRATE | D-GALACTOSE, 6-DEOXY- | BUTANAMIDE, N-FORMYL-2-HYDROXY-3-METHYL- | OXIRANE, 2,2'-[1,4-BUTANEDIYLBIS(OXYMETH | 1,4-DIETHOXYBUTANE |
| 7.79 | 1,2,3-THIADIAZOLE, 5-METHYL- | BUTANAMIDE, N-FORMYL-2-HYDROXY-3-METHYL- | BUTANE, 2,2'-[METHYLENEBIS(OXY)]BIS[2-ME | 4-METHYLTHIAZOLE | 1,2,4-BUTANETRIOL, TRINITRATE |