Determination of stabilisers in nitrocellulose-based propellants before and after ageing

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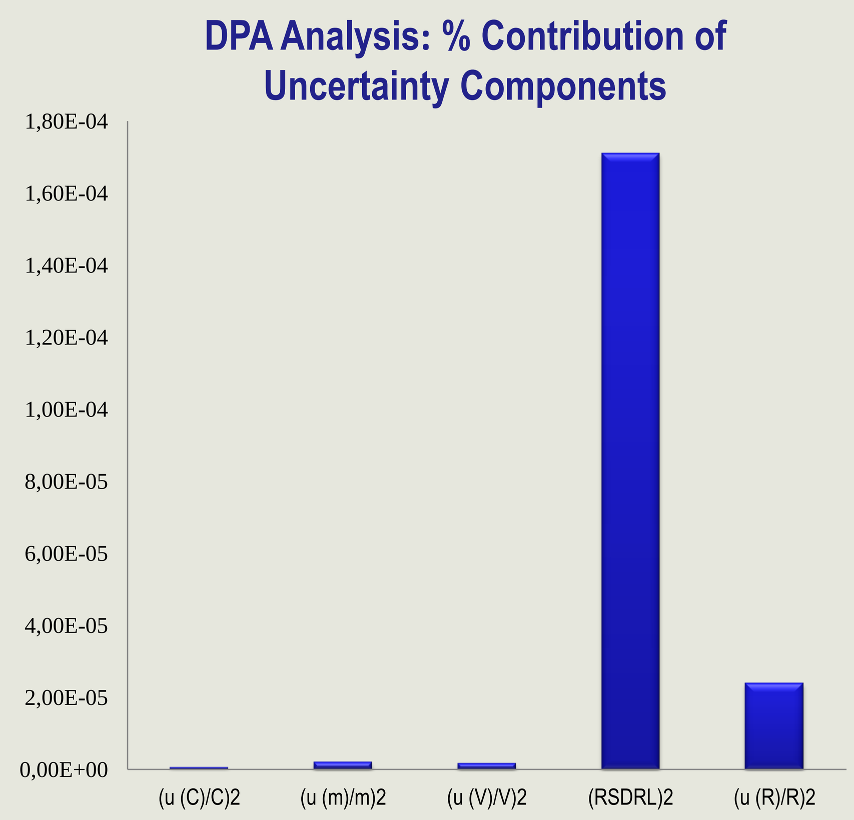
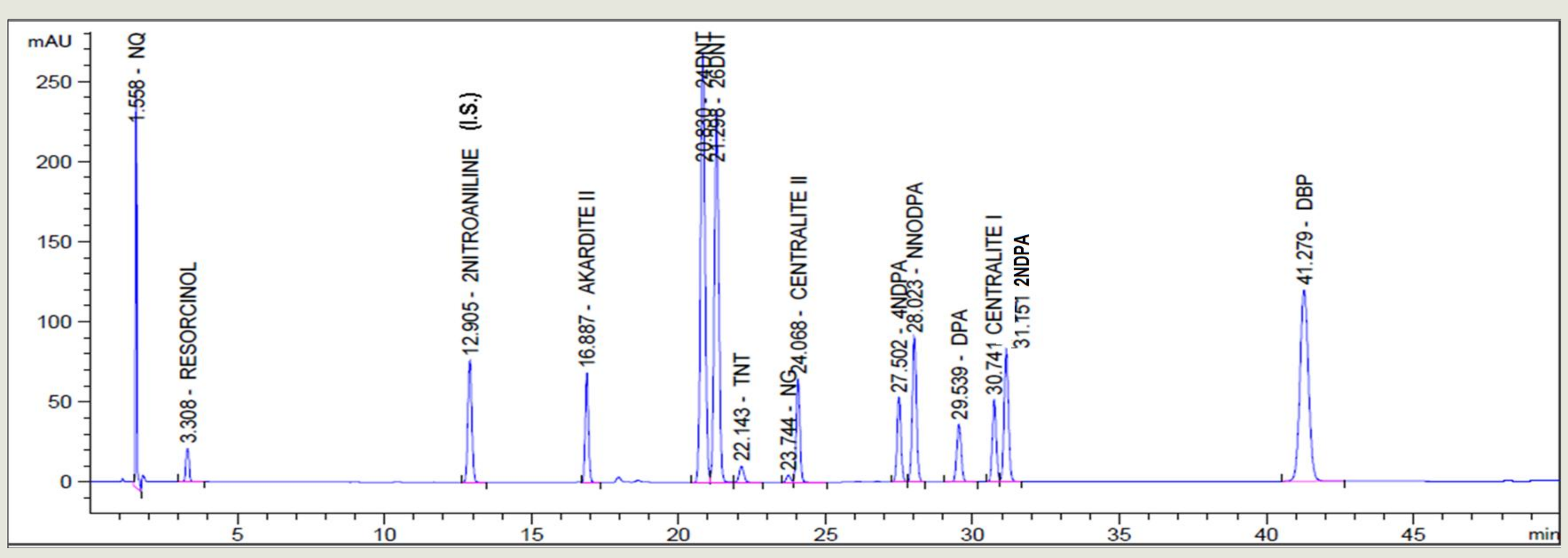
Smokeless powder has been developed in the 1800s in order to replace black powder and is the primary propellant in civilian and military ammunition. These types of propellants are nitrocellulose-based and they are divided into three categories (single, double, triple based). Each category contains key additives such as stabilisers, other energetic materials, plasticisers etc. The prediction of the lifespan of propellants is of high significance not only for economical and performance but most importantly for safety reasons. High temperatures (>30°C) or high moisture content (>65%) can lead to the degradation of stabilisers which subsequently can cause chemical instability and therefore self ignition. The National Guard Laboratory (NGL) was established in 2014 and its main purpose is to determine the stability of the propellants for the safety of civilians and military personnel. NGL uses two different techniques, Heat Flow Calorimetry (HFC) and High Performance Liquid Chromatography (HPLC) which are both validated [1]. HFC measures the decomposition rate (calculated from the recorded heat flow curve) and yields information regarding the stability of propellants as well as the prediction of their lifespan [2]. Using HPLC, qualitative and quantitative determination of five initial and two daughter stabilizers present in the propellant before and after artificial ageing (the ageing of propellants is carried out artificially by HFC) is evaluated. From the results obtained separately by the above mentioned techniques is possible to predict whether the propellant is suitable for safe storage.

HPLC ANALYSIS OF PROPELLANT COMPONENTS

CHROMATOGRAPHIC CONDITIONS	
HPLC	Agilent Infinity 1260
Detector	Agilent DIODE ARRAY
Wavelength	230nm
Column	Zorbax Eclipse XDB C8 (3.5μm) 150x 4.6mm
Column Temperature	40°C
Sample Temperature	5°C
Internal Standard	2-Nitroaniline
Calibration	Curve for each compound 10-300mg/L





Chromatographic Separations of Smokeless Powder Additives

Recovery, Repeatability, Reproducibility obtained from the spiked samples at spiking level 0.2%

STABILISERS	%RECOVERY	RSD_r	RSD_{RL}	u_c	u_{exp}(%)
Akardite II	95.75	0.493	2.830	0.31	1.7
Centralite II (MC)	99.67	0.558	1.081	0.56	2.9
4NDPA	97.92	1.179	2.777	0.75	4.0
NODPA	98.24	1.149	2.569	0.76	3.9
DPA	99.20	0.817	1.767	0.55	2.8
Centralite I (EC)	98.94	0.983	2.371	0.65	3.3
2NDPA	94.16	2.145	2.603	1.32	7.2

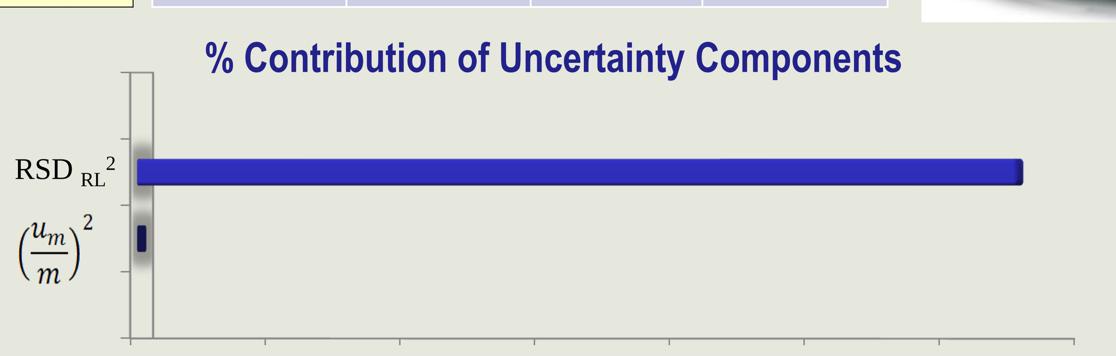
HEAT FLOW CALORIMETRY

Table: Required period $t_m = t_{25} e^{\frac{E_1}{(RT_m)-C}}$ and Heat Flow $P_I = P_{71} e^{\frac{E_1\left(\frac{1}{T_{71}}-\frac{1}{T_m}\right)}{R}}$ for different experimental temperature T_m.

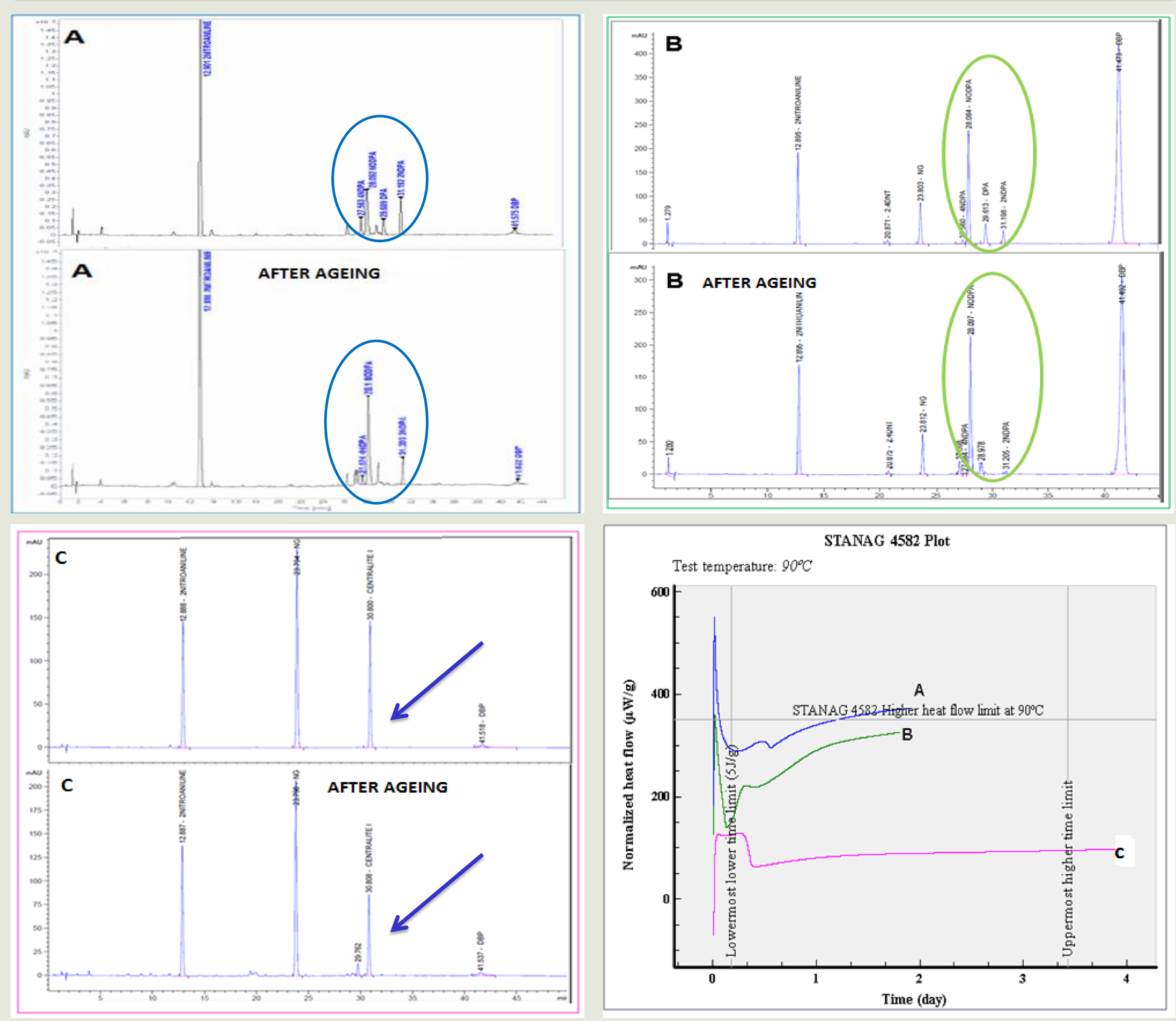
T °C	T_m days	P_I μW/g
60	123	9.8
65	64.9	18.5
70	34.8	34.5
75	19.0	63.1
80	10.6	114.0
85	5.98	201.0
90	3.43	350.0

HFC EXPERIMENTAL CONDITIONS	
HFC	TAM III, TA Instruments
Minicalorimeters	24
Vials	Glass 4ml
Artificial Ageing	90°C

RSD_r	RSD_{RL}	u_c	u_{exp}(%)
1.4	4.87	9.3	5.1



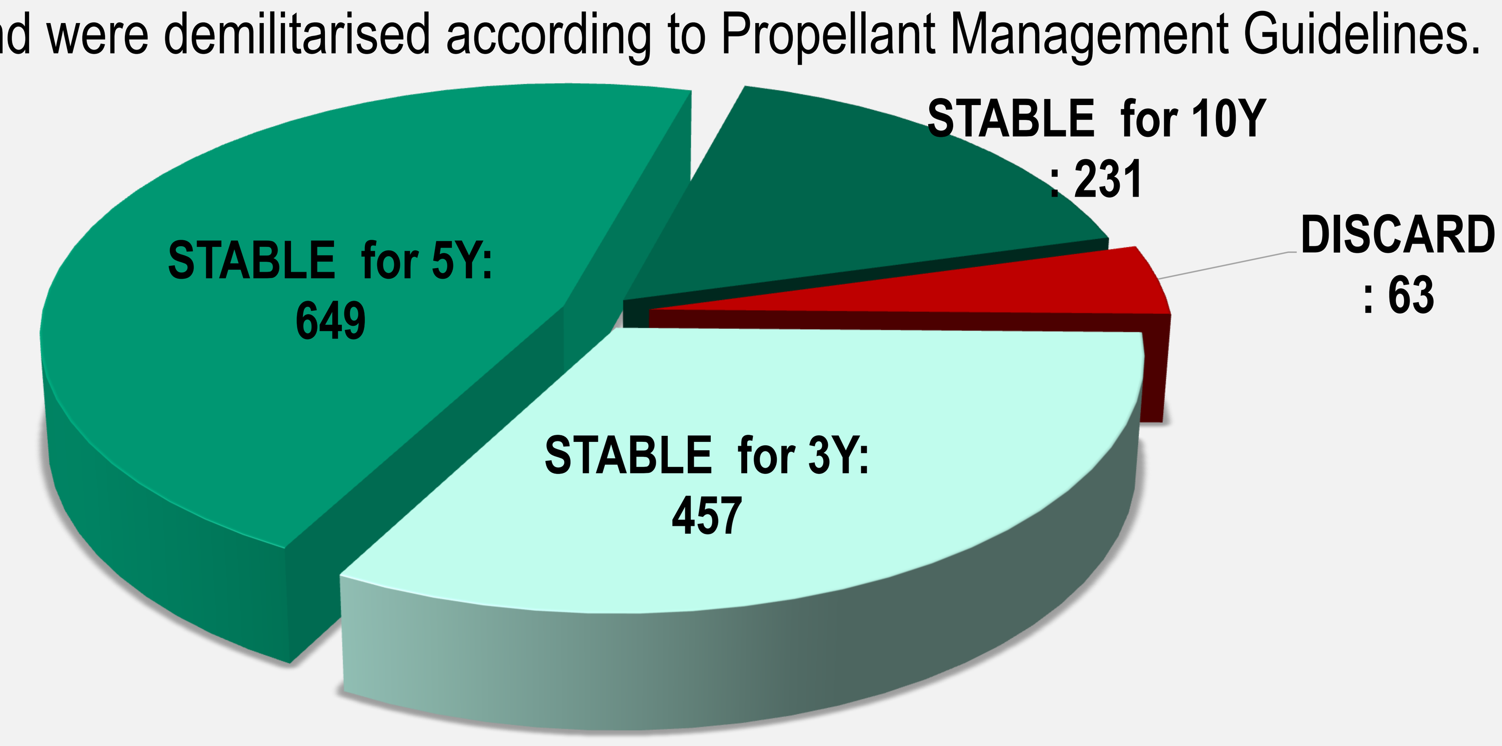
CORRELATION OF HPLC / HFC



SAMPLE	% DPA	% NNODPA	% EC	% EFFECTIVE STABILISER >0.2%	HFC μW/g	AFTER AGEING % DPA	AFTER AGEING % NNODPA	AFTER AGEING % EC	AFTER AGEING % EFFECTIVE STABILISER >0.2%	EVALUATION
A) Mortar shell 105mm	0.14	0.16	-	0.28	371.1	-	0.27		0.23	DISCARD
B) Cartridge shell 0.50mm	0.33	0.85	-	1.05	324.6	-	1.06		0.90	STABLE for 5Years at 25°C
C) Mortar shell 120 mm	-	-	1.45	1.45	99.89			0.89	0.89	STABLE for 10Years at 25°C
D) Cartridge 0.38''	-	0.13	-	0.11	-	-	-	-	-	DISCARD

CONCLUSIONS

- The prediction of shelf-life of ammunitions is significant not only for economical reasons but also for their performance and most importantly for the safety of civilians and military personnel.
- HFC method was verified based on the STANAG and the HPLC method was validated based on the same guidelines but was converted to a multi-analyte method.
- The samples can be discarded from HPLC before or after ageing according to the amount of "Effective Stabiliser" or from the HFC when maximum heat flow exceeds the upper limit of the method.
- Up to date the NGL has analysed 1400 ammunition batches where only 5% were unstable and were demilitarised according to Propellant Management Guidelines.



Reference:
1. NATO Allied Ordnance Publication (AOP)48, *Explosives, Nitrocellulose based propellants, stability test procedure and requirements using stabilizer depletion*, Ed.2 ,2008.
2. NATO Standardization Agreement STANAG 4582, *Explosives, Nitrocellulose based propellants, stability test procedure and requirements using Heat Flow Calorimetry*, Ed.1, 2007.

EURACHEM 29-30 MAY 2017, NICOSIA CYPRUS