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(Edition 2)

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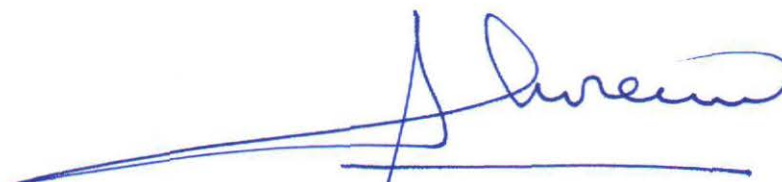# EXPLOSIVES, NITROCELLULOSE-BASED PROPELLANTS, STABILITY TEST PROCEDURES AND REQUIREMENTS USING STABILIZER DEPLETION

AOP-48

October 2008

AOP-48
(Edition 2)

NORTH ATLANTIC TREATY ORGANIZATION

NATO STANDARDIZATION AGENCY (NSA)

NATO LETTER OF PROMULGATION

1. AOP-48 - (Edition 2) – EXPLOSIVES, NITROCELLULOSE-BASED PROPELLANTS, STABILITY TEST PROCEDURES AND REQUIREMENTS USING STABILIZER DEPLETION is a NATO/PfP UNCLASSIFIED publication. The agreement of nations to use this publication is recorded in STANAG 4620 Edition 1.

2. AOP-48 (Edition 2) is effective upon receipt.

Promulgated on 3 October 2008

Juan A. MORENO
Vice Admiral, ESP(N)
Director, NATO Standardization Agency

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NATION	SPECIFICATION RESERVATIONS

RECORD OF CHANGES

Change Date	Date Entered	Effective Date	By Whom Entered

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CHAPTER 1

1. INTRODUCTION

1.1   It is a characteristic property of nitrocellulose-based propellants that the nitric ester constituents e.g. nitroglycerin, nitrocellulose, undergo a slow decomposition even at ambient temperatures. The degradation products formed, unless removed, can cause a reduction in chemical stability which can lead to cook-off / self-ignition due to the exothermic nature of the reactions involved. In addition they can lead to a loss of calorific value, changes in ballistic properties and cracking in large diameter charges.

1.2   Small amounts of stabilizing compounds are included in propellant formulations, either singly or as mixtures, in order to react with the degradation products, thus reducing the probability of the adverse effects noted above.

1.3   The chemical stability of propellants is normally assessed by observing their behaviour at elevated temperatures. Many tests such as the Abel Heat Test, Taliani Test, Methyl Violet Test, Bergmann-Junk Test, Vacuum Stability Test, Weight Loss Tests, Time to Cook Off, Heat Flow Calorimetry, Stabilizer Depletion Rates, etc. have been used for this purpose.

1.4   Stability tests based on stabilizer depletion are performed by first artificially ageing either at one single temperature (single-temperature ageing procedure) or at a number of different temperatures (multi-temperature ageing procedure), followed by the determination of the stabilizer depletion.

1.5   The single-temperature ageing procedure has shown to be a cost-effective method to assure that a propellant is sufficiently stable to be stored for 10 years at ambient storage conditions (25°C) – this at least for propellants consisting of well-known and generally used propellant components. For propellants of new formulations, in particular with stabilizers and other relevant components which were not used before in propellant formulations, more elaborate methods, such as the multi-temperature ageing procedure, have to be used.

1.6   The stabilizer depletion method, when conducted at a number of different temperatures (multi-temperature ageing procedure), offers the advantage of being able to determine the rate of the degradation processes, the temperature dependence of the reactions taking place and hence to assess the chemical life (safe storage life) at a particular temperature. Using this data, it is possible to develop a single-temperature ageing procedure and sentencing criteria for establishing whether a propellant of a specific composition will remain chemically stable at ambient temperature for some minimum time.

1.7   In Edition 1 of this AOP as well as in earlier STANAGs based on stabilizer depletion using single-temperature ageing, different ageing temperatures, ageing periods and sentencing criteria were applied to different propellant types. One reason for such differences was to take into consideration that specific propellant types are inherently less stable than propellants of other compositions (e.g. that the nitroglycerin-containing double-base propellants are significantly less stable than the nitroglycerin-free single-base propellants). From today's point of view, however, such differences do not make sense and should be avoided. This applies in particular for the qualification of a propellant, where the requirements necessary to fulfil the propellant's tasks have to be met irrespective of the propellant type which has finally been chosen. Therefore, identical ageing conditions and sentencing criteria are applied for all propellant types in Edition 2 of this AOP.

1.8   Furthermore, a fixed ageing temperature was provided in the single-temperature ageing procedures of Edition 1 of this AOP as well as in the earlier stabilizer depletion STANAGs. In the stability test based on Heat Flow Calorimetry (STANAG 4582), however, the test temperature can

be freely chosen from within the range 60°C and 90°C, resulting in a test duration of between 123 days (at 60°C) and 3.43 days (at 90°C) to ensure sufficient chemical stability for an isothermal storage of a minimum of 10 years at 25°C. For Edition 2 of this AOP, the possibility to run the single-temperature ageing at different temperatures as well as the respective test conditions are adopted from STANAG 4582.

1.9   Regarding the multi-temperature ageing procedure, Edition 1 of this AOP as well as STANAG 4527 used a two step regression procedure, based on calculation of reaction rate constants for pseudo zero and pseudo first order kinetics, followed by an Arrhenius-extrapolation for the reaction kinetic that gave the better fit. This procedure contained several sources of uncertainties and errors. In particular the decision as to which type of kinetics should be used was often unclear while considerably influencing the result of the evaluation. For Edition 2 of this AOP, a sequential or simultaneous one-step regression method is introduced which simultaneously analyses all ageing data, thereby finding the optimal reaction order thus yielding more accurate results.

1.10   It has to be noted that AOP-48 (stabilizer depletion), STANAG 4582 (Heat Flow Calorimetry) and STANAG 4556 (Vacuum Stability Test) investigate different physical-chemical processes connected with propellant ageing. The three methods therefore inherently might produce differing or even contradictory stability assessments.

1.11   The procedures described in this AOP cover most of the nitrocellulose-based propellant types which are in service today. There might be, however, a few unusual propellant compositions for which these procedures are not applicable, e.g. for some double-base propellants stabilized with magnesium oxide and / or calcium carbonate rather than with organic stabilizers, for some triple-base propellants without stabilizers, or for some propellants with very low initial stabilizer contents (below 0.5 % initial stabilizer). Chemical stability of such propellants has to be checked by another technique not based on stabilizer depletion, e.g. STANAG 4582 (Heat Flow Calorimetry) or STANAG 4556 (Vacuum Stability Test). Caution also should be taken with propellants stabilized with the less effective stabilizers ethyl centralite (EC) and/or methyl centralite (MC) alone, for which the methods described in AOP-48 Ed.2 might overestimate chemical stability.

CHAPTER 2

2.   SCOPE

2.1   The aim of this AOP is to standardize stability test procedures for nitrocellulose-based propellants using stabilizer depletion. This AOP also describes an approach for assessing the chemical life and the temperature dependence of stabilizer consumption rates for nitrocellulose-based propellants. Edition 1 of this AOP merged and replaced the following STANAGs: 4117, 4527, 4541 and draft STANAG 4542. In Edition 2 of this AOP, all procedures have been revised in order to eliminate inconsistencies between the different procedures and in order to incorporate the latest findings in the field of propellant stability.

2.2   The test procedures were developed to facilitate cross-procurement and provide a means by which countries can satisfy themselves that propellants received from abroad will remain chemically stable, if stored at ambient temperatures (25°C), for a minimum of ten (10) years. The test procedures were also developed to facilitate assessment of the chemical life (safe storage life) of nitrocellulose-based propellants for qualification purposes. This AOP does not address any other possible effects, such as changes of physical, mechanical and ballistic properties, which alter the service life of the respective nitrocellulose-based propellants.

2.3   This AOP will be reviewed upon the request of a participating nation. If any changes are proposed, the national delegate of the submitting country shall request that the Chairman of CASG AC/326 SG/1 includes this as an agenda item for the next meeting of the Subgroup.

2.4   Requests to revise AOP-48 must be accompanied by supporting documentation and should be presented to the Chairman of CASG AC/326 SG/1 for inclusion on the agenda of the next meeting of the Subgroup. Subgroup 1 will approve the revisions of this AOP. Such revisions will be provided to the Custodian Nation and to the International Staff Secretary for publication. Switzerland is the Custodian Nation for this document.

CHAPTER 3

3.　　DEFINITIONS

3.1　　INITIAL STABILIZERS ("parent stabilizers") are stabilizers that were incorporated in the propellant formulation during manufacture.

3.2　　DAUGHTER STABILIZERS are substances with stabilizing capabilities that were not included in the propellant formulation but were produced from the initial stabilizers during propellant manufacture or ageing. Most stabilizer depletion products fall into this class.

> NOTE 1: Certain stabilizers can appear both as initial stabilizer (incorporated in basic formulation) and as daughter stabilizer (produced from initial stabilizer), this even in the same propellant. Typical examples for such stabilizers are 2NDPA, 4NDPA, pNMA and pNEA – they can be used as initial stabilizers but are also formed from DPA, AKA-II, MC or EC.

3.3　　EFFECTIVE STABILIZER is a defined term which is used to assess the stability in the single-temperature test and is defined as follows:

3.3.1　　The content of "effective stabilizer" is calculated from the contents of all initial stabilizers listed in Table 1 (except if they are used as surface moderants) and the content of N-nitrosodiphenyl-amine as follows:

For propellants without diphenylamine **as well as for propellants with diphenylamine and other stabilizers**:

> Effective stabilizer = Σ (contents of initial stabilizers)

For propellants with **diphenylamine only**:

> Effective stabilizer = content of diphenylamine + 0.85 N-nitrosodiphenylamine

> NOTE 2: In case of propellants with more than one stabilizer, it makes sense to add the contents of all initial stabilizers together as all stabilizers contribute to the overall propellant stability and not only the most reactive stabilizer. As in the first phase of propellant ageing, the most reactive stabilizer is depleted first and at a higher rate than the less reactive stabilizer(s), the effective stabilizer depletion within the single-temperature test period will always be faster than in the period thereafter. Thus, this approach can be regarded as conservative as it assumes that the less reactive stabilizer(s) which deplete later are consumed at the same high rate as the most reactive stabilizer which depletes first.

> NOTE 3: By convention, daughter stabilizers do not contribute to the amount of "effective stabilizer", even if they still show some stabilizing effects. This approach ensures the necessary margin of safety of the method. Even propellants with all effective stabilizer consumed show some remaining chemical life just due to stabilizing effects of daughter stabilizers. The only daughter product included in the "effective stabilizer" is N-nitroso-diphenylamine if produced from diphenylamine and if no other initial stabilizers are present. The reason for this exception is that DPA is generally consumed much faster than other stabilizer types, this despite the proven fact that a propellant stabilized with DPA is by no means less stable if compared to the equivalent propellant with another, slower consuming stabilizer (see also Figure 2 in Section 7.4). Thanks to the excellent stabilizing properties of the daughter stabilizers of DPA, time to autocatalysis will be more than five times longer than the time until DPA is fully consumed in a DPA-stabilized propellant. In order to take this faster decomposition rate into account, propellants containing DPA alone are treated here as exceptions allowing for the inclusion of the primary daughter stabilizer N-nitrosodiphenyl-amine, weighed by its difference in molecular mass.

3.4 <u>PERCENTAGE EFFECTIVE STABILIZER</u> is the amount of effective stabilizer found, expressed as a percentage by weight of the propellant sample.

3.5 <u>INITIAL LEVEL</u> is the percentage of effective stabilizer found in the propellant sample prior to ageing.

CHAPTER 4

4. GENERAL METHODOLOGY

4.1 Stability testing of nitrocellulose-based propellants is carried out by determination of stabilizer depletion after artificial ageing of the propellants at temperatures and durations corresponding to 10 years of natural ageing at ambient storage conditions (25°C). This testing should guarantee that the amount of stabilizer in the propellant would not drop below a safety level after its storage for 10 years. Stabilizer contents in the samples of propellants are determined by high performance liquid chromatography (the preferred method) or by another suitable method that gives equivalent precision and is able to differentiate between different stabilizers, their daughter products and other propellant ingredients.

4.2 Stabilizers have to be incorporated homogeneously. The content of stabilizers which are used as surface moderants must not be included in the "effective stabilizer". If a substance is used both as stabilizer and as surface moderant in a specific propellant, special measures have to be taken (e.g. specific analysis of the undeterred core of the propellant grains, subtraction of the amount of surface moderant from the analysed total content, or stability assessment with another method, such as STANAG 4582 or STANAG 4556).

4.3 Artificial ageing is carried out using either a single-temperature ageing procedure or a multi-temperature ageing procedure. A flow diagram showing the suggested procedure to apply this AOP is given in Figure 1.

4.4 The single-temperature ageing procedure is used for propellants consisting of well-known and generally used propellant components and stabilizers defined in Table 1. The ageing can be performed at any temperature between 50°C and 90°C. Table 2 defines the corresponding ageing times which are considered equivalent to 10 years of storage at 25°C. Ageing time is considerably shorter for higher temperatures. Lower temperatures, however, will better represent the ageing at ambient conditions. Due to the very conservative activation energy assumption made to calculate the ageing times in Table 2, even propellants which exhibit satisfactory chemical stability in-service may fail the sentencing criteria (see Chapter 6) of the single-temperature procedure, in particular if tested in the higher temperature range. In such cases, further examination of the propellant is advisable: Either the single-temperature test should be repeated at a lower temperature (e.g. 60°C or 50°C), or the safe storage life should be assessed by using the multi-temperature procedure.

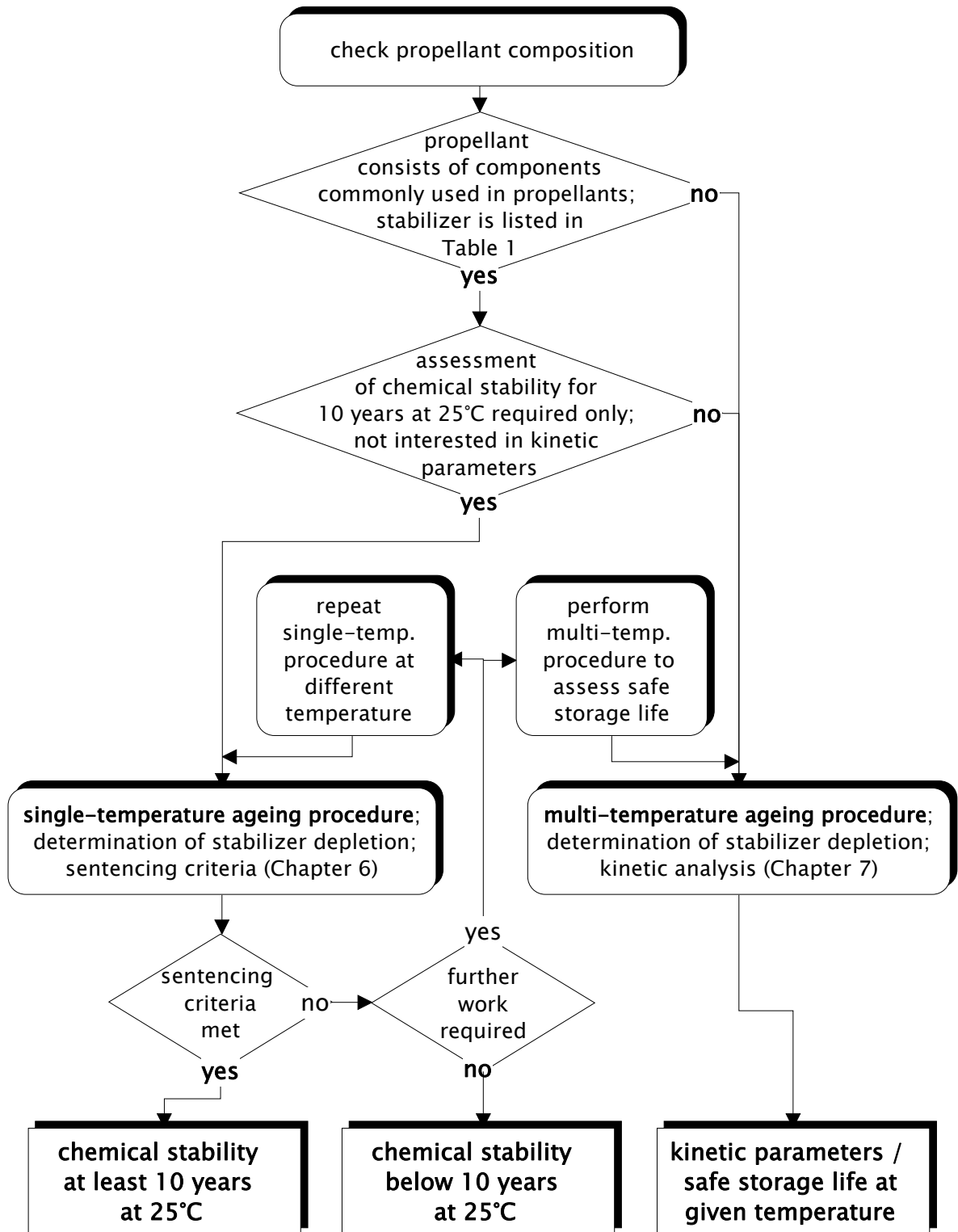> NOTE 4: For the single-temperature ageing procedure, the "effective stabilizer" concept is used.

FIGURE 1: Flow diagram of stability assessment based on stabilizer depletion

TABLE 1: List of stabilizers suitable for single-temperature ageing procedure

Name	Other Names	Abbreviation
Diphenylamine		DPA
2-Nitro-diphenylamine		2NDPA
Ethyl Centralite	Centralite-I; Carbamite; N,N'-Diethyl- N,N'-diphenyl-urea	EC
Methyl Centralite	Centralite-II; N,N'-Dimethyl- N,N'-diphenylurea	MC
Akardite-II	N-Methyl-N',N'-diphenylurea	AKA-II
p-Nitro-N-methylaniline		pNMA, MNA
Resorcinol		

NOTE 5: The stabilizers listed in Table 1 differ significantly regarding reactivity, stabilizing efficiency and usage. DPA, 2NDPA, EC, MC, AKA-II, pNMA and resorcinol have been used for decades in numerous NATO/PfP nations. For all these stabilizers, at least sufficient stabilizing ability for nitrocellulose-based propellants was established.

DPA is the most reactive and thus fastest depleting stabilizer. 2NDPA and AKA-II deplete considerably slower, whereas EC and MC are consumed slower again. If a combination of these stabilizers is used, they deplete consecutively: DPA always depletes first, then 2NDPA and AKA-II, and latest EC and MC.

Caution: Under certain circumstances and due to the lower depletion rates, chemical stability of propellants stabilized with EC and/or MC solely might be overestimated in both AOP-48 Ed. 2 single-temperature and multi-temperature sequences. It thus is recommended that chemical stability of propellants containing EC and/or MC as the only stabilizers is checked by another technique not based on stabilizer depletion, e.g. STANAG 4582 (Heat Flow Calorimetry) or STANAG 4556 (Vacuum Stability Test).

Table 1 has been limited to stabilizers which are incorporated in propellants which are already qualified and introduced in NATO/PfP nations. Alternative stabilizers can be added to Table 1 as soon as they comply with this restriction. One such candidate would be triphenylamine (TPA) which already has been incorporated in experimental propellants demonstrating good stabilizing properties.

TABLE 2: Conditions for single-temperature ageing procedure

Temperature [°C]	Ageing Time [days]	Temperature [°C]	Ageing Time [days]
50	301	70	34.8
55	191	75	19.0
60	123	80	10.6
65	64.9	85	5.98
65.5	60.9	90	3.43

NOTE 6: Table 2 contains ageing temperature and ageing duration corresponding to 10 years of isothermal storage at 25°C, calculated by assuming an activation energy of 120 kJ/mol above 60°C and of 80 kJ/mol below this temperature, as defined in STANAG 4582.

The corresponding ageing times can be calculated for any temperature above 60°C using Equation 2 given in STANAG 4582 which writes

$$t_m = t_{25} \cdot \exp\{E_1/(R \cdot T_m) - C\}$$

with t_{25} = 3652.5 days (10 years), T_m = test temperature in K, E_1 = 120 kJ/mol, R = 0.00831447 kJ/(K·mol) and C = 46.713.

For temperatures below 60°C, the corresponding ageing times t_m can be calculated from

$$t_m = t_{25} \cdot \exp\{E_2/(R \cdot T_m) - D\}$$

with E_2 = 80 kJ/mol and D = 32.272.

For T_m = 60°C, both equations result the t_m value of 123 days as already listed in Table 2.

NOTE 7: For surveillance purposes, this ageing matrix might be adapted as follows: If the surveillance interval differs from 10 years, this interval (as t_{25} in days) can be used in the first equation in NOTE 6 to calculate the required ageing time at the desired ageing temperature. If the real activation energy of a certain propellant type is known from multi-temperature measurements, also the activation energy assumption E_1 for the range above 60°C might be replaced by this measured value. It is, however, not advisable to also change the activation energy assumption E_2 for the range below 60°C as otherwise the safety margin is reduced.

4.5   Multi-temperature artificial ageing is used for propellants with stabilizers not listed in Table 1, for samples failing to meet the criteria of the single-temperature ageing procedure, as well as for more accurate safe storage life assessments (the latter can be performed for all different nitrocellulose-based propellants).

4.6   For the <u>multi-temperature ageing procedure</u>, the propellants shall be aged for a minimum of four different durations at each of a minimum of three different temperatures. The temperatures selected should lie in the range 40°C to 80°C and there should be at least a 10°C difference between each selected temperature. The ageing periods shall be selected such that the "optimum region" of 10 % to 90 % stabilizer depletion is covered as well as possible (meaning that the majority of the aged samples should not only lie within this range but also be spread over the entire range) – this in particular if only three temperatures have been chosen. If ageing is performed at more than three temperatures, it is acceptable that samples aged at the lowest temperature only cover a part of the optimum range (e.g. with a conversion rate between 10 % and 50 %).

NOTE 8: For the multi-temperature ageing procedure, the "effective stabilizer" concept is not applicable because the decomposition kinetics of "effective stabilizers" are not well defined. For this reason, exclusively the individual initial stabilizers are evaluated.

NOTE 9: If more than one initial stabilizer is present and should be assessed, it has to be assured that the chosen range for propellant ageing covers the depletion of all these initial stabilizers.

4.7   Both the procedures – single-temperature and multi-temperature ageing – use the same methods and apparatus for ageing and preparation of propellants and for the determination of stabilizer contents. These common test methods are described in Chapter 5. Evaluation of results for the single-temperature procedure is described in Chapter 6. For multi-temperature ageing, see Chapter 7. Test data sheets for single-temperature ageing procedures are included in Chapter 8. For multi-temperature ageing procedures, see Chapter 9. Typical chromatographic separations

and conditions are included in Chapter 10. An example of the kinetic analysis of the multi-temperature procedure is given in Chapter 11.

4.8   This AOP calls for the use of substances and test procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from the statutory obligations relating to health and safety at any stage during use.

CHAPTER 5

5.   TEST PROCEDURES

5.1   ARTIFICIAL AGEING

5.1.1   General description

5.1.1.1 Results of numerous studies clearly demonstrate that both ageing rate and ageing reaction mechanism of propellants strongly depend on ageing conditions, in particular on

–   loading density (containers fully filled / partly filled),

–   tightness of seal (containers unsealed / loosely sealed / airtight sealed), and

–   size of propellant grains / blocks (propellant in original size / cut into pieces / ground).

5.1.1.2 The main reasons for this are changes in reaction pathways due to higher oxygen levels in the sample (for lower loading densities or leaking seals) or due to reduced moisture levels (drying of propellant in case of unsealed containers or if seals are leaking).

5.1.1.3 The influence of these conditions on the ageing rate can not only be striking but also can go in both directions, with tendencies towards increased ageing rates with higher loading densities, better tightness and larger propellant grain or block sizes.

5.1.1.4 Therefore, conditions of sample preparation and artificial ageing should be as close as possible to the real ageing condition of the respective propellant in the ammunition system. As far as feasible, the propellant should be aged in its original condition, with grinding only if necessary and with allowance of larger pieces for rocket propellants. Furthermore, the loading density should be as realistic as possible.

5.1.1.5 In order to allow for different circumstances, several possible ways of propellant ageing are described here:

–   in cartridges of the appropriate calibre, sealed by an inert projectile,

–   in sealed glass or metal vials (e.g. heat flow calorimeter vials or larger sealed vials),

–   in glass tubes with stoppers,

–   in sealed polymer-coated aluminium bags,

–   in conditioning boxes or wrapped into foil.

5.1.1.6 For small size gun propellants (e.g. small and medium calibre), ageing in cartridges or fully filled and hermetically sealed vials (according to STANAG 4582) is the recommended method. For propellants of larger size (e.g. bulk propellants, solid rocket propellants, stick propellants) ageing in sealed, polymer-coated aluminium bags or in conditioning boxes (according to STANAG 4581) is recommended.

5.1.1.7 The National Authorities are however, free to choose any other ageing method as listed in 5.1.1.5 and to vary the propellant sample/air ratio (loading density) for specific natures of ammunition.

5.1.2   General directions (for all possible ageing methods)

5.1.2.1 It is a basic requirement that the materials of the sample container and seal used do not react with the propellants and their decomposition products. For most of the container types listed in 5.1.1.5, a sufficient compatibility can be assumed. In particular, no incompatibility reactions between propellants and glass containers or polymer-coated aluminium bags were reported.

Sometimes, diffusion of propellant ingredients into the polymer-layer of the polymer-coated aluminium bags, into polymeric seals (vials) or into sealant grease (glass tubes with stoppers) can be found. If in doubt (e.g. for ageing in metal cartridges), chemical compatibility between propellant and container material has to be checked.

5.1.2.2 The ageing conditions (e.g. container type and loading density) chosen must be kept constant for all samples within the series in order to avoid fluctuations in the decomposition reactions between the different samples.

5.1.2.3 All propellant sample preparation and ageing details shall be fully recorded on the data sheet and also shall be mentioned in resulting reports.

5.1.2.4 It must be established that the sample subjected to ageing is representative for the batch or bulk of propellant in test. If the volume of the sample tube or container is too small to fulfil this, a larger ageing container should be used instead, or multiple samples containers should be used for each ageing step. If this is impossible or regarded as inappropriate, a sufficiently large amount of the propellant should be cut or ground and the sample should be taken from a well mixed fraction in order to achieve the required sample homogeneity.

> NOTE 10: Grinding of propellant markedly changes ageing behaviour and should be avoided whenever possible. Cutting into medium sized pieces, on the other hand, is a more acceptable alternative which might help to avoid grinding in most cases.

5.1.2.5 Since the ageing depends somewhat on the moisture content, it is advisable to determine and record the moisture content by an appropriate method (e.g. Karl Fischer).

5.1.2.6 Single-temperature ageing procedure is carried out with at least two propellant samples heated at one temperature for one duration.

5.1.2.7 Multi-temperature ageing procedure is carried out with at least two propellant samples for each combination of temperature and duration of artificial ageing.

5.1.2.8 Ageing takes place in a suitable thermostated heating bath, heating block or oven which is capable of maintaining a specified mean temperature to $\pm 0.2°C$ for the required duration for all aged samples.

5.1.2.9 After removing the samples from the heating bath, heating block or oven, the effectiveness of the seal during ageing should to be checked (e.g. by weighing the filled containers before and after ageing) and reported.

> NOTE 11: For longer ageing periods at higher temperatures, absolutely perfect sealing is difficult to obtain, this in particular for glass vials and glass tubes. In small glass vials (heat flow calorimetry vials of volumes up to 4 ml), weight losses of below 0.2 % with respect to the total propellant weight is usually obtainable. For larger, fully filled glass vials or flasks, weight losses between 0.1 % and 0.5 % (or up to 2 % if not properly sealed) have to be taken into account. For glass tubes with stoppers (e.g. "NATO tubes"), weight losses will be considerably higher (typically 0.5 % to 2 % weight loss after the single-temperature sequences defined in Table 2). Heat-sealed polymer-coated aluminium bags are usually very tight as expressed by weight losses of below 0.1 % (except for rare cases where propellant components migrate into the polymer, leading to particular delamination of the polymer from the aluminium, followed by leaking of the bags – weight losses of 0.2 % to 0.6 % then result; similarly high weight losses are also obtained if the bags are either not tightly heat sealed or if they are closed by gluing rather than by heat sealing). Properly sealed ammunition cartridges are very tight as seen from typical weight losses of below 0.1 % with respect to the total propellant weight. It has to be taken into account that higher weight loss values mean a considerable loss of moisture, residual solvents and other volatile components such

as nitroglycerin, which changes the sample composition and likely affects ageing rate and reaction mechanism.

5.1.3   Ageing in ammunition cartridges

5.1.3.1 For this ageing method, original ammunition cartridges with inert projectiles are used.

NOTE 12: If it is not intended to check overall stability of the propellant in the system, explosive or pyrotechnic components such as igniters, primers, tracers, etc. should be removed from the cartridge prior to filling with propellant. Otherwise, if such explosive or pyrotechnic components are not removed, appropriate safety precautions should be taken.

5.1.3.2 For this ageing method, the original ammunition cartridges are filled with the typical amount of sample propellant and then sealed with an inert projectile. The cartridges are placed in the oven in such a manner as to ensure that the entire volume of the cartridges is maintained at the specified temperature for the specified duration.

NOTE 13: This method gives the best representation of the real ageing conditions.

5.1.4   Ageing in sealed glass or metal vials

5.1.4.1 For this ageing method, glass or metal vials that can be hermetically sealed have to be used. The vials must have a minimum volume of 2 cm^3.

NOTE 14: As described in 5.1.2.4, significantly larger volumes would be preferred. However, much larger vials, especially those made of glass, often tend to leak if fully filled with propellant and if aged at high temperatures, whereas the small heat flow calorimeter vials have been found to almost always remain sealed during ageing conditions listed in Table 2.

5.1.4.2 The vials are filled with propellant up to the top so that the amount of air inside is minimal before sealing. The loading density is thus approx. 0.8 to 1.1 g/cm^3. Alternatively the loading density of the ammunition defined for the propellant in test may be used. The vials are then placed in an upright position in the heating apparatus in such a manner as to ensure that the entire volume of the vial is maintained at the specified temperature for the specified duration.

NOTE 15: This ageing method is identical to STANAG 4582 regarding sample preparation, sample container, loading density and ageing temperature/duration profiles. Therefore, it is the recommended ageing method at least for small size gun propellants (e.g. small and medium calibre). This ageing method can also be applied to larger sized propellants (e.g. large calibre gun propellants, stick propellants) if it can be managed to place representative amounts (see 5.1.2.4.) of these propellants into sealed vials (e.g. by cutting and/or use of larger or multiple vials).

5.1.5   Ageing in glass tubes with stoppers

5.1.5.1 Ageing can also be performed in glass tubes with glass stoppers. Examples are:

– the "NATO-tube" with defined dimensions (length 152.4 mm, diameter 25.4 mm) leading to a volume of approx. 45 cm^3;

– scaled-down "NATO-tubes" (for example for reduction of the sample size from 20 to 2 grams whilst maintaining the overall dimensions of the tube or at least its loading density);

– other glass tubes with glass stoppers.

5.1.5.2 The glass tubes are filled with the desired amount of propellant and closed. Traditionally, 20 grams of the propellant sample are filled into the original "NATO-tube" resulting in a loading density of approx. $0.4 - 0.5$ g/cm^3. The glass stoppers are then fit without force or pressure. A non-reactive grease or other suitable material is often used to seal. Apart from this "established procedure", other loading densities and closing techniques are also possible. The tubes are then placed in an upright position in the heating apparatus in such a manner as to ensure that the entire volume of the heating tube is maintained at the specified temperature for the specified duration.

> NOTE 16: This ageing method (ageing in "original NATO-tubes") was used in Edition 1 of AOP-48 as well as in the earlier STANAGs (4117, 4527, 4541, and draft STANAG 4542) and therefore might still be preferred by some nations due to historic reasons. It has to be noted, however, that ageing in stoppered glass tubes represents rather poorly the real ageing conditions in ammunition, as the propellant's loading density is usually too low and as it is difficult (or even impossible) to obtain an airtight seal with glass stoppers.

> NOTE 17: The reduction in tube size from the dimensions described in 5.1.5.1 to one tenth of its volume significantly reduces both required sample amount and safety risks, which might be important in particular for experimental propellants. It was reported that this scaling-down has no significant effect on stabilizer depletion within the timescale and ageing environment of the STANAG 4117 / 4541 tests.

5.1.6 Ageing in polymer-coated aluminium bags

5.1.6.1 For this ageing method, polymer-coated, heat-sealable aluminium bags are used (e.g. 30 x 30 cm bags according to specifications of MIL-B-1341 G Class 1 "Barrier Materials, Watervapor-Proof, Grease-Proof, Flexible, Heat-Sealable"). This method is also applicable for larger propellant grains as well as for propellant sticks, blocks or solid rocket propellants.

5.1.6.2 The bags are filled up to $20 - 30$ % of their volume with sample propellant. Excess air is removed by flattening the empty part of the bags before heat-sealing the bags according to the manufacturer's specifications. The bags are then placed in the heating oven for the specified duration.

> NOTE 18: The main advantage of this ageing method is, apart from the possibility to also age block propellants, that gas evolution during ageing does not cause excessive pressure build-up followed by seal leakage as often appears with glass tubes or vials. Here, evolved gases just inflate the bags. Furthermore, an air/propellant ratio similar to real ammunition can be adjusted. Therefore, this ageing method is recommended for propellants of larger size (e.g. block propellants, solid rocket propellants, stick propellants) which otherwise have to be ground prior to ageing.

5.1.7 Other ageing methods for block propellants

5.1.7.1 If ageing of block propellants in polymer-coated aluminium bags (5.1.6) turns out to be inappropriate, further ageing methods are possible: (i) Close wrapping of the propellant blocks into foil, or (ii) cutting the propellant block in order to fit into conditioning boxes. The wrapped blocks or condition boxes are then placed in the heating oven for the specified duration.

5.2   DETERMINATION OF EFFECTIVE STABILIZER

5.2.1   General description

5.2.1.1 The stabilizers may be determined by any appropriate analytical procedure. High Performance Liquid Chromatography (HPLC), with suitable chromatographic conditions, has been shown to be suitable and a typical procedure is described below. HPLC is the preferred technique, other analytical methods (e.g. gas chromatography for centralites) are allowed if they show equivalent precision and are able to differentiate between different stabilizers, their daughter products and other propellant ingredients.

5.2.1.2 A procedure for sample preparation based on total solution is described. However, alternative extraction procedures may be used if they also achieve quantitative recovery of stabilizers. Synthetic mixtures containing nitrocellulose may be used to demonstrate complete recovery of the stabilizers.

5.2.1.3 The propellant is dissolved in acetonitrile and the nitrocellulose present is precipitated. The percentage effective stabilizer is then determined.

5.2.1.4 A sample of propellant from each heating container shall be analysed.

5.2.1.5 At least two samples of unaged propellant shall be analysed for comparison.

5.2.2   Reagents

5.2.2.1 Acetonitrile, HPLC quality.

5.2.2.2 2 % aqueous calcium chloride solution.

5.2.2.3 All initial stabilizers present in propellant sample (see Table 1); purity 99 % or better.

5.2.2.4 N-nitrosodiphenylamine (N-NO-DPA), if diphenylamine is used as a stabilizer in the propellant. Check the purity by HPLC prior to use. If more than one peak is observed, recrystallise from ethanol (analytical grade).

5.2.2.5 Samples of the principal degradation products to aid identification of peaks, which may appear in chromatograms and cause interference with the determination of stabilizers. These may include:

for diphenylamine:

> N-nitrosodiphenylamine
>
> 2-nitrodiphenylamine
>
> 4-nitrodiphenylamine
>
> N-nitroso-2-nitrodiphenylamine
>
> N-nitroso-4-nitrodiphenylamine
>
> 2,2'-dinitrodiphenylamine
>
> 2,4-dinitrodiphenylamine
>
> 2,4'-dinitrodiphenylamine
>
> 4,4'-dinitrodiphenylamine
>
> N-nitroso-2,4'-dinitrodiphenylamine
>
> N-nitroso-4,4'-dinitrodiphenylamine

for 2-nitrodiphenylamine:

    N-nitroso-2-nitrodiphenylamine

    2,2'-dinitrodiphenylamine

    2,4-dinitrodiphenylamine

    2,4'-dinitrodiphenylamine

for 4-nitrodiphenylamine:

    N-nitroso-4-nitrodiphenylamine

    2,4-dinitrodiphenylamine

    2,4'-dinitrodiphenylamine

    4,4'-dinitrodiphenylamine

for triphenylamine:

    2-nitro-triphenylamine

    4-nitro-triphenylamine

    2,2'-dinitro-triphenylamine

    2,4-dinitro-triphenylamine

    2,4'-dinitro-triphenylamine

    4,4'-dinitro-triphenylamine

for ethyl centralite:

    2-nitro ethyl centralite

    4-nitro ethyl centralite

    2,2'-dinitro ethyl centralite

    2,4-dinitro ethyl centralite

    2,4'-dinitro ethyl centralite

    4,4'-dinitro ethyl centralite

    N-nitroso-N-ethylaniline

    2-nitro-N-ethylaniline

    4-nitro-N-ethylaniline

    4-nitro-N-nitroso-N-ethylaniline

    2,4-dinitro-N-ethylaniline

for methyl centralite:

    2-nitro methyl centralite

4-nitro methyl centralite

2,2'-dinitro methyl centralite

2,4-dinitro methyl centralite

2,4'-dinitro methyl centralite

4,4'-dinitro methyl centralite

N-nitroso-N-methylaniline

2-nitro-N-methylaniline

4-nitro-N-methylaniline

4-nitro-N-nitroso-N-methylaniline

2,4-dinitro-N-methylaniline

for akardite-II:

N-nitroso-akardite-II

2-nitro-akardite-II

4-nitro-akardite-II

+ principal degradation products of diphenylamine

for pNMA:

4-nitro-N-nitroso-N-methylaniline

2,4-dinitro-N-methylaniline

NOTE 19: Some of these stabilizers and their daughter products, in particular if from the family of aromatic nitro compounds, aromatic amines and N-nitrosamines, are very toxic / carcinogenic. Appropriate precautions have to be taken while handling these substances.

5.2.2.6 In many cases most of the degradation products listed above will not be present in samples aged under conditions of this test. Occasionally, if excessive degradation has occurred, some trinitro and tetranitro derivatives may also be present. At specific conditions (e.g. long term natural ageing), other products could also be produced.

5.2.3   Apparatus

5.2.3.1 A High Performance Liquid Chromatographic system. This system should include a suitable UV detector, column and solvent system.

5.2.3.2 Suitable data accumulating and processing system.

5.2.4   Sample preparation and extraction procedure

5.2.4.1 Preparation of samples before analysis (after heating): Homogenise the individual aged propellant samples (and also the non-aged reference sample). If required, cut or grind the propellants before homogenisation so that a representative sample can be taken. Propellants that

are surface coated with the same substance as used as stabilizer might require other sample preparation (e.g. removal of coated layer).

5.2.4.2 Accurately weigh about 1 gram of propellant from each of the aged samples into 500 cm^3 flasks, and add 250 cm^3 of acetonitrile to each sample. Stopper the flasks and dissolve the propellant by shaking / stirring for a minimum of 4 hours at room temperature avoiding exposure to direct sunlight. An ultrasonic bath may be used in order to assist dissolution. In this case, temperature has to be kept below 40°C.

5.2.4.3 To each flask add 50 cm^3 of a 2 % aqueous solution of calcium chloride to precipitate the nitrocellulose.

5.2.4.4 Allow the precipitate to settle for at least 1 hour. If possible, the samples should be analysed immediately, otherwise they should be kept in cool dark conditions (5 ± 3°C) to reduce any further reaction of the stabilizer.

5.2.4.5 If the samples have been stored under cool conditions, allow them to return to room temperature. Take a portion of the supernatant liquid from each sample and centrifuge or filter through a 0.5 μm PTFE (Teflon) filter.

5.2.4.6 Samples should not be stored for more than 24 hours prior to analysis. If total analysis cannot be completed within this time period, samples may be stored for up to 5 days provided the conditions described in 5.2.4.4 are met and reference samples are also analysed at regular intervals.

> NOTE 20: The precipitation of NC prior to introduction into the chromatographic system is primarily performed to extend column life and prevent possible interference with analyte detection from the gradual elution of NC during the course of the run. Precipitation of NC during the sample preparation may not be necessary, if a gradient or post-analysis column clean-up is used. Additionally, minor adjustments to the sample size, and resulting sample concentration, can be made provided that equivalent results are demonstrated.

5.2.5   Determination of stabilizers by High Performance Liquid Chromatography (HPLC)

5.2.5.1 Determine the amount of effective stabilizer present in each sample of the supernatant liquid as a percentage of the propellant sample using a suitable HPLC separation procedure.

5.2.5.2 The column and solvent combinations used shall be capable of fully resolving (base line separation) stabilizers from any degradation products and soluble propellant ingredients.

5.2.5.3 The column shall be maintained at a constant temperature to within $\pm$0.5°C. Column temperature not exceeding 40°C is recommended in order to avoid decomposition of stabilizer daughter products.

5.2.5.4 A detector wavelength between 210 nm and 254 nm has been found to be suitable; however, a wider wavelength range or a diode array system for peak identification or an alternative type of detector may be employed depending on the chromatographic conditions.

5.2.5.5 Internal or external standards may be used for quantitative analysis providing the following conditions are met:

5.2.5.6 Internal standard(s) used shall have a chemical and physical behaviour similar to the component(s) being analysed. They shall be resolved (base line separation) from any neighbouring peaks. The internal standard shall be added at the dissolution stage described in 5.2.4.2. It is important that the relative response factors do not change over the concentration range to be determined.

5.2.5.7 External standard(s). The concentration of the solutions of stabilizers used shall cover the concentration range in the samples to be analysed.

5.2.6   <u>Reporting</u>

5.2.6.1 For each sample, calculate the effective stabilizer content as a percentage of the original propellant sample. Correct the result with the weight loss which occurred during ageing if necessary.

5.2.6.2 Report details of the chromatographic conditions and the results in the form outlined in data sheet at Chapter 8 (for single-temperature ageing procedure) or Chapter 9 (for multi-temperature ageing procedure).

5.2.6.3 Provide copies of the chromatograms obtained for the standard(s) used and the propellant sample, as received and after ageing.

> NOTE 21: Chapter 10 shows typical chromatograms and experimental conditions for the separation of the different stabilizers from their possible daughter products using HPLC.

CHAPTER 6

6.   ACCEPTANCE CRITERIA FOR SINGLE-TEMPERATURE AGEING PROCEDURE

6.1   Nitrocellulose-based propellants will be judged according to the following criteria:

6.2   Criterion 1: Maximum decrease in effective stabilizer during ageing (in % of initial level) ≤ **80 %**

        Criterion 2: Minimum percentage of effective stabilizer remaining after ageing ≥ **0.2 %**

6.3   The propellant will remain chemically stable for a minimum of 10 years of storage at an ambient temperature (25°C) if, after single-temperature ageing according to conditions listed in Table 2, both criteria are met.

6.4   The above criteria were derived from ageing studies on a range of propellants in NATO service. The assessment is a conservative estimate for minimum storage time and the actual service chemical life of a propellant may be considerably longer. It is known that certain propellants may fail to meet these criteria although they exhibit satisfactory chemical stability in-service. This failure is then a result of the overly conservative activation energy assumption made to calculate ageing times at the respective temperatures. For this reason, a failure to meet 10 years life as determined by this test must not be used in isolation to sentence the propellant. A further examination of the propellant at a lower temperature (e.g. 60°C or 50°C) or by multi-temperature ageing procedure is recommended in such cases (see Figure 1).

6.5   Storage of propellant at mean temperature greater than ambient will result in increased consumption of stabilizer(s) and can lead to a reduced safe chemical life. If it is known that the propellant is subjected to a prolonged storage at temperatures above ambient, it is recommended that the relevant National Authority perform additional surveillance testing at earlier than 10 years after procurement. The required surveillance interval for storage above 25°C can be calculated using the second equation in NOTE 6 (surveillance interval $t_m = t_{25} \cdot \exp\{E_2/(R \cdot T_m) - D\}$, with t_{25} = 3652.5 days (10 years), E_2 = 80 kJ/mol and D = 32.272).

CHAPTER 7

7.   CALCULATION OF CHEMICAL LIFE FROM MULTI-TEMPERATURE AGEING PROCEDURE

7.1   THEORETICAL CONSIDERATIONS

7.1.1   Depending on the decomposition characteristics of the main ingredients of a propellant (nitrocellulose, nitroglycerin) and on the rate of reaction between the stabilizer and the gaseous decomposition products, the resulting reaction order of stabilizer depletion usually ranges between zero and two.

7.1.2   Since some condensed degradation products of the propellant which did not react with the stabilizer show an autocatalytic effect, even formally negative reaction orders may be found in some cases.

7.1.3   Therefore the evaluation of multi-temperature ageing data should be preferably based on a nth order reaction of stabilizer depletion, which means estimation of best values for activation energy, frequency factor and reaction order.

7.1.4   The rate of a nth order reaction is defined by:

$$-\frac{dc}{dt} = kc^n \tag{1}$$

c   = fractional concentration

c_0 = initial concentration

n   = reaction order

k   = reaction rate constant [s^{-1}]

t = reaction (ageing) time [s]

By separation of variables, integration and rearrangement Equation 2 is obtained:

$$c^{1-n} = c_0^{1-n} - (1-n)kt \tag{2}$$

7.1.5   Since stabilizer depletion in propellants is a heterogeneous (gas / solid phase) reaction, reduced (dimensionless) concentration units are used, as it is common in thermal analysis with heterogeneous kinetics:

$$c = S/S_0 \qquad c_0 = S_o/S_o = 1 \tag{3}$$

S = stabilizer content [%]

S_0 = initial content of stabilizer [%]

> NOTE 22: The advantage of this transformation is that the k-values are no longer depending on the concentration unit chosen. Furthermore, they refer to relative stabilizer depletion rates, which are in accordance with the equally relative acceptance criterion 1 (see Chapter 6). It has to be noted, however, that these k-values differ from the concentration dependent k-values, as used conventionally for homogenous reactions and therefore found in standard kinetic textbooks. The concentration dependent k-values are obtained by multiplying the concentration independent reaction rate constants used here with the factor S_0^{n-1}.

7.1.6   Introducing Equation 3 into Equation 2 and rearrangement gives:

$$S = S_0\left[1-(1-n)kt\right]^{\frac{1}{1-n}} \tag{4}$$

7.1.7   The temperature dependence of the reaction rate constant k is described by the Arrhenius equation:

$$k = Ae^{\frac{-E}{RT}} \tag{5}$$

T = ageing temperature [K]

E = activation energy [kJ/mole]

A = frequency factor [s^{-1}]

R = gas constant [0.00831447 kJ/(K·mole)]

7.1.8   Introducing Equation 5 into Equation 4 results in:

$$S = S_0\left[1-(1-n)Ae^{\frac{-E}{RT}}t\right]^{\frac{1}{1-n}} \tag{6}$$

7.1.9   From Equation 6 follows that the ageing time is given by:

$$t = \frac{1}{A}e^{\frac{E}{RT}}\left[\frac{1-(S/S_o)^{1-n}}{1-n}\right] \tag{7}$$

7.1.10   The corresponding ageing temperature equals to:

$$T = \frac{E}{R\ln\left\{\dfrac{A(1-n)t}{1-(S/S_0)^{1-n}}\right\}} \tag{8}$$

NOTE 23: Equations 6, 7 and 8 are not defined for n = 1 as this would result in a division by zero. These equations, however, are continuous also in the vicinity of n = 1 and could be transferred into specific algebraic functions for n = 1 using the rule of l'Hospital/Bernoulli. For the numerical treatment of the problem, however, this is not required as n = 1 can be avoided by choosing n-values very close (but not equal) to 1, e.g. 0.99999 or 1.00001. This yields equivalent results to a pure 1st order reaction treatment without occurrence of the "division by zero"-problem.

NOTE 24: Equations 6, 7 and 8 are meant to describe the experimental data and to extrapolate the stabilizer depletion rate to standard storage conditions thus yielding safe storage life. They are not meant to be used for (over)interpretations regarding reaction mechanism. In fact, evaluation of stabilizer depletion data can yield negative n values despite the fact that nth order reactions with negative n are not described in the literature meaning that strictly speaking this approach would be inadmissible in such cases. Significantly negative values of n in principle indicate other (autocatalytic) reaction types and would require a more elaborate kinetic treatment. But even in these cases the formal application of nth order kinetics give sufficiently reliable extrapolations to ambient temperature.

7.2   EVALUATION OF DATA

7.2.1   In the evaluation, the unknown kinetic parameters E, A and n have to be calculated from the stabilizer depletion data. This can be done either in a sequential or in a simultaneous regression method.

7.2.2   In the sequential method, the ageing data (stabilizer depletion for all temperatures) are subjected to a least-square fitting using the natural logarithmic form of Equation 7. Thereby, the optimum n-value is determined first (n_{opt}; n-value which fits the data best). For this optimum n-value, E and A are calculated. This procedure is described in Chapter 11. Software which is capable of performing this calculation in an easy way was written and is maintained by the custodian nation. This software, named "AgeKin", can be obtained from the CNAD ammunition safety group management website (https://di.hq.nato.int/casg/; restricted access).

7.2.3   In the simultaneous method, all three parameters (n, A and E) are optimised simultaneously by fitting the natural logarithmic form of Equation 6 to the data. For that, a suitable routine (e.g. Levenberg-Marquardt Algorithm) has to be used. Most modern mathematics software packages contain such routines for simultaneous multi-parameter fitting. Some of them, however, call for relatively good starting values of the kinetic parameters. In most cases the following prediction procedure will be sufficient: Take as first starting value estimates 130 kJ/mole for E and 0.5 for n. Select one of the intermediate storage temperatures and roughly estimate the time t needed for 50 % stabilizer depletion ($S/S_0 = 0.5$). Solve Equation 7 for A, and calculate the starting value for A using the above values for E, n and t.

7.2.4   The kinetic model assumptions used here are valid only for the depletion of the initial stabilizer but not for the "effective stabilizer". In case of DPA, the content of N-nitrosodiphenylamine cannot be included (see also Section 7.4.2). If more than one initial stabilizer is present, evaluation is usually done on the most reactive stabilizer solely, unless a more complex approach is used (see also Chapter 7.5).

7.2.5   Stabilizer depletion in nitrocellulose-based propellants is typically described by values of the reaction order n ranging between -1.0 and +2.0. n values outside this range have to be regarded as suspicious and should only be accepted if it has been established that they are not caused by experimental errors or insufficient coverage of the data field (see also Section 7.2.7). Erroneously high n values result in too high values of t_{25} and T_{10} (as defined in Section 7.3.1).

7.2.6   The standard deviation of the fit (SD; see Chapter 11, Equation 12 if sequential method is used) can be used as a measure of the quality of the evaluation. Standard deviation increases due to experimental errors (mainly incorrect storage temperatures and errors / uncertainties of stabilizer analysis), and, if a large temperature range is covered, due to the slight temperature dependency of the fitting parameter E (activation energy) which is assumed to be constant in the model used. Low standard deviations are more difficult to obtain as more data points and/or test temperatures are included in the fit. Standard deviation values up to 20 % (3 test temperatures), up to 25 % (4 test temperatures), and up to 30 % (more than 4 test temperatures) are considered to be acceptable and compatible with the kinetic model. If larger standard deviation values are calculated, this may indicate a more complex reaction and a more detailed investigation will be necessary.

7.2.7   In order to avoid problems during evaluation of multi-temperature data, the rules listed below should be followed:

(i) <u>Constant temperature:</u> The specified storage temperatures should be correct and constant within ±0.2°C for the required duration and for all samples. Deviations by 0.5°C or more will considerably deteriorate the quality of the evaluation. In fact, deviating storage temperatures were found to be the main cause of unsatisfactory high standard deviations.

(ii) <u>Coverage of "optimum region":</u> The "optimum region" of 10 % to 90 % stabilizer depletion should be covered as well as possible. At least at two of the test temperatures, stabilizer depletion should be measured up to the 80 % to 95 % range – this since the combination of

inconsistent data and coverage of only part of optimum stabilizer depletion range (e.g. only 10 % to 50 %) might result in implausibly high n_{opt} values ("over-fitting").

(iii) <u>Points with very small or very high stabilizer depletion:</u> Stabilizer depletion points of below 5 % or above 95 % are sometimes influential or deteriorate the quality of the evaluation. Thus, points with stabilizer depletion below 5 % should only be added to the fit after it has been established that they do not increase the standard deviation considerably. Furthermore, all but the first of consecutive data points with more than 95 % stabilizer depletion should be omitted.

(iv) <u>Points with stabilizer content above initial value:</u> In regions of low stabilizer depletion it can happen that, due to experimental uncertainty, stabilizer content values S of aged samples above the initial stabilizer content S_0 are obtained. This results in the appearance of "forbidden" mathematical operations (logarithm of negative value) which makes evaluation impossible. Such points also have to be omitted before evaluation of data.

7.3   CALCULATION OF CHEMICAL LIFE

7.3.1   Using the obtained best values for n, A and E, two quantities should be calculated:

1) t_{25} = storage time [years] at 25°C after which a critical stabilizer depletion is reached (calculation from Equation 7; results from Equation 7 have to be divided by 31,556,925 in order to convert units from s into years).

2) T_{10} = temperature [°C] for a 10-years storage after which a critical stabilizer depletion is achieved (calculation from Equation 8; a value of 273.15 has to be subtracted from results obtained from Equation 8 in order to convert units from K into °C).

NOTE 25: The values obtained for chemical life will be dependent on the amount of stabilizer depletion considered acceptable and shall be agreed between the purchaser and the manufacturer. A stabilizer depletion of 80 % ($S/S_0 = 0.2$; as used as criterion 1 of the single-temperature ageing procedure, Chapter 6) is appropriate for most cases and can be used as a guideline.

7.4   <u>TREATMENT OF PROPELLANTS WITH STABILIZERS OF VERY LOW OR VERY HIGH REACTIVITY</u>

7.4.1   Due to the differences in stabilizer reactivity, t_{25}- and T_{10}-values obtained for propellants with different stabilizers cannot be directly compared with each other.

7.4.2   Propellants with highly reactive and efficient stabilizers (such as DPA; see Figure 2) inherently result in lower t_{25}- and T_{10}-values which does not mean that they are less stable than propellants with stabilizers of lower reactivity and thus higher t_{25}- and T_{10}-values. For <u>propellants stabilized with DPA only</u>, the standard approach which only regards depletion of parent DPA is in fact too conservative and does not represent the real stability of these propellants. Nevertheless, the simple evaluation as described above (analysis of DPA depletion only) should be performed first, whereas the resulting t_{25} and T_{10} values have to be regarded as "lower limits of the real stability" (since they do not take stabilizing properties of DPA daughter products into account). In most cases, this will be sufficient since t_{25}-values of well above 10 years are also obtained for 80 % depletion of parent DPA. If, however, this result is regarded as insufficient or if a more accurate assessment of chemical life of these propellants is required, a more complex kinetic model which takes DPA daughter products into account has to be employed (which also will need much longer storage time to cover the optimal region also for all included daughter products). In such cases it must be stated which model and which requirements were used.

7.4.3   On the other hand, propellants with stabilizers of much lower reactivity (such as EC or MC, see Figure 2) might result in very high t_{25}- and T_{10}-values. In some cases, e.g. for triple-base propellants stabilized with EC or MC, implausible extremely high t_{25}- and T_{10}-values might even

indicate that the stabilizers do not react at all or at least not efficiently enough with the nitrogen oxides produced by propellant ageing. In such cases, chemical stability has to be checked by another method, e.g. STANAG 4582 (Heat Flow Calorimetry) or STANAG 4556 (Vacuum Stability Test).
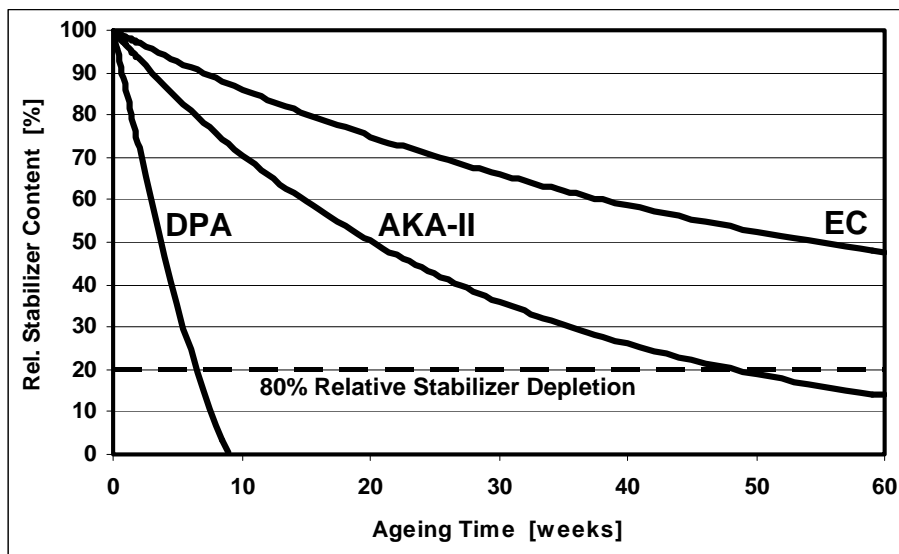

FIGURE 2: Relative depletion of different stabilizers in a reference propellant matrix at 70°C. The three single-base propellants are identical regarding formulation (including the use of the same nitrocellulose batch; with the incorporation of different stabilizers as the only exception) as well as regarding geometry (small single perforated grains). Initial stabilizer content is 1.5% absolute for all samples. In this reference propellant, DPA depletes approximately 5 times faster than AKA-II and approximately 15 times faster than EC, resulting in t_{25}-values of 37 years (DPA), 180 years (AKA-II), and 450 years (EC). In spite of these totally different stabiliser depletion rates and t_{25}-values, all three propellants fulfil the applied stability tests, including STANAG 4582 (Heat Flow Calorimetry) and STANAG 4556 (Vacuum Stability Test) with rather similar test results (spread of results in each test is less than factor 2). This indicates that the three propellants have at least similar "overall" chemical stabilities.

7.5 TREATMENT OF PROPELLANTS WITH MORE THAN ONE STABILIZER

7.5.1 Depending on time and effort which can be invested into the collection and analysis of multi-temperature data of propellants with more than one stabilizer, different approaches might become applicable.

7.5.2 Most propellants with more than one stabilizer are very stable, so that sufficient coverage of depletion of all present initial stabilizers requires excessive ageing times (e.g. of up to several years at 60°C). Therefore, sufficient coverage of optimum region of depletion usually is only available for the most reactive stabilizer which then makes the simplest but very conservative approach (A), in which the most reactive stabilizer is assessed solely by n^{th} order kinetics, being the only one applicable.

7.5.3 If, however, sufficient coverage is available for all initial stabilizers, more elaborate kinetic models which take the depletion of all initial stabilizers into account and thus yield more realistic chemical life predictions can be used. Whereas many of these models are very complex and require a lot of experience, two relatively simple approaches often yield satisfactory results:

7.5.4 If, on one hand, reactivities and depletion rates of the initial stabilizers are similar (such as for pNMA and 2NDPA), approach (B) can be used in which the simple n^{th} order analysis is performed on the sum of all initial stabilizers ("effective stabilizer").

7.5.5 If, on the other hand, reactivities of the initial stabilizers differ so much that they deplete consecutively (e.g. for DPA and AKA-II; DPA and EC or MC; AKA-II and EC or MC), approach (C) can be employed in which the depletion of the individual stabilizers is modelled one after the other, but each of them still with the simple n^{th} order analysis.

7.5.6 If approaches (B) and (C) fail, more complex models (D) have to be chosen.

7.5.7 It has to be stated which approach has been used.

7.5.8 The application of the nth order kinetic evaluation in approaches (A) to (C) of course requires that the conditions as already described for the standard case with only one stabilizer apply, in particular that the standard deviation obtained from the fit lies below the respective limits given in Section 7.2.6.

7.5.9 Approaches (A) to (D) are explained in more detail below (see also Figure 3):

(A) Performing the simple n^{th} order analysis on the <u>most reactive stabilizer only</u>. This only requires sufficient coverage of depletion range for the most reactive stabilizer. The resulting t_{25}- and T_{10}-values are very conservative and have to be regarded as "lower limits of the real stability" (as they do not take stabilizing properties of the other, slower depleting stabilizers into account). In most cases, however, this will be sufficient since t_{25}-values of well above 10 years are also obtained for 80 % depletion of the most reactive ones of the currently used initial stabilizers.

(B) Performing the simple n^{th} order analysis on the <u>sum of all initial stabilizers</u> ("effective stabilizer"). This procedure requires sufficient coverage for the depletion of "effective stabilizer" and gives best results if all initial stabilizers have similar depletion rates. The resulting t_{25}- and T_{10}-values are much more realistic than in approach (A).

(C) Analyzing the depletion of <u>all initial stabilizers</u> individually and consecutively by performing the simple n^{th} order analysis on each of them (here for simplicity described for only two stabilizers, e.g. stabilizer 1 = DPA and stabilizer 2 = AKA-II or EC). In the first step, depletion of the more reactive stabilizer 1 is analysed such as in approach (A). In the second step, the timescale for the less reactive stabilizer 2 has to be corrected in such a way that this timescale commences when stabilizer 2 starts depleting. Then the nth order model is applied to stabilizer 2 as well. The safe storage life t_T at a given temperature T is easily calculated as the sum of the time during which only stabilizer 1 depletes plus the time for the required depletion for stabilizer 2 (here it has to be taken into account that, in order to be compliant with the single-temperature test, "80 % stabilizer depletion" applies to 80 % of the sum of the two initial stabilizers; as stabilizer 1 is fully depleted soon after stabilizer 2 starts, the tolerable amount of stabilizer 2 depletion is lower by the amount necessary to achieve this requirement). The temperature for 10 years storage (T_{10}) then can be calculated numerically by searching the temperature at which the safe storage life is exactly 10 years. This procedure requires sufficient coverage for the depletion of all initial stabilizers and can only be applied if the initial stabilizers deplete consecutively (distinctively one after the other). The resulting t_{25}- and T_{10}-values are then much more realistic than in approach (A).

(D) Employment of a more complex kinetic model which takes the depletion of all initial stabilizers (and possibly also of some daughter products) into account. No guidelines can be given as specific solutions have to be sought for each individual case.
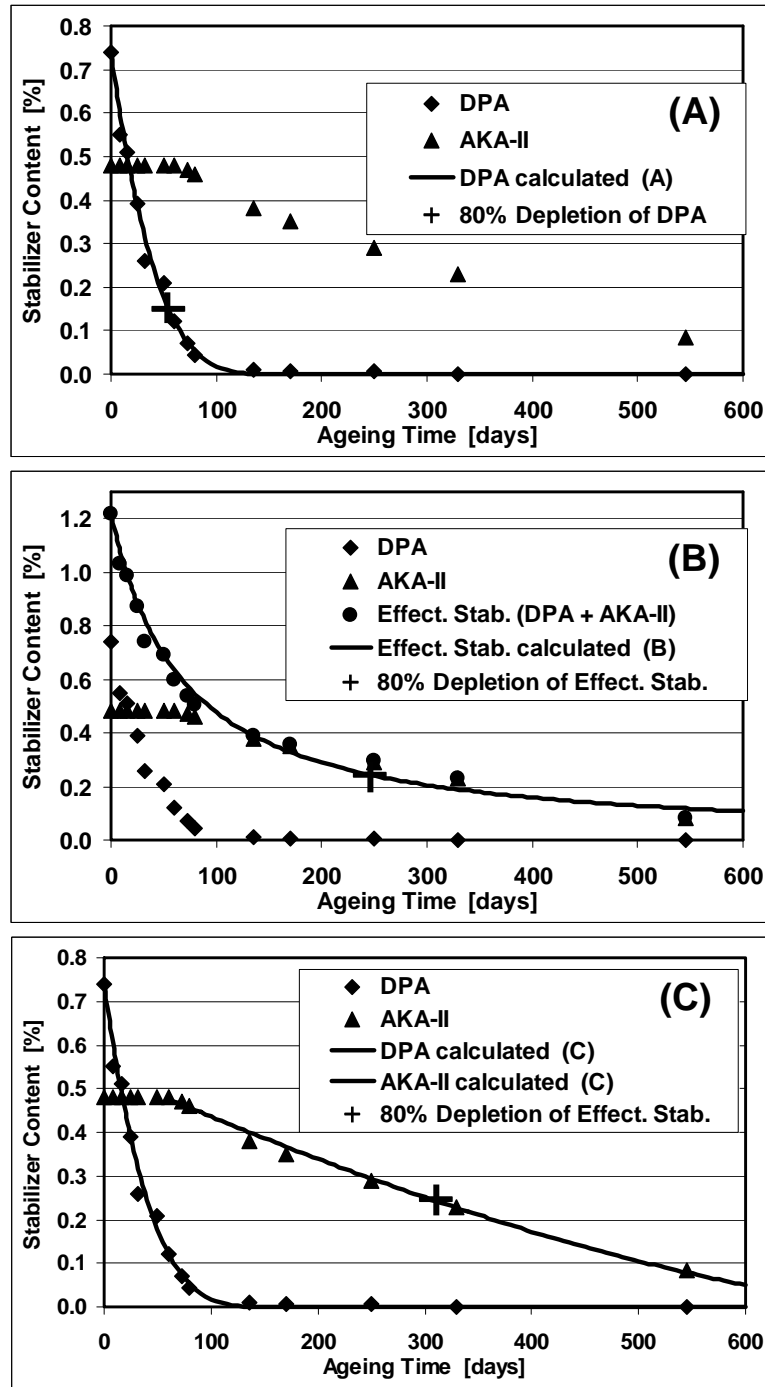
FIGURE 3: Different possible methods for kinetic analysis of the multi-temperature ageing data of a single-base propellant stabilised with 0.75 % DPA and 0.5 % AKA-II. Propellant formulation was optimized for highest possible chemical stability. Data were collected at 60°C, 70°C, 80°C, and 90 °C. For simplicity only the 70°C data are shown here.

(A) n^{th} order analysis of the most reactive stabiliser DPA only (thereby ignoring the presence of the second stabilizer AKA-II). This most simple approach allows for a good quality of fit and yields the lowest t_{25}-value (most conservative result); approx. 200 years for 80% DPA depletion.

(B) n^{th} order analysis of the "Effective Stabiliser" which is the sum of the initial stabilisers DPA + AKA-II. This approach is possible but not ideal for these data thus giving a markedly worse (but still acceptable) quality of fit. Here a much higher t_{25}-value of approx. 950 years for 80% DPA + AKA-II depletion is obtained.

(C) Individual and consecutive treatment of the depletion of DPA and AKA-II with the nth order approach, thereby starting analysis of AKA-II depletion at the time when 80 % of the DPA is consumed. This approach is excellently suited for the present data thus allowing for a good quality of fit. Here the highest but most realistic t_{25}-value of approx. 1,300 years for 80% DPA + AKA-II depletion results.

7.6 OPTIMISATION OF AGEING TIMES

7.6.1 It is practically impossible to achieve an efficient data field – as outlined in Section 4.6 and Section 7.2.7 – without intermediate evaluation and optimisation of the ageing times.

7.6.2 The following procedure is therefore recommended:

1) Store 6 (double) samples at the highest temperature chosen and at the nearest temperature below.

2) Store 5 (double) samples at the lower temperatures.

3) Remove double samples at the two highest temperatures from storage after about 10 and 20 % of the time defined in Table 2 (e.g. after 1 and 2 days for 80°C and 3 and 7 days for 70°C).

4) Estimate provisional values for E and A fixing n at 0.5 as outlined in Chapter 7.2.

5) Replace S/S_0 in Equation 7 by (100-D) / 100 (D = stabilizer depletion in % of the initial content).

6) Calculate ageing times from this equation for:
   D = 30 % / 50 % / 70 % and 90% for both highest temperatures, as well as for
   D = 10 % / 30 % / 50 % / 70 % and 90 % for the ageing temperatures below.
   Round the times calculated to the next day.

   NOTE 26: Since in the evaluation of data the initial value of stabilizer content (S_0) is considered as invariable it must be known with a higher reliability than the individual values after ageing. Therefore for each ageing temperature two unaged samples should be analysed. The mean value is then used in the evaluation.

8. <u>DATA SHEETS FOR SINGLE-TEMPERATURE AGEING PROCEDURE</u>

AOP-48 DATA SHEET 1
FOR SINGLE-TEMPERATURE AGEING PROCEDURE

Report Reference Number:
(Unique Reference Number)   Page 1 of 2 Pages

TEST SITE INFORMATION	**SPECIMEN INFORMATION**
Laboratory: (Name of laboratory) **Date:** (Date that form was completed) **Date Tested:** (Date of test period) **POC:** (Point of contact)	**Propellant:** (Type of propellant) **Identification:** (Trade name and/or identity code) **Manufacturer:** (Name of manufacturer) **Lot, Batch or Consignment Number:** **Date of Manufacture or Receipt:** **Special Storage Conditions:** (If applicable)
TEST CONDITIONS	**COMPOSITION**
Sample Preparation (Before Ageing): (Include details of cutting, grinding, drying or solvent removal, if applicable)	(Composition and percentages)
	Comments:
Sample Preparation (After Ageing): (Details of extraction if different to that described in 5.2.4) **Standard Used:** (State whether internal or external)	**Data Sent To:** (Name and address of person receiving this information)

**AOP-48 DATA SHEET 2
FOR SINGLE-TEMPERATURE AGEING PROCEDURE**

Report Reference Number:

(Unique Reference Number)   Page 2 of 2 Pages

AGEING CONDITIONS

Sample Confinement (Container type and sealing):
Loading Density (g/cm^3):
Temperature (°C):
Duration (days) :

CHROMATOGRAPHIC CONDITIONS

If not HPLC, State Method:
Column Dimensions: Solvent System:
Column Packing:
Column Temperature (°C):
Detector and Wavelength: Flow Rate:
Stabilizers Analysed (List of stabilizers):

RESULTS

N o.	Weight			% Stabi-lizer 1 (name of stabilizer 1)	% Stabi-lizer 2 [*] (name of stabilizer 2)	% Stabi-lizer 3 [*] (name of stabilizer 3)	% N-NO-DPA [*] (* delete when in-appropriate)	% Effective Stabilizer
	Before Ageing /g	After Ageing /g	Loss /%					
Unheated								
1		--	--					
2		--	--					
3		--	--					
4		--	--					
Mean Values (A)								
Aged								
1								
2								
3								
4								
Mean Values (B)								

Stabilizer contents of aged samples have to be corrected for weight loss.

Percentage Effective Stabilizer after ageing (B):

Decrease in Effective Stabilizer (A-B):

Percentage Decrease (A-B) x 100:
$$\text{Percentage Decrease} = \frac{(A-B) \times 100}{A}$$

CHAPTER 9

9.   DATA SHEETS FOR MULTI-TEMPERATURE AGEING PROCEDURE

AOP-48 DATA SHEET 1
FOR MULTI-TEMPERATURE AGEING PROCEDURE

Report Reference Number:
(Unique Reference Number)   Page 1 of 3 Pages

TEST SITE INFORMATION	**SPECIMEN INFORMATION**
Laboratory: (Name of laboratory) **Date:** (Date that form was completed) **Date Tested:** (Date of test period) **POC:** (Point of contact)	**Propellant:** (Type of propellant) **Identification:** (Trade name and/or identity code) **Manufacturer:** (Name of manufacturer) **Lot, Batch or Consignment Number:** **Date of Manufacture or Receipt:** **Special Storage Conditions:** (If applicable)
TEST CONDITIONS	**COMPOSITION**
Sample Preparation (Before Ageing): (Include details of cutting, grinding, drying or solvent removal, if applicable) **Sample Preparation (After Ageing):** (Details of extraction if different to that described in 5.2.4) **Standard Used:** (State whether internal or external)	(Composition and percentages) **Comments:** **Data Sent To:** (Name and address of person receiving this information)

AOP-48 DATA SHEET 2
FOR MULTI-TEMPERATURE AGEING PROCEDURE

Report Reference Number:

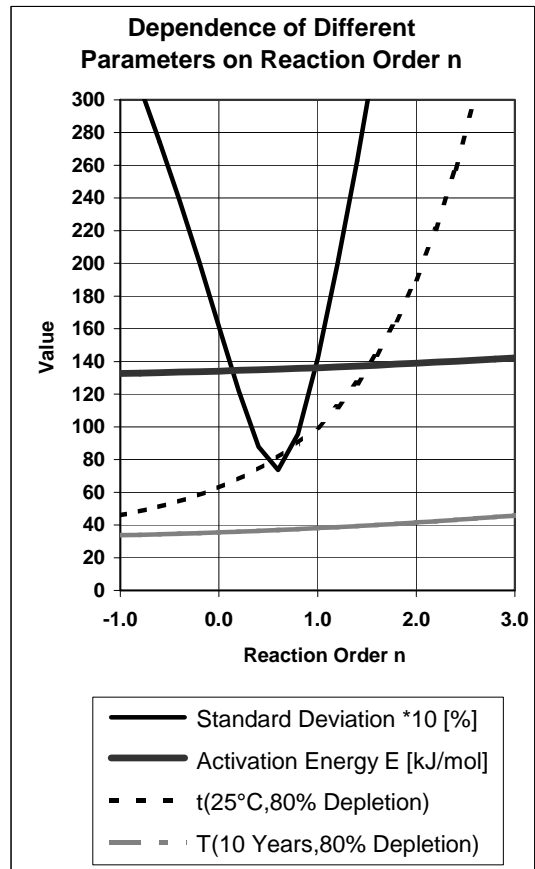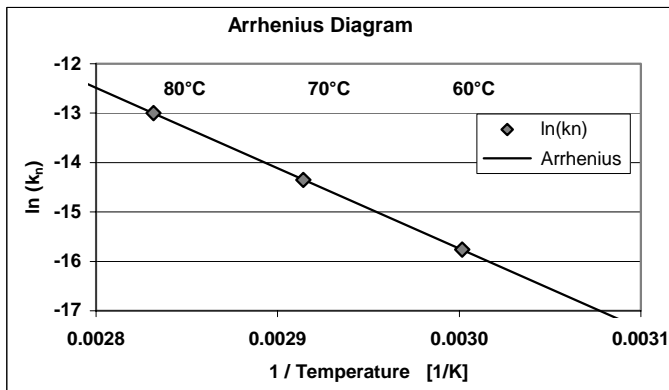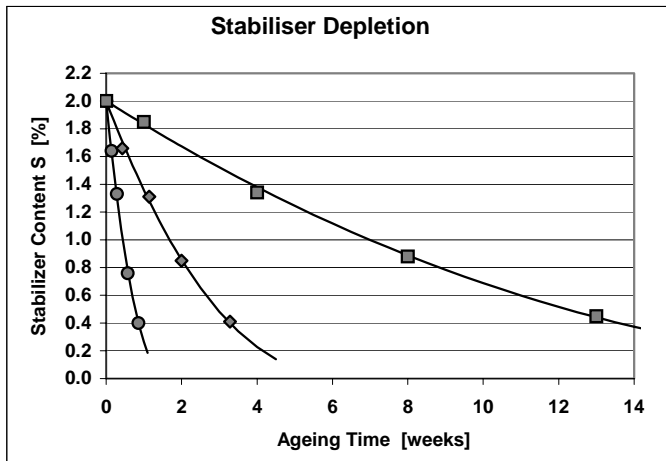(Unique Reference Number)   Page 2 of 3 Pages

AGEING CONDITIONS

Sample Confinement (Container type and sealing):
Loading Density (g/cm^3):
Temperatures (°C):

CHROMATOGRAPHIC CONDITIONS

If not HPLC, State Method:
Column Dimensions: Solvent system:
Column Packing:
Column Temperature (°C):
Detector and Wavelength: Flow rate:
Stabilizer Analysed:

RESULTS (1)

Ageing time / d	% Weight Loss Sample 1	% Weight Loss Sample 2	% Weight Loss Mean Value	% Stabilizer Sample 1	% Stabilizer Sample 2	% Stabilizer Mean Value
Unheated						
			--			--
			--			--
			--			--
T_1 / K						
T_2 / K						
T_3 / K						
T_4 / K						

AOP-48 DATA SHEET 3
FOR MULTI-TEMPERATURE AGEING PROCEDURE

Report Reference Number:
(Unique Reference Number)   Page 3 of 3 Pages

RESULTS 2 (Output of Computer Program for Kinetic Analysis)

Temperature Range Incuded in Fit:	40°C - 80°C	Optimum Reaction Order n:	0.58
Relative Standard Deviation of Fit:	7.3%	**Activation Energy E_A:**	**135.3** kJ/mol
		Frequency Factor A:	2.2955E+14 s^{-1}

	For 50% Stabiliser Conversion:	**For 80% Stabiliser Conversion:**
Safe Storage Life at 25°C ($t_{25°C}$):	**41** Years	**81** Years
Temperature for 10 Years Life ($T_{10\ Years}$):	**33** °C	**37** °C

Stabiliser Depletion

Arrhenius Diagram

Dependence of Different Parameters on Reaction Order n

Standard Deviation *10 [%]
Activation Energy E [kJ/mol]
t(25°C,80% Depletion)
T(10 Years,80% Depletion)

CHAPTER 10

10.   TYPICAL CHROMATOGRAPHIC SEPARATIONS AND CONDITIONS

All chromatograms in this chapter are made from artificial blends of stabilizers and daughter products and not from aged propellants. In real samples (from aged propellants), additional peaks from other propellant ingredients may appear, and not all of the daughter products are usually found.
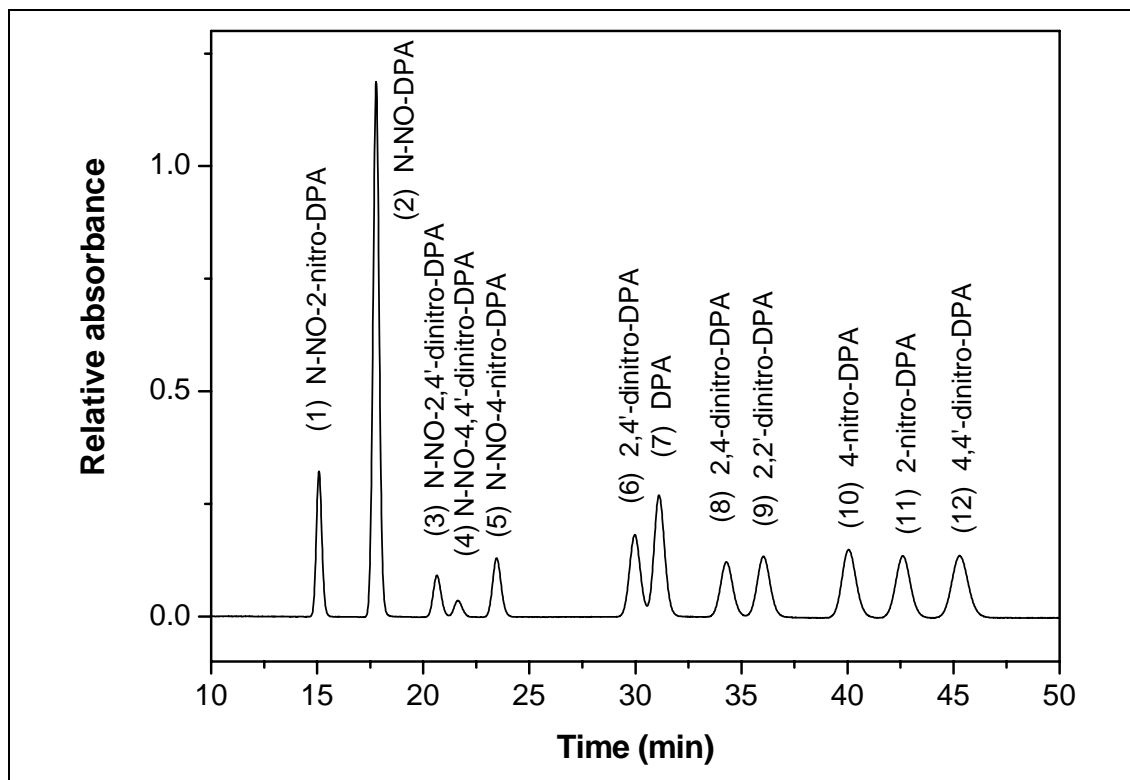
10.1   DIPHENYLAMINE (DPA)

FIGURE 4: Chromatogram of diphenylamine (7) and daughter products N-nitroso-diphenylamine (2), 2-nitro-diphenylamine (11), 4-nitro-diphenylamine (10), N-nitroso-2-nitro-diphenylamine (1), N-nitroso-4-nitro-diphenylamine (5), 2,2'-dinitro-diphenylamine (9), 2,4-dinitro-diphenylamine (8), 2,4'-dinitro-diphenylamine (6), and 4,4'-dinitro-diphenylamine (12). The two other possible daughter products N-nitroso-2,4'-dinitro-diphenylamine (3) and N-nitroso-4,4'-dinitro-diphenylamine (4) which were not observed so far are given as well.

CONDITIONS:

- Sample: Artificial mix of stabilizer and daughter products

- Column: Supelco Supelcosil ABZ +plus, 3 μm, 150 x 4.6 mm

- Detector: UV at 254 nm

- Mobile phase: Acetonitrile/Methanol/Water (14%/25%/61%)

- Flow rate: 1.5 cm³/min

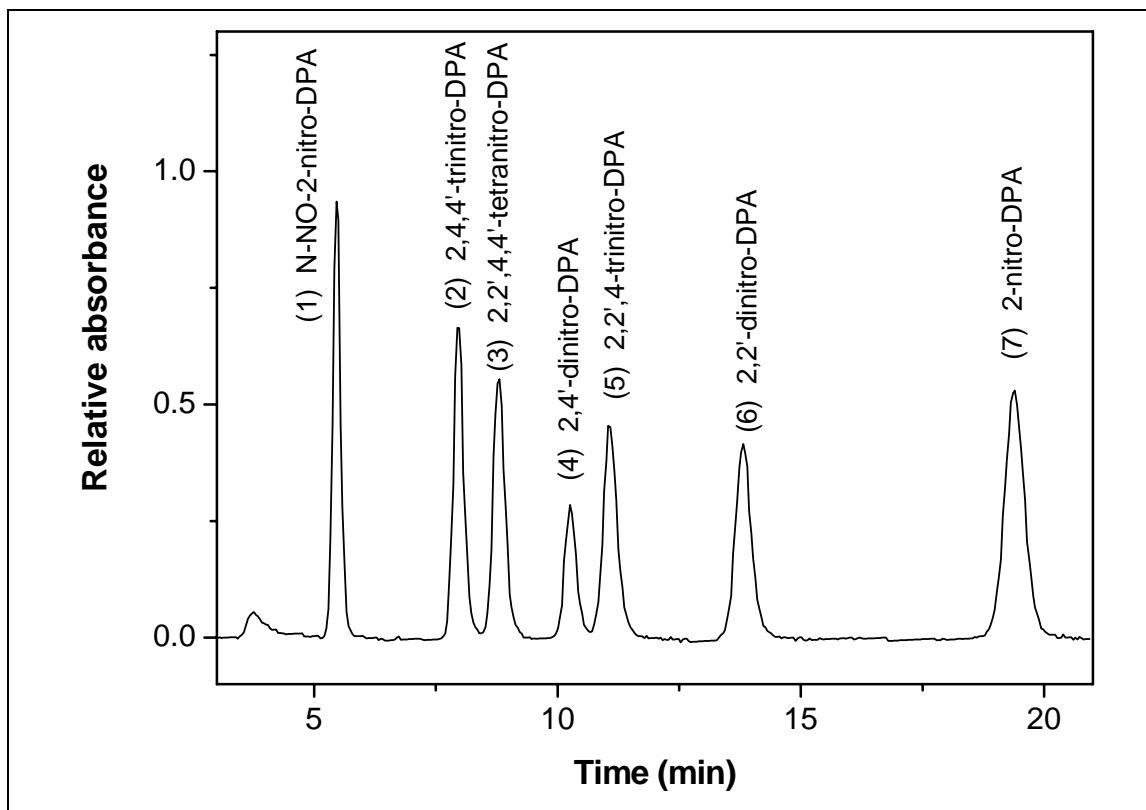- Temperature: 35°C

10.2   2-NITRO-DIPHENYLAMINE (2NDPA)

FIGURE 5: Chromatogram of 2-nitro-diphenylamine (7) and daughter products N-nitroso-2-nitro-di-phenylamine (1), 2,2'-dinitro-diphenylamine (6), 2,4'-dinitro-diphenylamine (4). The tri- and tetra-nitrated products 2,2',4-trinitro-diphenylamine (5), 2,4,4'-trinitro-diphenylamine (2), 2,2',4,4'-tetranitro-diphenylamine (3) are also given. 2,4-dinitro-diphenylamine is missing in the chromatogram – this potential daughter product was not observed in propellants so far.

CONDITIONS:

- Sample: Artificial mix of stabilizer and daughter products
- Column: Lichrospher RP C-18, 4 μm, 250 x 4 mm
- Detector: UV at 225 nm
- Mobile phase: Methanol/Water (67%/33%)
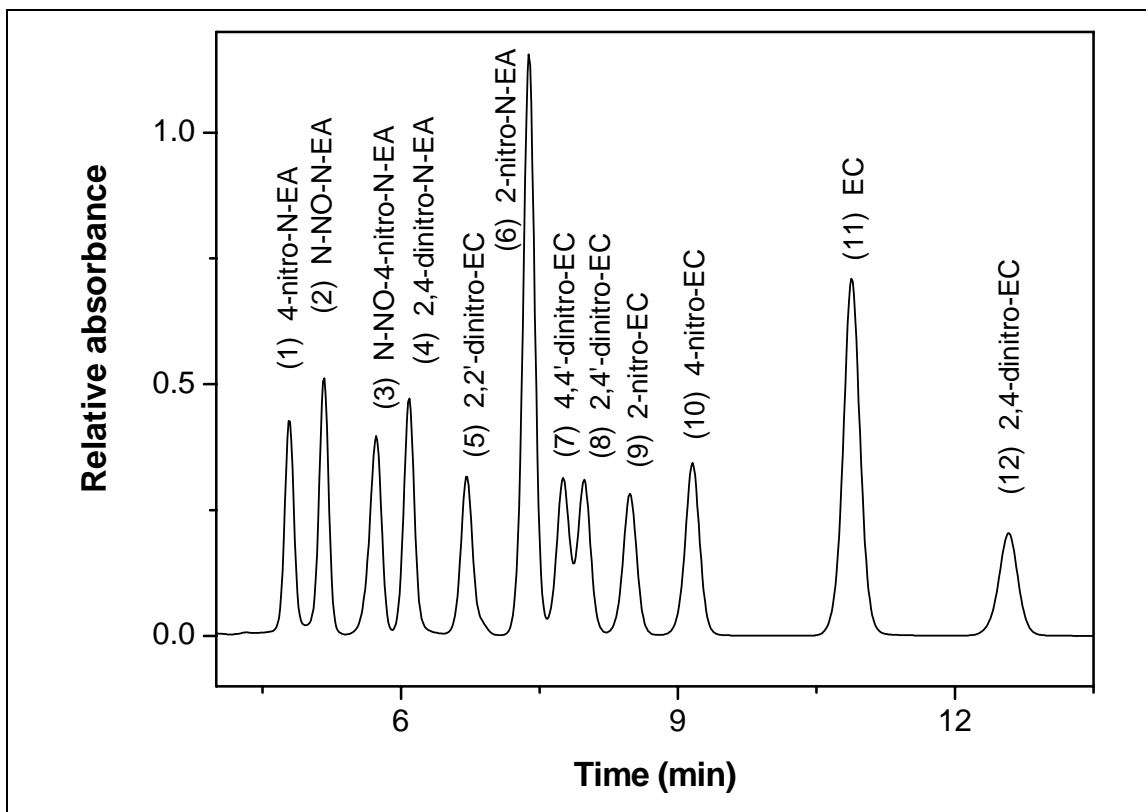- Flow rate: 1.2 cm³/min
- Temperature: 25°C

10.3   ETHYL CENTRALITE (EC)

FIGURE 6: Chromatogram of ethyl centralite (11) and daughter products 2-nitro ethyl centralite (9), 4-nitro ethyl centralite (10), 2,2'-dinitro ethyl centralite (5), 2,4-dinitro ethyl centralite (12), 2,4'-dinitro ethyl centralite (8), 4,4'-dinitro ethyl centralite (7), N-nitroso-N-ethylaniline (2), 2-nitro-N-ethylaniline (6), 4-nitro-N-ethylaniline (1), 4-nitro-N-nitroso-N-ethylaniline (3), and 2,4-dinitro-N-ethylaniline (4). The two other possible daughter products, N-ethylaniline and 2-nitro-N-nitroso-N-ethylaniline, were not observed in propellants so far.

CONDITIONS:

- Sample: Artificial mix of stabilizer and daughter products

- Column: Lichrospher Superspher, 4 μm, 250 x 4.6 mm

- Detector: UV at 254 nm

- Mobile phase: Acetonitrile/Water (58%/42%)

- Flow rate: 1.0 cm³/min

- Temperature: 28°C
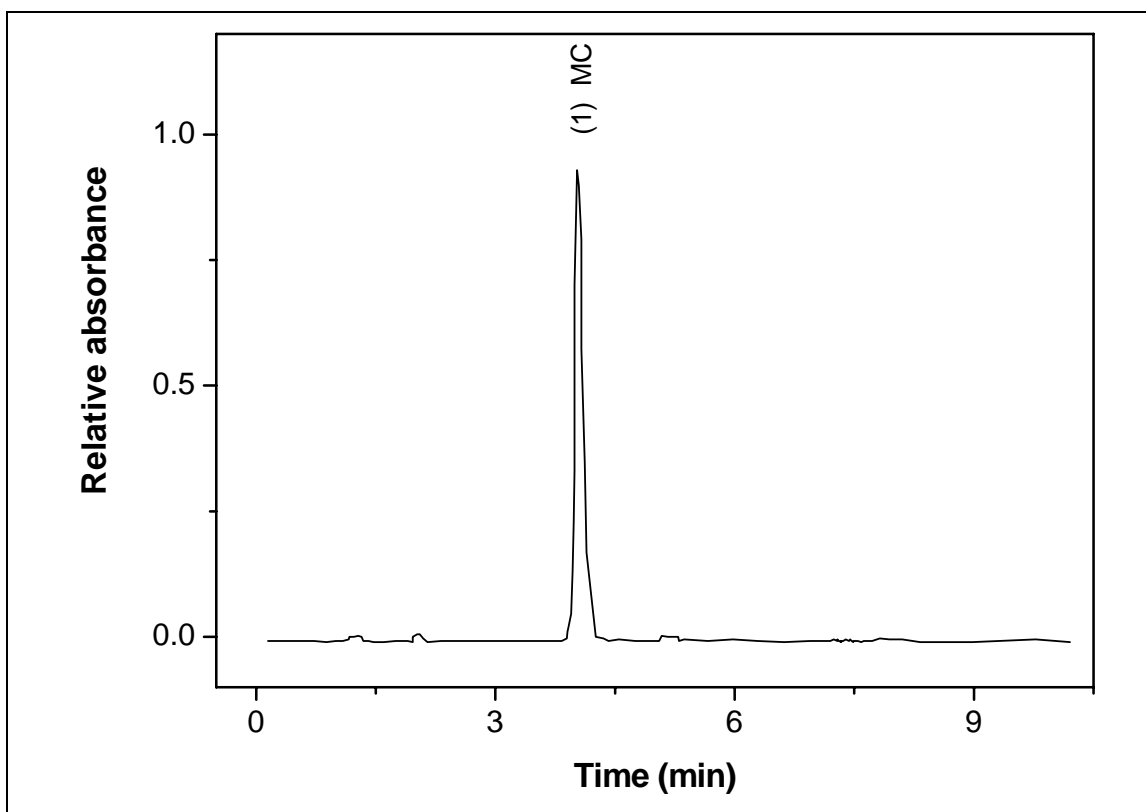
10.4   METHYL CENTRALITE (MC)

FIGURE 7: Chromatogram of methyl centralite (1). No daughter products are shown as no such products were available.

CONDITIONS:

- Sample: Solution of pure stabilizer
- Column: Waters Spherisorb ODS-2, 5 μm, 15 cm
- Detector: UV at 230 nm
- Mobile phase: Acetonitrile/Water (65%/35%)
- Flow rate: 1.0 cm³/min
- Temperature: 22°C
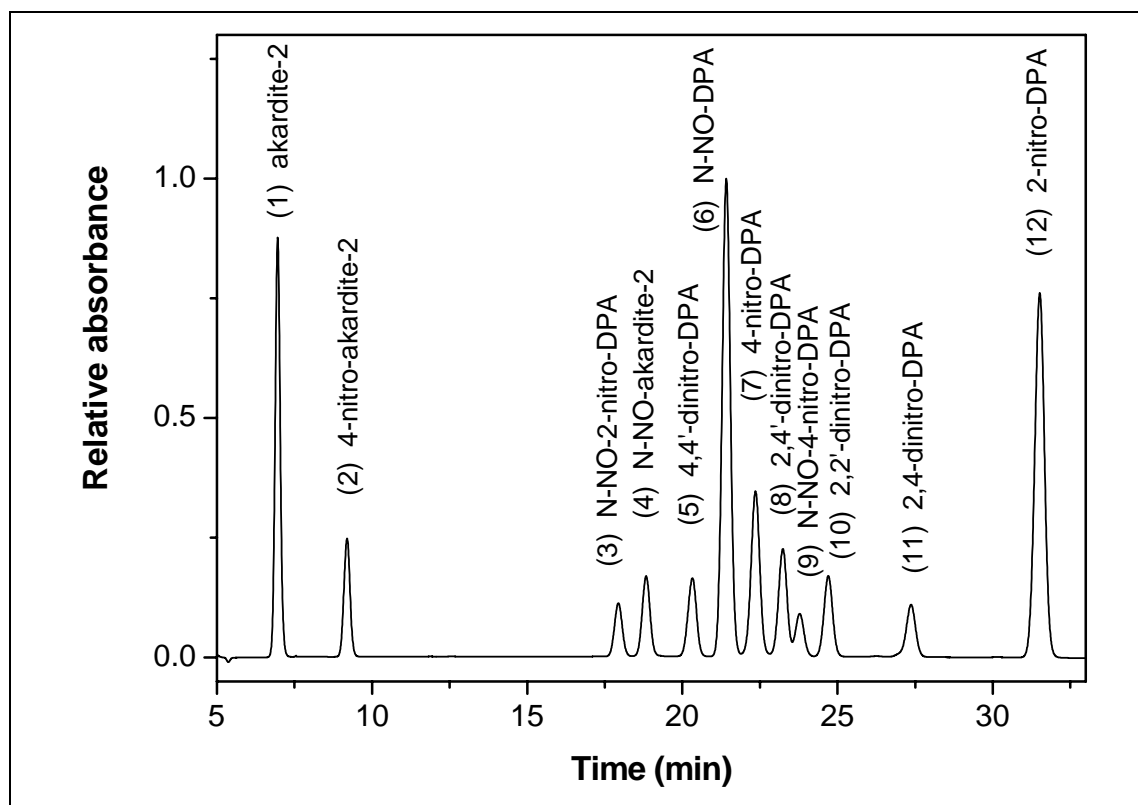
10.5   AKARDITE-II (AKA-II)

FIGURE 8: Chromatogram of akardite-II (1) and daughter products N-nitroso-akardite-II (4), 4-nitro-
akardite-II (2) and the principal degradation products of diphenylamine, namely N-nitroso-
diphenylamine (6), 2-nitro-diphenylamine (12), 4-nitro-diphenylamine (7), N-nitroso-2-nitro-
diphenylamine (3), N-nitroso-4-nitro-diphenylamine (9), 2,2'-dinitro-diphenylamine (10),
2,4-dinitro-diphenylamine (11), 2,4'-dinitro-diphenylamine (8), and 4,4'-dinitro-diphenylamine
(5). 2-nitro-akardite-II as well as dinitro-akardites were not observed so far in propellants.
Please note that N-nitroso-akardite-II is not stable under sunlight. Therefore all solutions
should be stored in dark.

CONDITIONS:

- Sample: Artificial mix of stabilizer and daughter products

- Column: Waters Symmetry C18, 5 μm, 250 x 4.2 mm

- Detector: UV at 220 nm

- Mobile phase: Acetonitrile/Water/Methanol/Tetrahydrofurane (linear gradient in 35 min; initial:
                  30.5%/56.5%/8.0%/5.0%; final: 50.0%/44.5%/3.0%/2.5%)

- Flow rate: 1.0 cm³/min

- Temperature: 40°C
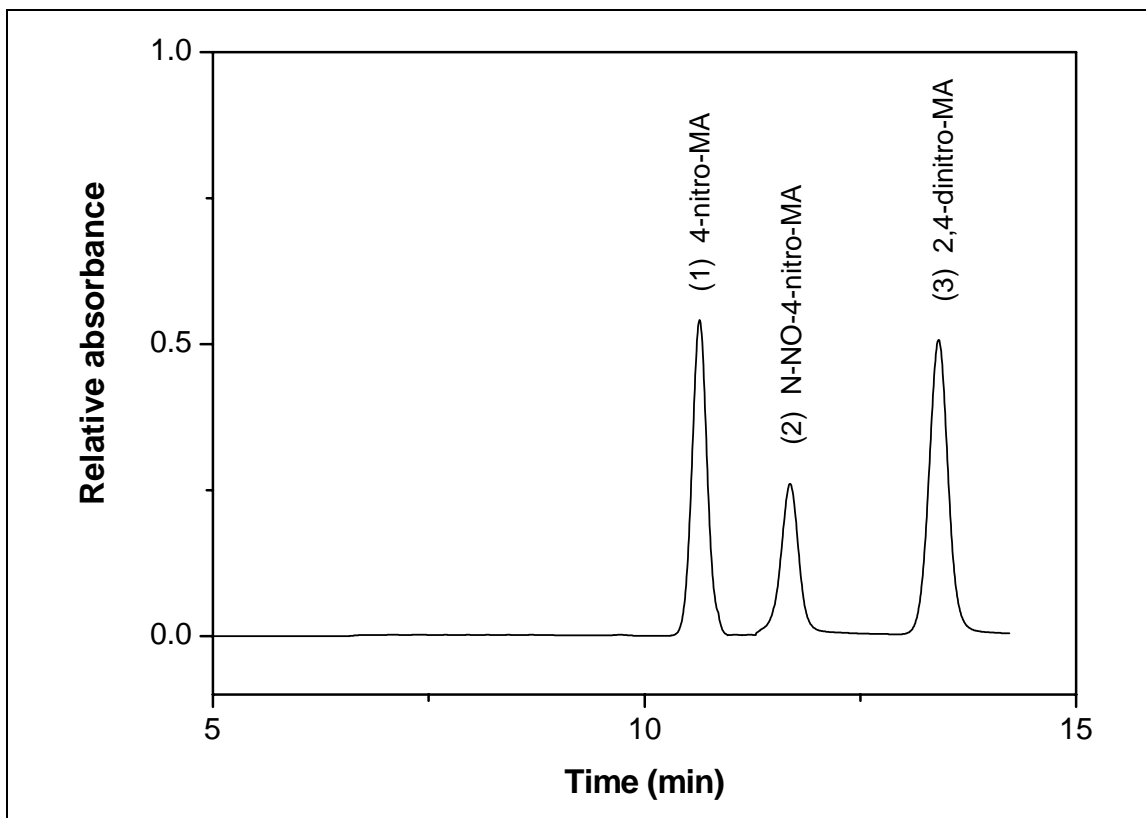
10.6   p-NITRO-N-METHYLANILINE (pNMA, MNA)

FIGURE 9: Chromatogram of 4-nitro-N-methylaniline (1) and daughter products 4-nitro-N-nitroso-N-methylaniline (2), 2,4-dinitro-N-methylaniline (3).

CONDITIONS:

- Sample: Artificial mix of stabilizer and daughter products
- Column: Supelcosil CN, 3 μm, 250 x 4.6 mm
- Detector: UV at 230 nm
- Mobile phase: Acetonitrile/Water (20%/80%)
- Flow rate: 1.0 cm³/min
- Temperature: 28°C

CHAPTER 11

11. EXAMPLE FOR CALCULATION OF CHEMICAL LIFE FROM MULTI-TEMPERATURE AGEING PROCEDURE

11.1 DESCRIPTION OF SEQUENTIAL EVALUATION TECHNIQUE

11.1.1 As mentioned in Section 7.2.2, the sequential method is based on a least-square fitting procedure of all ageing data (stabilizer depletion for all temperatures) in order to determine the optimum n-value, followed by calculation of the corresponding E and A values.

11.1.2 The least-square fitting procedure uses the natural logarithmic form of Equation 7

$$\ln(t) = \ln\left(\frac{1}{A}\right) + \frac{E}{RT} + \ln\left(\frac{1 - (S/S_o)^{1-n}}{1-n}\right) \tag{9}$$

11.1.3 To simplify matters we write:

$$y \quad = \quad a \quad + \quad bx \quad + \quad z \tag{10}$$

where: $\quad x = 1/T; \quad y = \ln t; \quad z = \ln\left(\frac{1 - (S/S_o)^{1-n}}{1-n}\right) \quad a = \ln(1/A); \quad b = E/R$

11.1.4 a and b are the coefficients of a linear regression. For a given value of n, they are calculated as follows:

$$b = \frac{N(\Sigma xy - \Sigma xz) - \Sigma x(\Sigma y - \Sigma z)}{N\Sigma x^2 - (\Sigma x)^2} \quad \text{and} \quad a = \frac{\Sigma y - b\Sigma x - \Sigma z}{N} \tag{11}$$

11.1.5 The relative standard deviation (SD) of the linear regression is calculated as:

$$SD = 100 * \sqrt{\frac{\Sigma(a + bx + z - y)^2}{N - 3}} \tag{12}$$

11.1.6 The best value of n (n_{opt}) can be found by adjusting n until SD reaches its minimum value.

11.1.7 For the optimum n-value, A and E are calculated as follows:

$$A = e^{-a}; \quad E = b \cdot R \tag{13}$$

11.2   EXAMPLE

11.2.1 The example is based on the following ageing / stabilizer depletion data:

T [°C]	t [d]	S [%]
80	1	1.64
80	2	1.33
80	4	0.76
80	6	0.40
70	3	1.66
70	8	1.31
70	14	0.85
70	23	0.41
60	7	1.85
60	28	1.34
60	56	0.88
60	91	0.45

S_0 = 2.00 % (mean value of six measurements)

N = 12 (number of points)

S = mean values of duplicate measurements

(discard all values where the stabilizer

depletion is < 10 % or > 90 %)

11.2.2 For n_{start}, a value of -0.99999 is chosen to avoid n = 1 (where Equation 9 is infinite) during the following evaluation.

11.2.3 For this starting n-value, the other two parameters (a and b) are calculated using Equation 11. The relative standard deviation (SD) for this n-value is calculated using Equation 12.

11.2.4 Then, the n-value is increased by 0.001, followed by calculation of the corresponding parameters a, b and SD. This has to be repeated until SD reaches its minimum. The minimum of the relative standard deviation represents the optimum n-value.

11.2.5 For this optimum n-value, A and E are calculated from a and b (Equation 13), followed by calculation of t_{25} and T_{10}, the latter using Equations 7 and 8 assuming 80 % depletion to be critical ($S / S_0 = 0.2$).

11.2.6 The so obtained values of A, E, SD, t_{25} and T_{10} for selected n-values are given in the following table:

n	A [s^{-1}]	E [kJ/mole]	SD [%]	t_{25} [Years]	T_{10} [°C]
-0.99999	5.7259E13	132.634	33.898	45.833	33.732
0.00001	1.2781E14	134.134	16.147	62.691	35.470
0.50001	2.1011E14	135.090	7.668	77.501	36.641
0.582	**2.2955E14**	**135.262**	**7.344** (minimum SD)	**80.569**	**36.854**
1.00001	3.7203E14	136.209	14.178	100.045	38.043
2.00001	1.4654E15	138.946	48.037	190.420	41.544

11.2.7   The runs of SD, E, t_{25} and T_{10} for n-values between -1 and 3 are given in Figure 10:

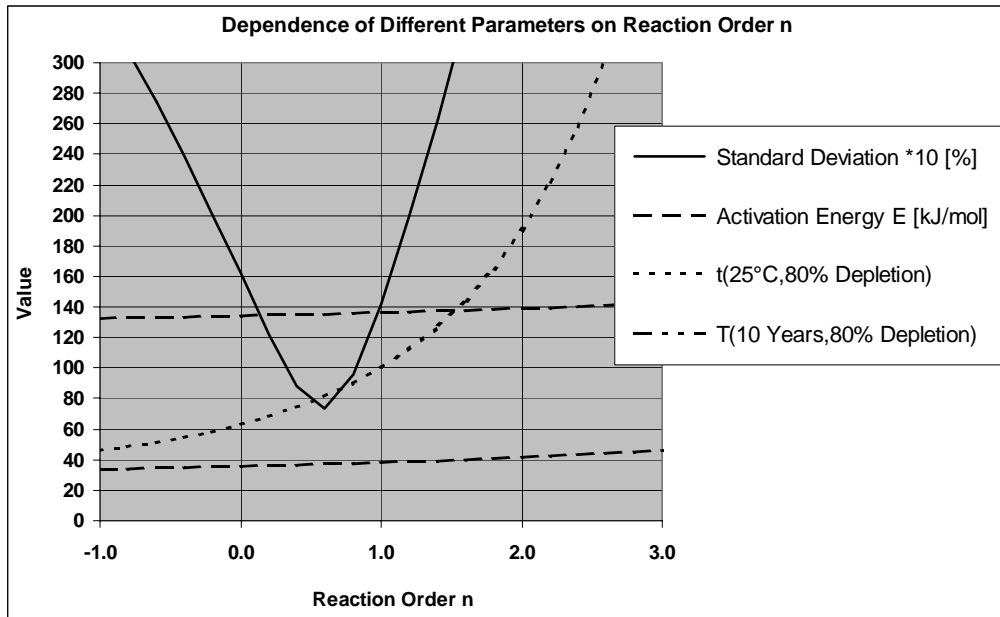**Dependence of Different Parameters on Reaction Order n**

FIGURE 10: SD, E, t_{25} and T_{10} in function of reaction order

NOTE 27: From Figure 10 it is evident that the obtained E-value is almost independent on the n-value chosen, whereas T_{10} depends slightly, t_{25} strongly on the reaction order n. It is therefore essential to use the optimum reaction order value, as otherwise marking deviations from the "effective" shelf life value will result. In particular, a difference in t_{25} of 60 % appears between 0th and 1st order treatment (the two possible n-values used in STANAG 4527 and Ed. 1 of this AOP).

11.2.8   Figure 11 shows the excellent coincidence between measured and recalculated (fitted) S-values as obtained if the optimum reaction order (here: n = 0.582) is used:
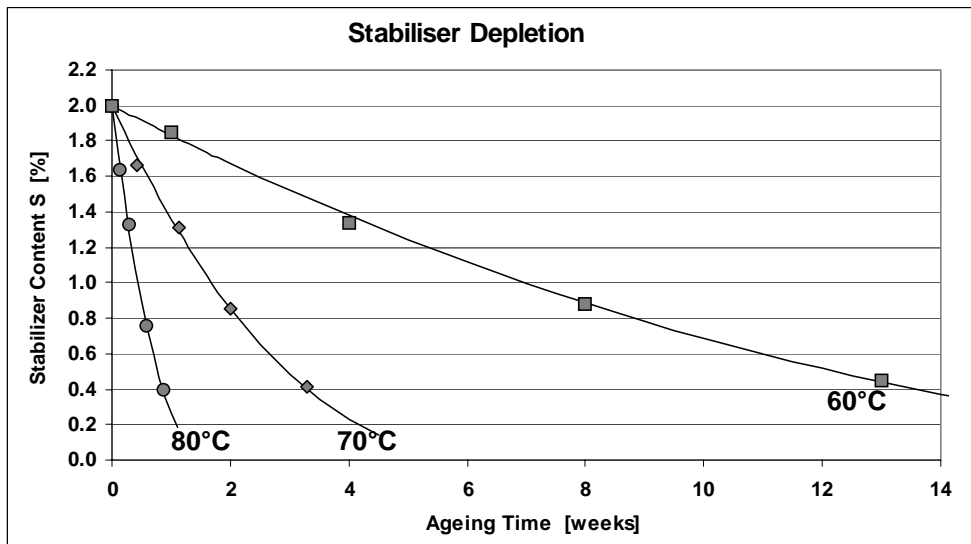
Stabiliser Depletion

FIGURE 11: Measured (dots) and recalculated stabilizer content values

11.2.9 Whereas Figure 11 already contains all relevant information also about the temperature dependence of stabilizer depletion, for some people it might be more convenient having an Arrhenius diagram such as given in Figure 12. The line within this diagram represents the k-values as calculated by Equation 5 using the overall optimum values for A and E obtained for the optimum reaction order n_{opt}. The points show the k-values calculated for every ageing temperature (using the same reaction order n_{opt}) individually by:

$$\ln k_T = (\Sigma z_T - \Sigma y_T)/N_T \tag{14}$$
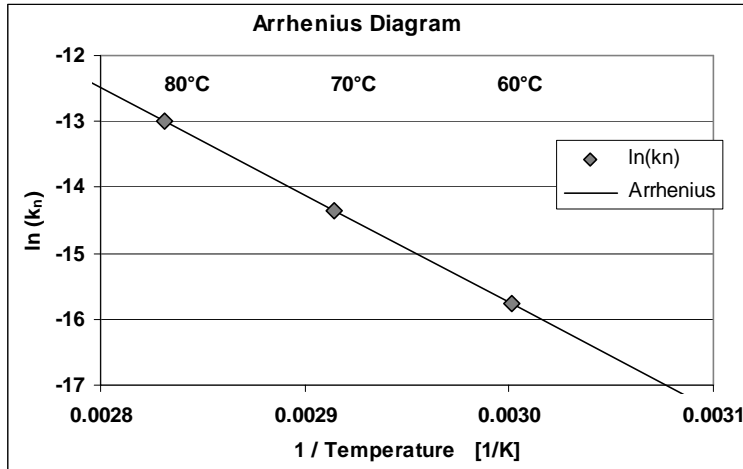
(T indicates data for one temperature only)

FIGURE 12: Arrhenius diagram with k-values for n = 0.582, calculated individually for each temperature (80°C, 70°C, and 60°C)