ANALYZING THE MIGRATION OF PLASTICIZERS IN POWDERS BY IMAGING SPECTROSCOPY

Heike Pontius, Manuela Dörich, Moritz Heil

Fraunhofer-Institut für Chemische Technologie (ICT),
Joseph-von-Fraunhofer-Straße 7, 76327 Pfinztal, Germany

Abstract

Granular propellants contain plasticizers or deterrents. With plasticizers mechanical characteristics are adjusted while deterrents have an influence on combustion. Both remain mobile inside the polymer matrix implying that they may migrate through the grain. That process will be intensified by higher temperatures. During their lifetimes propellants are exposed to different temperatures so migration processes might have a great influence on performance and safety.
First efforts have been made to develop technics and methods to determine the spatial distribution of plasticizers and deterrents inside propellants. This paper presents results realized with a FTIR microscope.

Paper 120, pages 120-1 to 120-10 in Proceedings of the 47rd International Annual Conference of ICT, 'Energetic Materials – Synthesis, Characterization, Processing', June 28 to August 1, 2016, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (ICT), D-76327 Pfinztal, Germany.

1. Introduction

There are several motives for the application of volatile organic compounds in granular propellants. First embedded plasticizers help to tune the desired mechanical characteristics of different propellants by softening the structure induced by the polymer binder. Second effective deterrents act as combustion moderators when being coated on the surface. The deterrent penetrates into the grain up to a certain depth. At the beginning of the combustion progress when the burning surface is large, it retards the burning rate, but later the diminishing concentration of the deterrent leads to an increase of the burning rate compensating the decreasing burning surface.

Since the binders are not cured the organics remain mobile inside the polymer matrix. Surface coatings may migrate into the grain resulting in an unacceptable increase of burning rate and higher pressure when firing the weapon. Plasticizers may form irregular profiles or quit the material completely which means that the mechanical properties of the ammunition cannot be maintained.

During their lifetime propellants are exposed to different temperatures which may exceed the moderate temperatures during regular storage afar. Even a small temperature increase can cause a faster migration process resulting in large changes in concentration. Moreover the presence of other liquid ingredients like nitroglycerin in the propellant matrix can stimulate the migration.

The purpose of their application can no longer be gained when deterrent or plasticizer molecules have left their places inside the binder matrix, diluting all over the propellant or exuding to the surface. The migration problem is concerning both the performance and the safety lifetime of a munition and so it is a sensitive issue when looking for stability.

Does a change in the characteristics of a propellant arise from an altered distribution of deterrent or plasticizer? To give an answer to that question primarily it has to be looked if the spatial distribution has changed. It is necessary to develop technics and methods to determine deterrents and plasticizers in energetic systems in spatial resolution. In this paper first studies in this field will be presented.

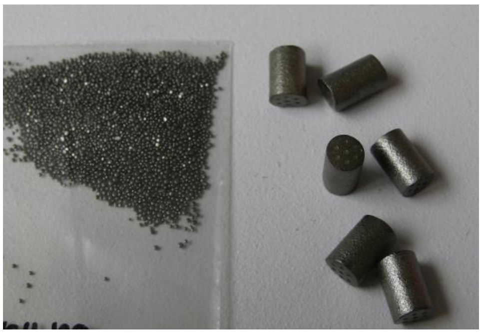
2. Experiments

2.1 Analytical method

Infrared (IR) microscopy was chosen as first analytical method. A Bruker Optics Hyperion 3000 microscope mounted on a FTIR spectrometer Vertex 70 was used in this study. The IR spectrometer is working in the 10.000 cm^{-1} to 380 cm^{-1} range with a resolution of 0.4 cm^{-1}.

2.2 Materials

For first investigations three propellants were chosen: Ball powder KP 13414, MRCA Q5560 propellant, and a seven hole low temperature coefficient propellant from ICT. The ball powder and the MRCA Q5560 have dibutylphthalate (DBP) as deterrent on the surface while the ICT propellant is containing DNDA-57 as plasticizer.

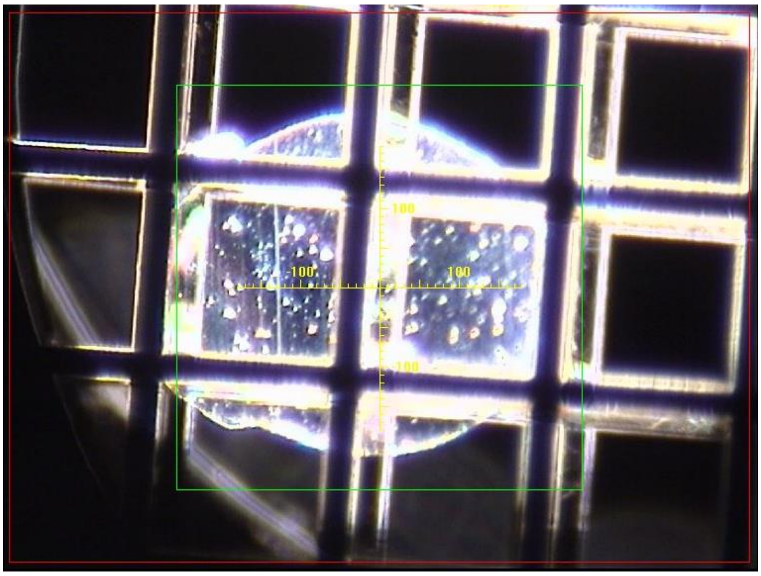


Picture 1: Ball powder KP 13414 and DNDA propellant in comparison

3. Results and discussion

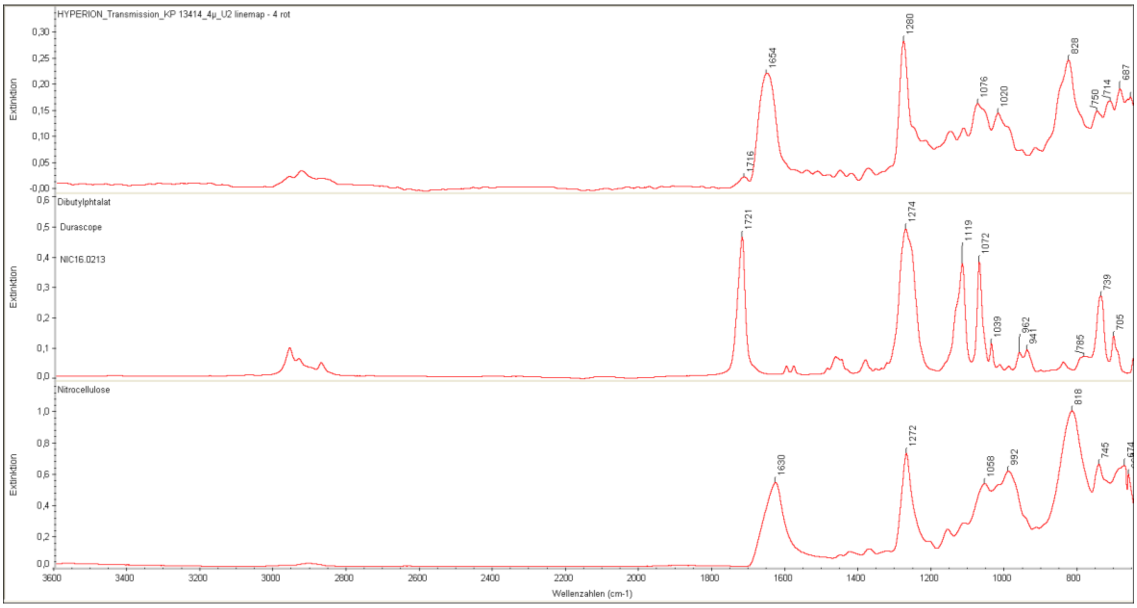
3.1 Ball powder KP 13414

The ball powder was placed in a two component adhesive and cured. Afterwards it was cut by a microtome into thin slices. The slices were fixed inside a micromesh. Since only one grain could be cured in one preparation it is not so easy to find a positon where the edge of the sliced grain is free accessible (see picture 2).



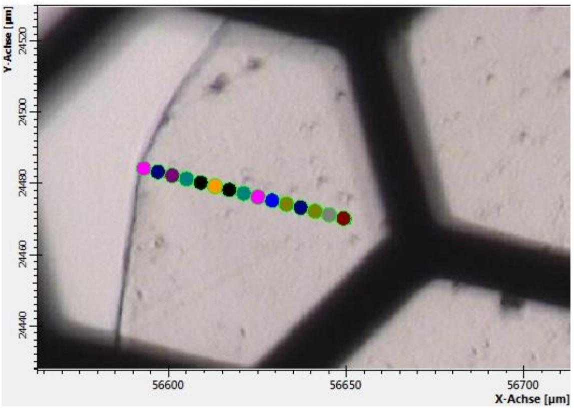
Picture 2: One slice of the ball powder KP 13414 fixed inside a micromesh shown by an UV/VIS-microscope. The width of the whole picture is 600 µm.

Picture 3 shows an IR reflection spectrum of the ball powder KP 13414 determined with ATR compared to its ingredients dibutylphthalate (DBP) and nitrocellulose (NC). The characteristic adsorption band of DBP at 1724 cm^{-1} appears at 1716 cm^{-1} in the spectrum of KP 13414.



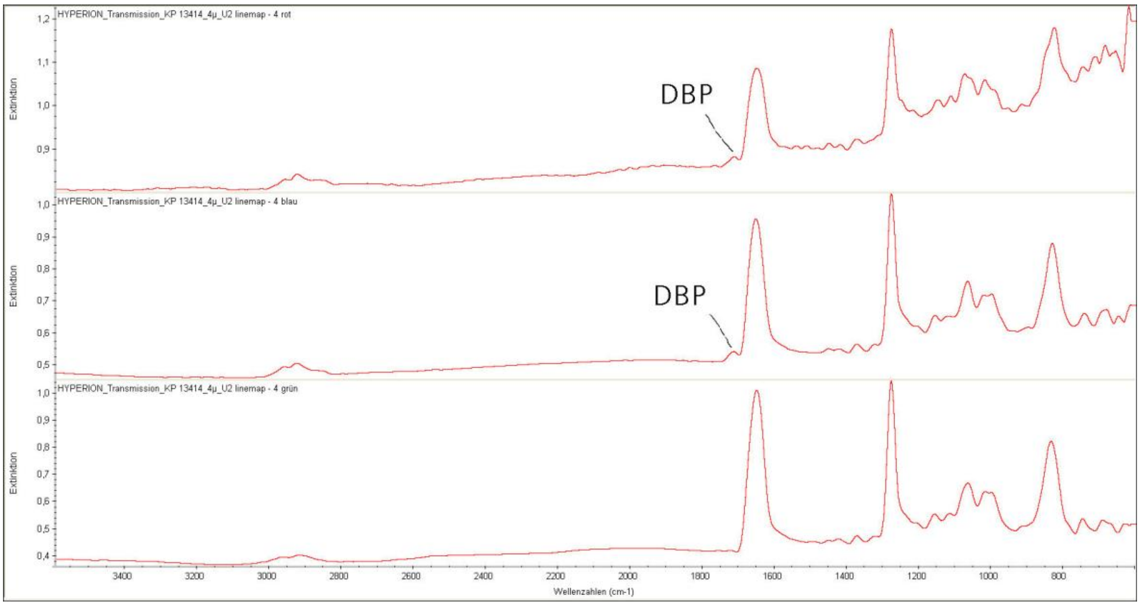
Picture 3: IR reflection spectrum (ATR) of ball powder KP 13414 (first IR spectrum) including dibutylphthalate DBP (second spectrum) and nitrocellulose (third spectrum).

Picture 4 shows the points inside the slice from which IR spectra were made. The bright border is the edge of the slice while the dark hexagon shows the metal micromesh in which the embedded slice is fixed.

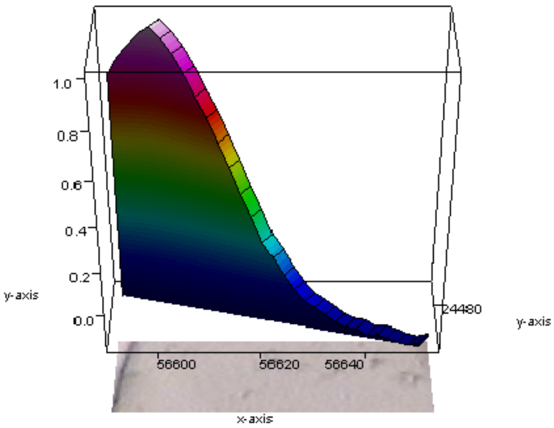


Picture 4: A 4 µm slice of ball powder KP 13414 on the table of the IR microscope. The round dots mark the points were one IR spectrum was made.

Picture 5 shows three selected spectra of KP 13414 at different depths. It is clearly visible that when coming deeper in the grain, the concentration of DBP is declining. This is also shown in picture 6.



Picture 5: IR transmission spectra of KP 13414 at different depths from the grain surface. In the first and the second spectrum dibutylphthalate (DBP) can be seen; in the third spectrum representing the deepest place measured inside the grain, there is no DBP detectable anymore.

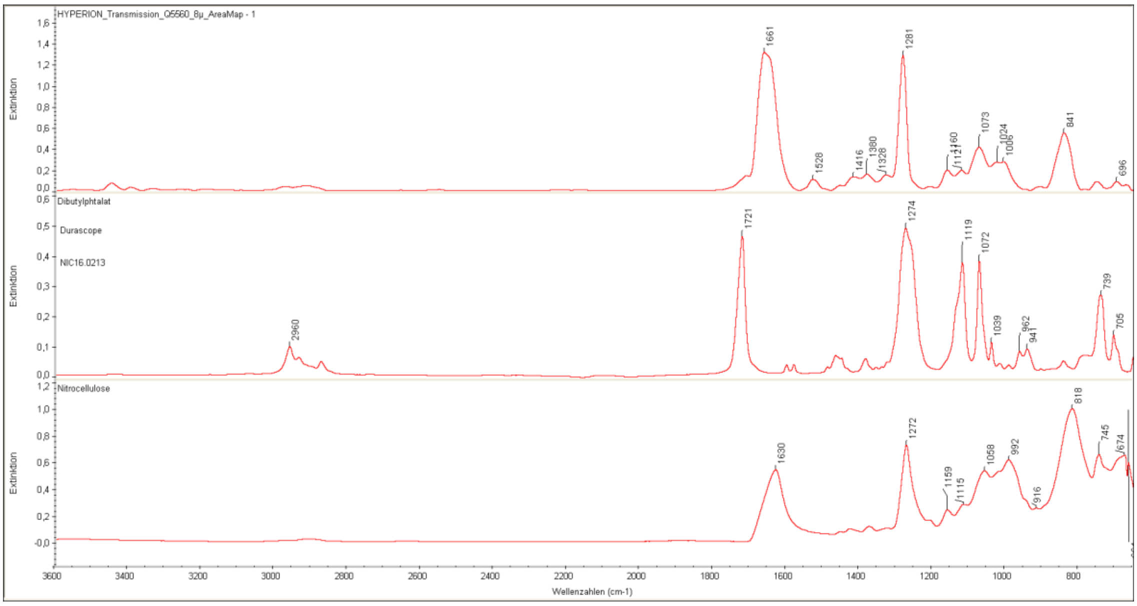


Picture 6: First increasing and then declining concentration of dibutyl-phthalate (DBP) inside a grain of ball powder KP 13414. The surface of the grain is located on the left side of the picture.

Since the adsorption band of DBP at 1716 cm^{-1} is not very high the next intent is to work with thicker microtome slices.

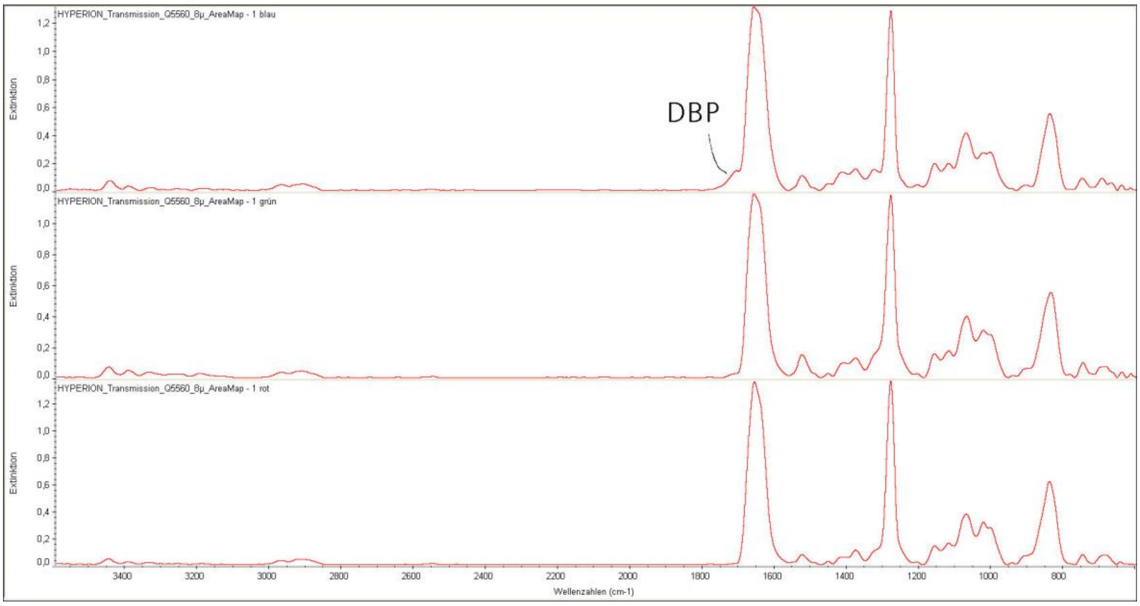
3.2 MRCA Q5560 propellant

Picture 7 shows an IR reflection spectrum of MRCA Q5560 as identified with ATR. The second and the third spectra are from the ingredients dibutylphthalate (DBP) and nitrocellulose (NC). There is little overlap of the characteristic adsorption bands of the deterrent with the matrix so in principle studies should be possible.

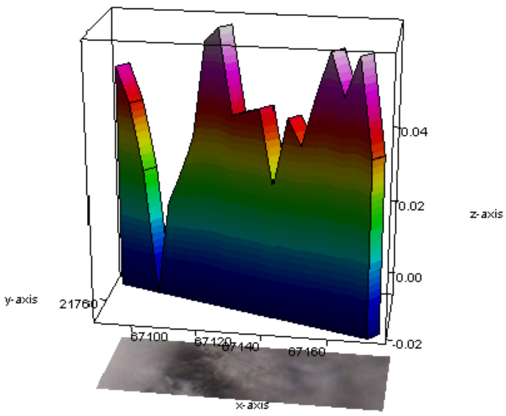


Picture 7: IR reflection spectrum (ATR) of MRCA Q5560 (first IR spectrum) including dibutylphthalate (second spectrum) and nitrocellulose (third spectrum).

But when exploring 4 µm microtome slices with the IR microscope it was not possible to find dibutylphthalate (DBP) inside the matrix. It could be detected when the thickness of the slice was raised to 8 µm indicating that the concentration of the surface coating decreased overall (picture 8). As shown in picture 9 it was not possible to find any constancy in the deterrent profile. Since the analyzed propellant is almost thirty years old it is likely that it has undergone natural aging and presents the expected migration.



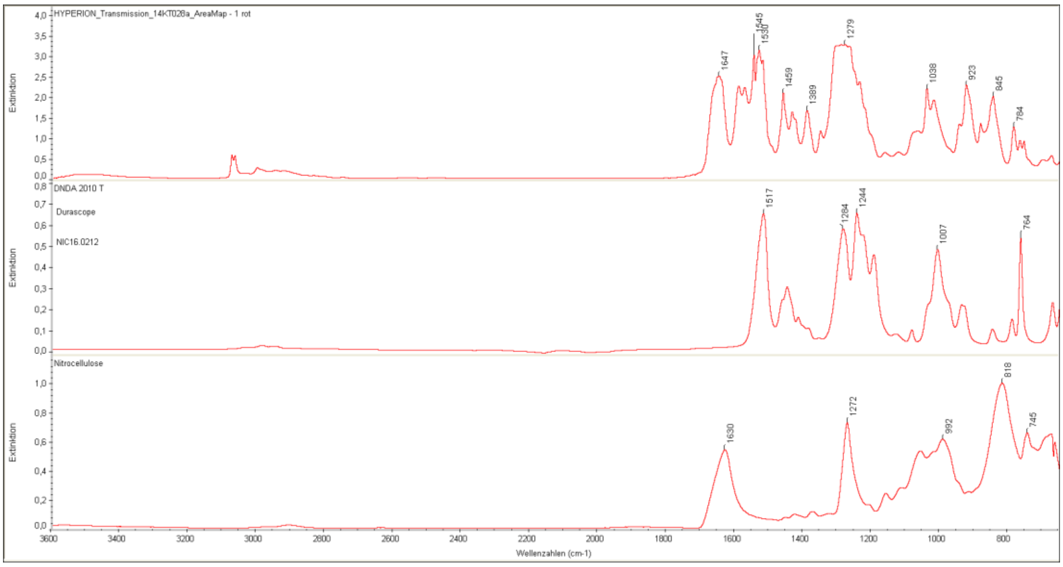
Picture 8: IR transmission spectra of MRCA Q5560 (8 µm slice) at different depths from the grain surface.



Picture 9: No constant declining of the concentration profile of dibutylphthalate (DBP) inside MRCA Q5560.
The surface of the grain is located on the left side of the picture.

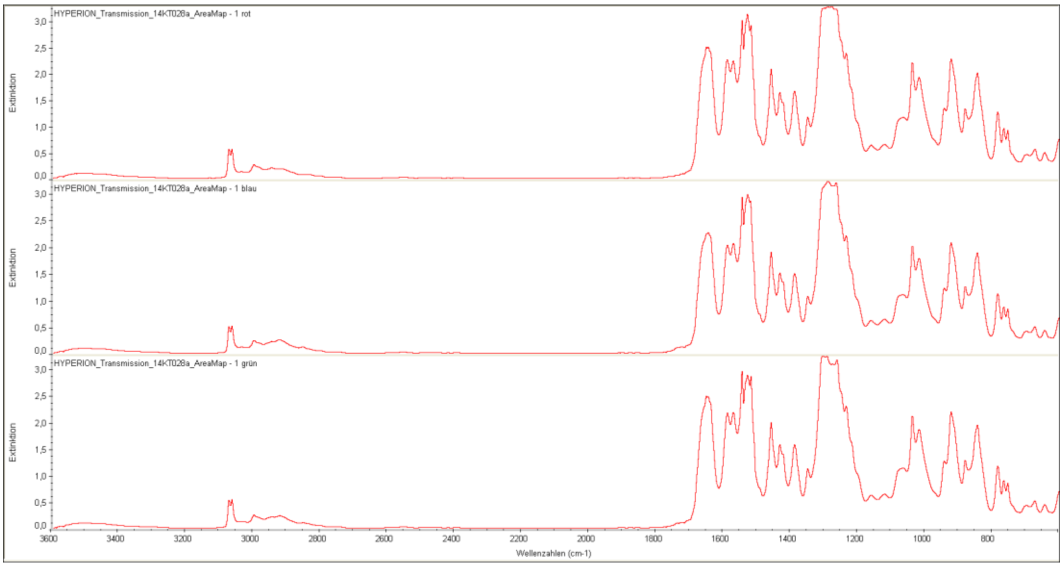
3.3 DNDA propellant

Picture 10 shows an IR reflection spectrum of the DNDA propellant determined with ATR compared to its ingredients: the plasticizer DNDA-57 and nitrocellulose (NC). The characteristic adsorption band of DNDA-57 at 1517 cm^{-1} appears at 1526 cm^{-1} in the spectrum of the propellant but it overlaps with the matrix.



Picture 10: IR reflection spectrum (ATR) of DNDA propellant (first IR spectrum) including DNDA-57 (second) and nitrocellulose (third spectrum).

Moreover the propellant grains are too soft to be cut with the standard microtome. When cutting it with a rotation microtome it smeared at first over the cut surface and blocked the holes. A better outcome is gained when the grains are frozen before cutting. But so far the achieved transmission spectra are oversaturated (see picture 11). For further analysis it is necessary to get thinner slices.



Picture 11: IR transmission spectra of the DNDA propellant taken at different depths from the grain surface. Differences can’t be seen since the transmission spectra are oversaturated.

4. Forecast

In further works other plasticizers and deterrents will be implied. The focus will be on the quantitative evaluation of the data. To induce higher migration rates the propellants will be stored at higher temperatures.
Moreover it is planned to track the reduction of plasticizers and deterrents also by the established method high pressure liquid chromatography (HPLC) to verify the quantitative evaluation with the IR microscope.
To get a better overview over the running processes other methods will be included also: mass loss tests at different temperatures, size exclusion chromatography (SEC), raman spectroscopy. This larger approach will help to get an evidence if migration is accompanied by the other reactions occurring inside the propellant over its lifetime and if a correlation between migration and mechanical properties of a propellant can be expected.