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Diphenylamine and derivatives as predictors of gunpowder age by means of HPLC and statistical models

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ABSTRACT

The gunpowder age is information of great importance that could help to establish safety regulations related to the propellants use and manipulation. In this work, a forced aging treatment (65 °C for 120 days) was applied to four gunpowders stabilized with diphenylamine (DPA). The evolution of DPA and derivatives (*N*-nitroso-DPA, 2-nitro-DPA, 4-nitro-DPA, and 4-4′-dinitro-DPA) concentration during the days was leaded by High Performance Liquid Chromatography (HPLC). The variation with time of the peak areas of these compounds was used to construct different statistical models that could predict the gunpowders age. These models were validated using nitrocellulose-based gunpowders of known manufacture date. Models that best predicted the gunpowder age provided prediction errors lower than 6, 4, and 2 years for single-base gunpowders with dinitrotoluene ($\geq 10\%\,(m/m)$), single-base gunpowders and double-base gunpowders, respectively.

1. Introduction

Smokeless gunpowders are propellants commonly classified by the number of active compounds present in their formulation. They can be classified as single-base, double-base, or triple-base gunpowders. Propellants based on nitrocellulose are usually described as single-base gunpowders, whereas mixtures of nitrocellulose with nitroglycerine are known as double-base gunpowders. On the other hand, triple-base gunpowders are composed of nitroguanidine as major component, nitrocellulose and nitroglycerine. Single and double-base gunpowders make up the vast majority of propellants used in firearms and triple-base smokeless gunpowders are used primarily in rockets and large caliber military grade weapons, whereby are difficult to obtain on the open market [1].

Some additives (such plasticizers, flame retardant, stabilizers, etc.) are added to the gunpowder formulation in order to modify/improve the gunpowder features. Active compounds mainly decompose to nitrogen oxides (NO and NO_2) that catalyze and accelerate the decomposition process, and may lead to self-heating and autoignition [2]. Stabilizers are added to gunpowders to stop such decomposition, being essential their addition in the gunpowders composition. Diphenylamine (DPA) and centralites (ethyl and methyl centralite) are the main stabilizers for nitrocellulose-based propellants, being DPA the most commonly used [3]. DPA ($(C_6H_5)_2NH$) may be added in different amounts (from 1 to $1.5\%\,(m/m)$) to gunpowders. In very few cases, a DPA derivative, such as 2-nitro-DPA, is used to stabilize gunpowders [4].

The DPA nitration process during smokeless gunpowder aging has already been reported in the literature [3,5]. DPA acts through a group of reactions that lead to the formation of nitrated DPA derivatives, mainly *N*-nitroso-DPA and to a minor extent mononitro and dinitro-DPA derivatives. Fig. 1 depicts the chemical structure of DPA and its main DPA derivatives. Theoretically, it would be possible to obtain, tri-, tetra- and hexanitro-derivatives, but they have only been observed in forced degradation processes [6].

The analysis of DPA and derivatives has been carried out by different analytical techniques. Mass Spectrometry (MS) has been applied for the determination of trace amounts of DPA, some DPA derivatives (*N*-nitroso-DPA, 4-nitroso-DPA, 2,4-dinitro-DPA, etc.), and other organic stabilizers (ethyl and methyl centralite) in smokeless gunpowders and also in gunshot residues [1,7,8]. Works with electrospray ionization MS [7], nanoelectrospray ionization MS [1], and desorption electrospray ionization MS [8] have been described for these purposes.

Ion Mobility Spectrometry [9] has been employed for the detection of DPA and some nitro derivatives in gunpowders, in addition to other compounds related with gunpowders, such as ethyl-centralite, nitroglycerine, trinitrotoluene and dinitrotoluene.

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Differential Pulse Polarography and Square-wave Voltammetry have been applied to the determination of *N*-nitroso-DPA, 2-nitro-DPA, 4-nitro-DPA, and 2,4-dinitro-DPA in a single-base solid propellant, obtaining detection limits ≤ 0.01 mg L^{-1} [6].

Chromatographic techniques have been widely employed up to date. Although Gas Chromatography has been used for the analysis of DPA and derivatives, this technique presents the disadvantage that the main derivative of DPA, *N*-nitroso-DPA, is thermally decomposed completely or partially during injection [10]. High Performance Liquid Chromatography (HPLC) with ultraviolet (UV) detection, using fixed wavelength [3,11], diode array detection (DAD) [10,12–14], or dual-amperometric detection [15]. However, the later detector has the disadvantage that *N*-nitroso-DPA cannot be measured directly, being necessary to determine its concentration through the data obtained for DPA, 2-nitro-DPA, and 4-nitro-DPA. HPLC-MS has been used to develop a method for the analysis of high potential explosives and two stabilizers (ethyl-centralite and DPA) collected from contaminated smooth surfaces without any pre-treatment [16]. This hyphenation has also been used to determine DPA and three DPA derivatives in smokeless gunpowders [17,18].

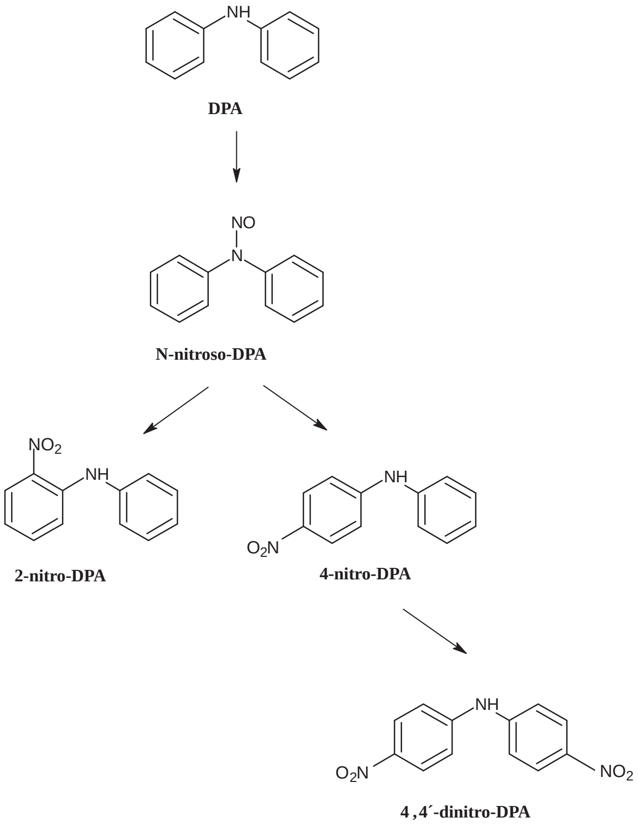

Fig. 1. Chemical structures of DPA and derivatives. Based on [6].

The goals of some of the above-mentioned studies have been either the determination of DPA [11] and two [15] or three [12,14] DPA nitrated derivatives formed during propellant aging by heating procedures in single-base gunpowders or the monitorization of the extent of stabilizer depletion. Moreover, some laboratories monitored the concentration of DPA and derivatives in propellants as a function of time with the aim of knowing the extent of gunpowder degradation. However, it is important to emphasize that a more general approach on gunpowder aging has not been achieved up to date. The goal of this research was to study the age prediction capability of several statistical models constructed on the base of the variation with time of HPLC peak areas obtained for DPA and its main derivatives after forced aging treatment of single-base and double-base gunpowders.

2. Material and methods

2.1. Instrumentation

HPLC 1100 equipment from Agilent Technologies (Palo Alto, CA, USA) with DAD detection was employed. ChemStation® software from Agilent Technologies was used. ProntoSIL column (C18, 250 × 4.6 mm, 5 μm particle size) from Scharlau (Barcelona, Spain) was used at a flow-rate of 1 mL min^{-1}; 40 °C, column temperature; 5 μL, sample injection volume; and four-step gradient of water (mobile phase A) and methanol (mobile phase B): from 25 to 40% B (10 min); from 40 to 55% B (10 min); from 55 to 70% B (10 min); and from 70 to 95% B (7.5 min). Hypersil ODS column (C18, 250 × 4.6 mm, 5 μm particle size) from Thermoquest Inc. (Cheshire, UK) was used at a flow-rate of 1.5 mL min^{-1}; 45 °C, column temperature; 10 μL, sample injection volume; and a mobile

Table 1
Gunpowder samples used in this work (composition and age were obtained from the official label).

	Minor components (< 5%)	Number of samples	Age of samples
Single-base gunpowders (Nitrocellulose)			
Without dinitrotoluene	Diphenylamine, graphite, potassium sulphate, and superficial agents.	2	29, 32
	Centralite, diphenylamine, flame retardant, and graphite.	3	25, 29, 30
	Dibutyl phthalate, diphenylamine, ethyl-centralite, graphite, potassium sulphate, sodium oxalate, and residual solvent.	5	18, 19*, 20, 28, 37*
	Camphor, diphenylamine, ethyl-centralite, graphite, and sodium sulphate.	1	31
With dinitrotoluene (> 10%, m/m)	Dibutyl phthalate, diphenylamine, graphite, and potassium sulphate.	2	12, 27
	Dibutyl phthalate and diphenylamine.	8	11, 13, 14, 21, 21, 22, 25, 34
	Dibutyl phthalate, diphenylamine, and sodium sulphate.	2	17, 22
Double-base gunpowders (Nitrocellulose + Nitroglycerin)			
Dibutyl phthalate, dinitrotoluene, diphenylamine, graphite, potassium nitrate, residual solvent, and sodium sulphate.		4	12, 13, 14, 15
Calcium carbonate, dibutyl phthalate, dinitrotoluene, diphenylamine, graphite, potassium nitrate, residual solvent, and sodium sulphate.		7	8, 14*, 17, 18, 19, 19, 20*
Centralite, diphenylamine, graphite, and potassium sulphate.		1	7
Centralite, diphenylamine, and graphite.		2	24, 25

* Gunpowders used in the forced aging study.

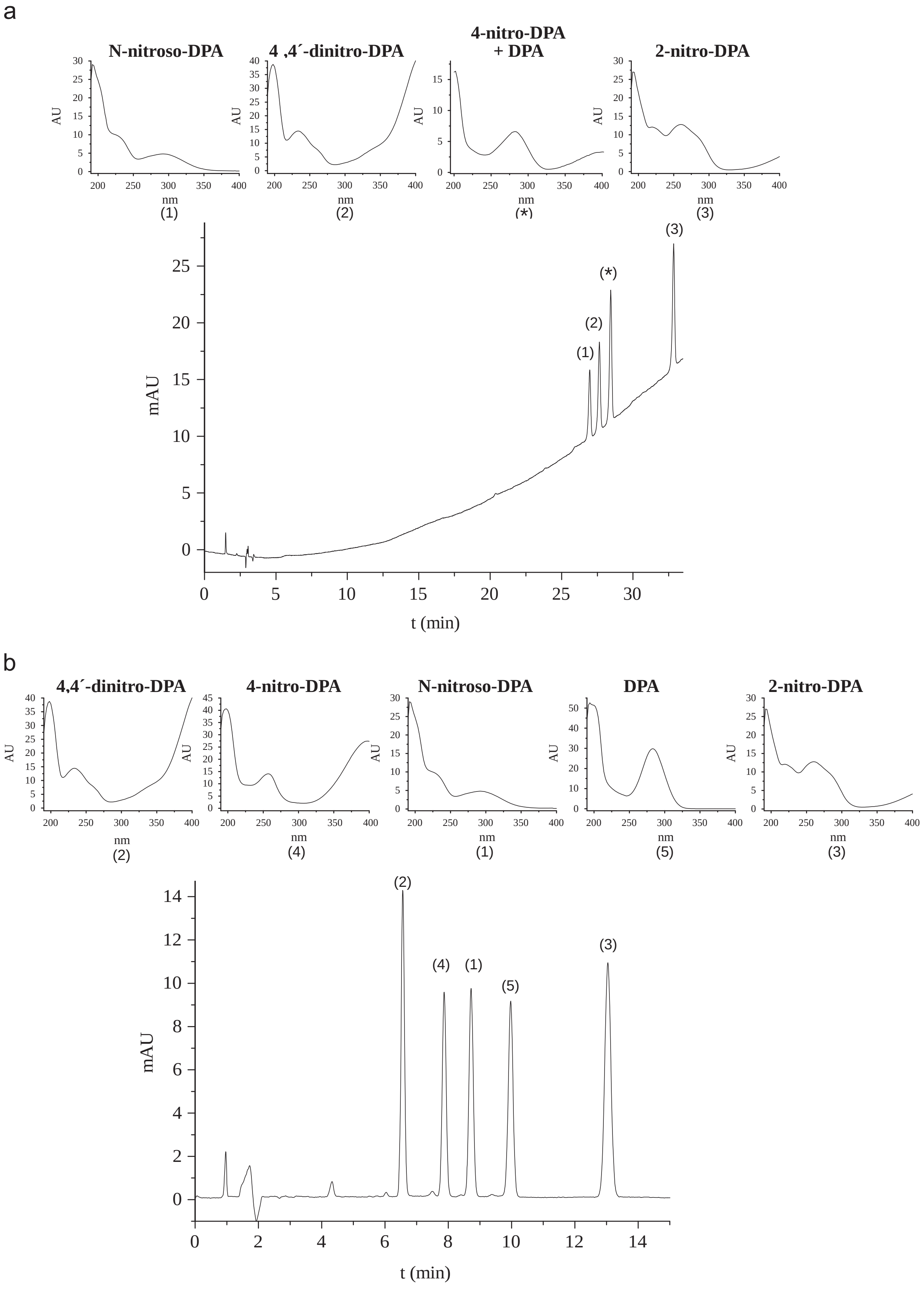

Fig. 2. Comparison of chromatograms obtained for the separation of a mixture of DPA and derivatives using two different chromatographic RP-HPLC methods: (a) ProntoSIL column; water (mobile phase A)/methanol (mobile phase B); gradient elution: from 25 to 40% B (10 min), from 40 to 55% B (10 min), from 55 to 70% B (10 min), and from 70 to 95% B (7.5 min); flow-rate: 1 mL min^{-1}; column temperature, 40 °C; UV detection, 230 ± 2 nm (reference at 550 ± 50 nm). (b) Hypersil ODS column; water/acetonitrile (52/48, v/v); flow-rate, 1.5 mL min^{-1}; column temperature, 45 °C; UV detection, 230 ± 2 nm (reference at 550 ± 50 nm).

phase water/acetonitrile (52/48, v/v) for isocratic separation. DAD detection at 230 ± 2 nm (reference at 550 ± 50 nm) was used for both chromatographic methods.

Statgraphics Centurion XV (StatPoint Incorporated, USA) was employed for the statistical analysis.

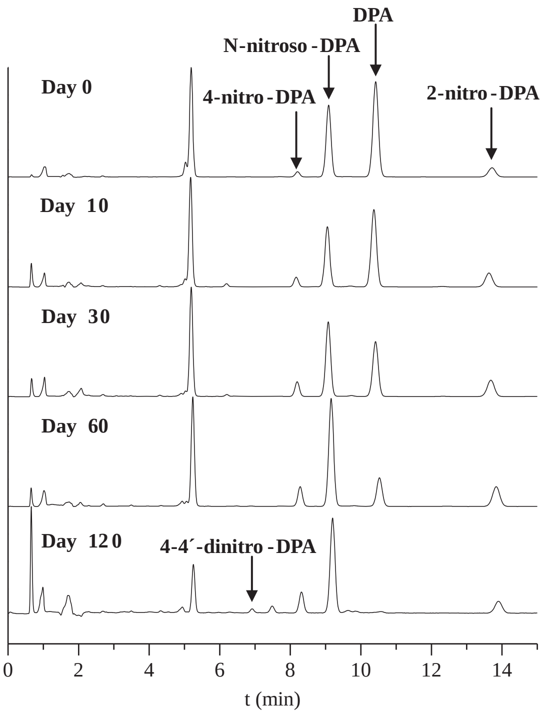

Fig. 3. Comparison of chromatograms corresponding to the methanolic extracts of double-base gunpowder subjected to forced aging treatment (65 °C) at different times of aging. Column: Hypersil ODS. The rest of chromatographic conditions as in Fig. 2(a).

2.2. Reagents and samples

Methanol (UV-IR-HPLC isocratic) was purchased from Panreac (Barcelona, Spain). Acetonitrile (HPLC grade) was supplied from Lab-Scan (Dublin, Ireland). DPA (100 mg L^{-1} in acetonitrile), *N*-nitroso-DPA (100 mg L^{-1} in methanol), 2-nitro-DPA (99.5% purity), and 4-nitro-DPA (99.0% purity), were supplied from Dr. Ehrenstorfer EQ Laboratories Inc. (Atlanta, GA, USA). 4,4′-dinitro-DPA (100 mg L^{-1} in methanol) was kindly provided by "La Marañosa" Institute of Technology (ITM) (Madrid, Spain). Ultrapure water was obtained from a Millipore Milli-Q gradient A10 water purification system from Millipore (Bedford, MA, USA). Methanolic individual standards (100 μg mL^{-1}) of DPA, *N*-nitroso-DPA, 2-nitro-DPA, 4-nitro-DPA, and 4,4′-dinitro-DPA were injected in the HPLC system for peak identification by comparing retention times and UV spectra.

Gunpowder samples were provided by Acuartelamiento San Juan del Viso (Madrid, Spain). Two single-base gunpowders of 19 and 37 years and two-double-base gunpowders of 14 and 20 years were used in the heating storage process. Thirty-three different smokeless gunpowders of known composition and manufacture age were used to validate the statistical models constructed (further details in Table 1).

2.3. Sample preparation

Duplicates of gunpowder samples (~100 mg) into labeled porcelain capsules were subjected at forced aging treatment (65 °C) in a laboratory oven. Samples at 0, 10, 20, 30, 45, 60, 90, and 120 days were extracted with 20 mL of methanol in an ultrasonic bath at room temperature (10 min). Centrifugation at 3450 g for 5 min was performed. Methanol extracts were analyzed by HPLC-DAD using the Hypersil ODS column.

Approximately 25 mg of the gunpowders used for statistical models validation were introduced into glass centrifuge screw top tubes and extracted with methanol (5 mL) in an ultrasonic bath for

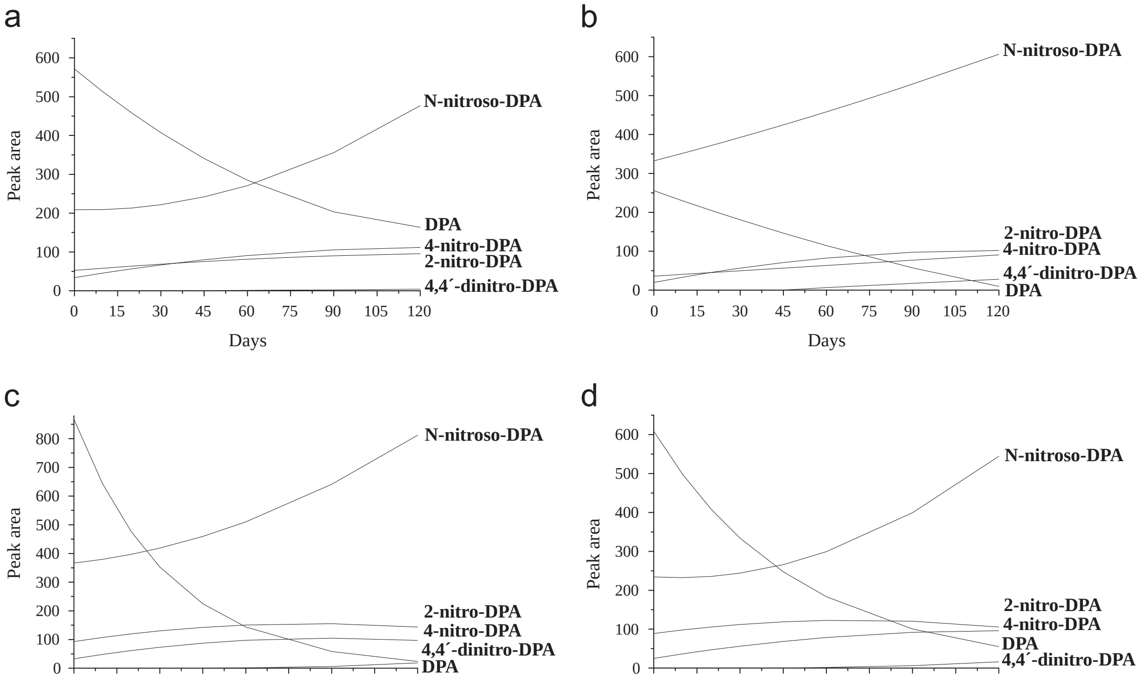

Fig. 4. Variation of total peak area of DPA and derivatives in gunpowders submitted to forced heating at 65 °C for 120 days. (a) Single-base gunpowder (19 years), (b) Single-base gunpowder (37 years), (c) Double-base gunpowder (14 years) and (d) Double-base gunpowder (20 years).

5 min at room temperature. Previous to the solution injection in the HPLC system, centrifugation at 3450 g for 5 min was carried out.

2.4. Data treatment

HPLC-DAD, using the Hypersil ODS column, limits of detection (LODs) for DPA and derivatives were obtained by injecting methanol solutions of DPA, *N*-nitroso-DPA, 2-nitro-DPA, 4-nitro-DPA, and 4,4′-dinitro-DPA over the range of concentrations near the expected LOD (0.5 to 10 mg L^{-1}). In all the analyses, the integrated peak areas were plotted against the injected concentrations of the DPA and its derivatives. The analyte concentration required giving a signal equal to the intercept of the straight line plus three times the standard error of the regression was given as the LOD. The LOD (mg L^{-1}) values calculated were: 0.1 (DPA), 0.1 (*N*-nitroso-DPA), 0.9 (2-nitro-DPA), 1.0 (4-nitro-DPA), and 0.3 (4,4′-dinitro-DPA).

Peak areas of DPA, *N*-nitroso-DPA, 2-nitro-DPA, and 4-nitro-DPA of the gunpowders heated at 65 °C for 0, 10, 20, 30, 45, 60, 90, and 120 days were used to construct different statistical models: univariate regression, ridge regression, partial least squares regression, multiple linear regression (logarithmic transformation), and multiple linear regression (square–root transformation). The ability of each model to predict the age of thirty-three validation samples was measured by calculating the Root Mean Square Error of Prediction (RMSEP), according to the expression:

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}}$$

where y_i is the reference value for the *i*th sample and $\hat{y}_i$ is the predicted value for the same sample; n is the number of validation samples.

3. Results and discussion

The HPLC-DAD analysis of a mixture of DPA, *N*-nitroso-DPA, 2-nitro-DPA, 4-nitro-DPA, and 4,4-dinitro-DPA was performed by two different chromatographic methods. The first method used a ProntoSIL column and a water/methanol mobile phase with a four-step gradient. The second method used a Hypersyl ODS column and an isocratic water/acetonitrile mobile phase (see Section 2.1 for detailed experimental conditions). Fig. 2 depicts the results obtained for both HPLC methods. Using the first method (Fig. 2(a)), the third chromatographic peak (retention time ~28.5 min) corresponded to a 4-nitro-DPA and DPA mixture, as can be observed in the corresponding UV spectra. The inadequate chromatographic separation and the large analysis time (~35 min) indicated the inefficiency of the ProntoSIL method. Furthermore, a change in the mobile phase composition (water/acetonitrile) led to similar results (data not shown). As a consequence, the HPLC method using a Hypersyl ODS column and a water/acetonitrile (52/48, v/v) mobile phase was tested. Fig. 2(b) depicts a chromatogram obtained with this second method. The characteristic UV spectrum of each peak demonstrated the complete separation of the five standards. In this case, the analysis was performed in about 14 min and the peaks of all standard studied were well-resolved. As consequence, this second method was chosen for the determination of DPA and the four derivatives studied in this work.

In order to study the DPA degradation, two single-base gunpowders of 19 and 37 years, and two-double-base gunpowders of 14 and 20 years, were subjected to forced aging treatment (65 °C for 120 days). Fig. 3 compares the chromatograms obtained for double-base gunpowder at different times of aging (0, 10, 30, 60, and 120 days). As can be observed, the peak corresponding to DPA decreases with time whereas the peaks assigned to its derivatives increase. Besides, it should be stressed the selectivity of the chromatographic method since peaks corresponding to other compounds (such as nitroglycerine) that could be present in the gunpowder do not interfere with the peaks of DPA and derivatives. Fig. 4 summarizes the peak area variation (replicates mean value) of DPA and derivatives as a function of time for the samples studied. For all gunpowders studied, except for the oldest single-base gunpowder (37 years), the effect of aging time in DPA and derivatives was quite similar: an exponential decrease of the DPA signal was observed, being the DPA decay more pronounced in the double-base gunpowder samples. As it was expected, peaks areas of DPA derivatives (*N*-nitroso-DPA, 2-nitro-DPA, and 4-nitro-DPA) increased with the storage time; this effect was more pronounced for the *N*-nitroso-DPA (the most immediate derivative of DPA). Only a weak signal of 4,4-dinitro-DPA was registered from day 60 of forced aging treatment in all the gunpowders. This could be expected since this compound is associated to a higher gunpowder aging. Finally, given the different behavior of the oldest gunpowder (37 years at starting this study), data of DPA and derivatives for this gunpowder were ignored for the next part of the study.

Table 2
Statistical models constructed to predict gunpowder age.

<table>
<tr><th>Statistical model</th><th>Var</th><th>n</th><th colspan="5">Best predictive model</th><th>R²</th></tr>
<tr><td>Univariate regression</td><td>2</td><td>20</td><td colspan="5">$\mathrm{Age} = \frac{\mathrm{Ln}(N\text{-nitro-DPA}/\mathrm{DPA}) + 2.1911}{0.081721}$</td><td>73.1</td></tr>
<tr><td>Multiple linear regression[a]</td><td>4</td><td>15</td><td colspan="5">$\mathrm{Age} = 7.01 - 0.00757 \times \mathrm{DPA} + 0.102 \times 2\text{-nitro-DPA} + 0.0428 \times 4\text{-nitro-DPA} + 0.0449 \times N\text{-nitro-DPA}$</td><td>99.8</td></tr>
<tr><td>Multiple linear regression (<i>logarithmic transformation</i>)[b]</td><td>2</td><td>18</td><td colspan="5">$\mathrm{Age} = 78.4332 - 29.3641 \times \log \mathrm{DPA} + 12.2029 \times \log 4\text{-nitro-DPA}$</td><td>99.2</td></tr>
<tr><td>Multiple linear regression (<i>square–root transformation</i>)[a,b]</td><td>2</td><td>11</td><td colspan="5">$\mathrm{Age} = 40.0363 - 1.3274 \times \sqrt{\mathrm{DPA}} + 0.71307 \times \sqrt{N\text{-nitro-DPA}}$</td><td>99.5</td></tr>
<tr><td>Ridge regression</td><td>4</td><td>19</td><td colspan="5">$\mathrm{Age} = 26.312 - 0.028404 \times \mathrm{DPA} + 0.021973 \times 2\text{-nitro-DPA} + 0.042502 \times 4\text{-nitro-DPA} + 0.023298 \times N\text{-nitro-DPA}$
(Ridge parameter = 0.07)</td><td>86.3</td></tr>
<tr><td>Partial least squares regression (3 components)</td><td></td><td></td><td>Component</td><td>% Variation in <i>X</i></td><td>Cumulative % of <i>X</i></td><td>% Variation in <i>Y</i></td><td>Cumulative % of <i>Y</i></td><td><i>R</i>-Squared</td></tr>
<tr><td></td><td>4</td><td>15</td><td>1</td><td>69.4168</td><td>69.4168</td><td>98.0236</td><td>98.0236</td><td>96.3942</td></tr>
<tr><td></td><td></td><td></td><td>2</td><td>7.5674</td><td>76.9843</td><td>1.2628</td><td>99.2864</td><td>96.0824</td></tr>
<tr><td></td><td></td><td></td><td>3</td><td>20.8001</td><td>97.7844</td><td>0.0533</td><td>99.3397</td><td>97.7844</td></tr>
</table>

[a] Backward selection of variables.

[b] Forward selection of variables; Var: number of variables taken to optimize the model; *n*: number of objects used to create the model (outliers have been excluded).

The gunpowders age submitted to the forced aging treatment was calculated taking into account a previous study [19] in which, it was estimated that 60 days at 65 °C for single-base gunpowders (30 days in the case of double-base gunpowders containing nitroglycerine) are equivalent to 10 years of aging at room temperature. Based on this criterion, it was possible to transform the days of forced aging treatment into the gunpowders age, if they were kept at room temperature. A data matrix was built with the calculated age of these gunpowders (objects) and the areas (variables) of those peaks assigned to DPA and derivatives, measured at each one of this time of aging treatment. In all cases, data followed a normal distribution (Skewness–Kurtosis normality tests) and were under statistical control at 95% confidence level (Hotelling's χ^2 and T^2 control charts).

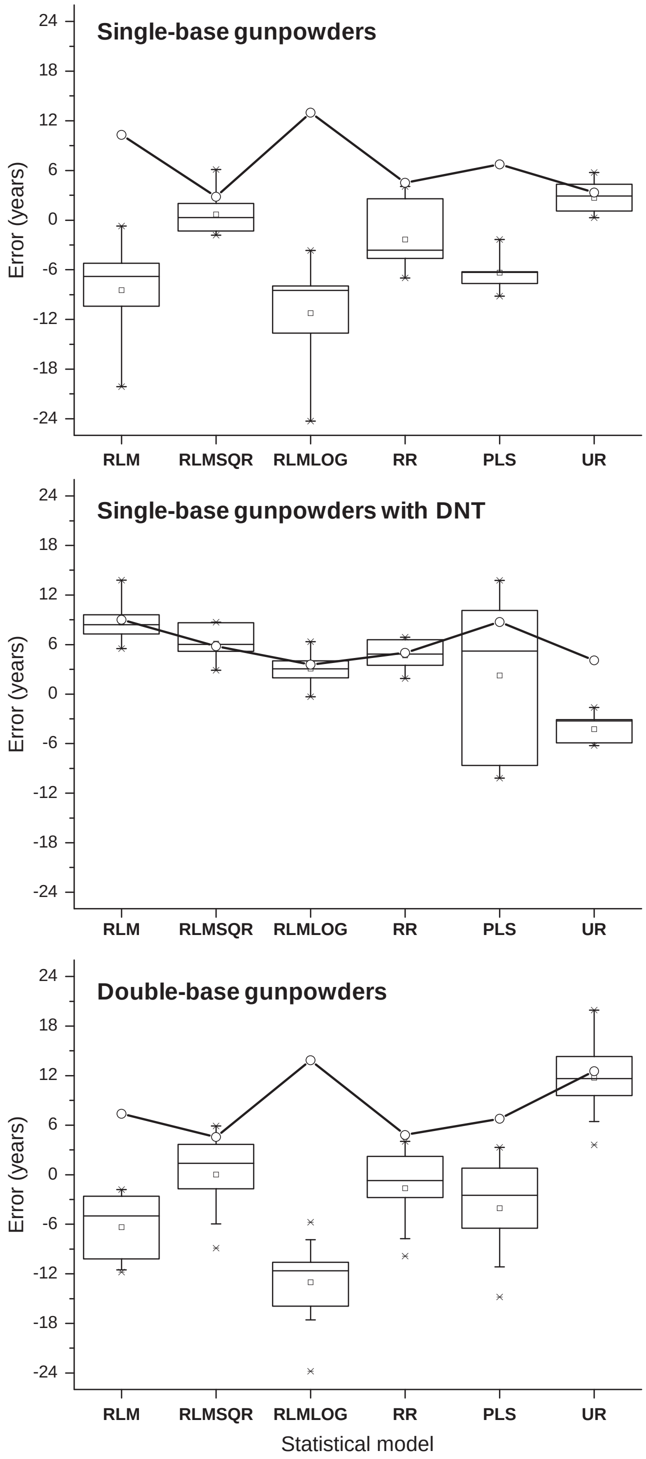

Fig. 5. Prediction errors obtained of gunpowder samples age through the different statistical models studied. Abbreviations: **RLM**, multiple linear regression; **RLM SQR**, multiple linear regression (square–root transformation); **RLM LOG**, multiple linear regression (logarithmic transformation); **RR**, ridge regression; **PLS**, partial least squares regression; and **UR**, univariate regression.

The statistical models evaluated were: univariate regression, multiple linear regression, multiple linear regression with both logarithmic or square–root transformation, and two variants of multiple linear regression (ridge regression and partial least squares regression), to overcome the problem of multicollinearity. Table 2 summarizes the statistical parameters of these models. It is important to mention that the statistical treatment itself selects those variables that contribute most to age prediction. The proportion of the variation in the dependent variable (age) accounted for the explanatory variables was better for multiple linear regression models ($R^2 > 99.2\%$), being univariate regression the model that worst work.

In order to check the prediction model performance, thirty-three gunpowders of known composition and manufacture date (Table 1) were used. Fig. 5 compiles both the errors obtained for the validation gunpowder samples when their age was predicted through the different regression models and the values of the estimation error RMSEP. According to these results, single-base gunpowders were classified in two groups, taking into account the presence or not of dinitrotoluene (> 10%, m/m) it their formulation. Lower errors of prediction (< 9 years) were observed for the gunpowders with dinitrotoluene content higher than 10% (m/m). These errors are always by excess, with the exception of the univariate model prediction, which seems to be useful from a security point of view. According to RMSEP values, best prediction regression models were multiple linear regression with square–root transformation of variables and ridge regression. The first model is based in a simple equation with only two variables: DPA and *N*-nitroso-DPA peak areas.

4. Conclusions

The separation and identification of DPA and four main derivatives (*N*-nitroso-DPA, 2-nitro-DPA, 4-nitro-DPA, and 4-4′-dinitro-DPA) was accomplished in less than 14 min by an HPLC-DAD method using a Hypersil ODS column and an isocratic water/acetonitrile (52/48, v/v) mobile phase.

A forced aging treatment (120 days at 65 °C) of two single-base and two-double-base gunpowders was performed. The variation in peak area of DPA, *N*-nitroso-DPA, 2-nitro-DPA, and 4-nitro-DPA obtained at different heating times was used to construct several statistic models which allow to predict the gunpowder age. The statistical model that best predicted the gunpowders age, according to RMSEP values and error (age) of prediction, was the multiple linear regression with square-root transformation.

Although specific studies for each gunpowder composition should be performed, results obtained in this study demonstrated the utility of DPA and derivatives to predict the gunpowder age.

The reported method gives to the forensic laboratories a useful tool that could help to estimate the gunpowders age and could help to the military laboratories to determine with acceptable prediction errors the gunpowder age in order to improve the protocols for a safe propellants manipulation.

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