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Multivariate optimization of the denitration reaction of nitrocelluloses for safer determination of their nitrogen content

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ABSTRACT

The nitrogen content is of paramount importance to predict the explosive or non-explosive character of nitrocellulose (NC), and hence its applications. There are still quite a few really effective analytical methodologies allowing its determination, due to great NC molecular complexity. One of the approaches giving access to nitrogen content consists in releasing the nitrogenic moieties through alkaline hydrolysis. For the first time, this work reports on the optimization of the denitration yield by means of an experimental design within reasonable ranges of sodium hydroxide concentration, temperature, and time. The experiments were conducted with non-explosive and explosive NC standards. An original capillary electrophoresis (CE) method was used to monitor nitrite and nitrate ions released during hydrolysis. Because of their very different chemical properties, denitration conditions were optimized separately for both sub-classes of NCs to maximize their denitration yields, applying desirability analysis on modeled denitration yields. Mild, safe, and robust optimized conditions were drawn. The denitration yields (95% for non-explosive NCs, 92% for explosive NCs) experimentally obtained under these conditions were in good agreement with model predictions. For practical purposes, correction factors based on these maximal denitration yields are proposed for the first time to correct the determination of nitrogen content, based on preliminary alkaline denitration. This new strategy was successfully applied to determine nitrogen contents of NCs in real explosive samples (smokeless gunpowders).

1. Introduction

Nitrocellulose (NC) is a nitrated ester polymer prepared by an esterification reaction between the hydroxyl groups of cellulose with nitric acid in nitric and sulfuric acid mixtures. This results in the replacement of hydroxyl groups of cellulose by nitro groups with a maximum theoretical number of 3 nitro groups per glucopyranose unit, corresponding to a nitrogen content of 14.14% (w/w). In practice, the nitrogen content cannot exceed 13.8%, representing a hydroxyl degree of substitution (DS) of 2.9 per glucose anhydride unit [1]. In fact, the synthesis of NCs having nitrogen content higher than 13.8%, apart from being expensive, led to the formation of unstable compounds such as sulfuric esters of cellulose [2]. Nitrogen content affects physical and chemical NC properties and determines its applications [1]. Indeed, NCs containing less than 12.5% nitrogen are widely used in daily products (printing inks, paints, lacquers, varnishes, filter membranes), whereas NCs having higher nitrogen contents are employed in the manufacturing of energetic materials, such as propellants and dynamites. These are classified according to the number of energetic materials in their composition [3,4]: (i) single-base propellants, which mainly contain NC, (ii) double-base propellants consisting of NC and nitroglycerin, and (iii) triple-base propellants containing NC, nitroglycerin, and nitroguanidine. Smokeless gunpowder formulations also contain other auxiliary compounds such as stabilizers (diphenylamine, ethyl-centralite, and methyl-centralite), flash suppressants, deterrents, plasticizers (dinitrotoluene, dibutylphthalate) and inert material (graphite) [3,4].

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Besides the many methods reported in the literature for the analysis of NC additives which are generally small molecules [4–11], analysis and characterization of NC itself remain much more challenging, due to its high molar mass, its inherent dispersity in both molar mass and functional groups, its lack of solubility in common organic solvents, and its risk management when handling. Classically, analysis and characterization of pure NC involve an armory of methods including long and tedious chemical ones such as Devarda's [12] vibrational spectroscopy [13,14], pyrolysis gas chromatography coupled to mass spectrometry [15], reversed phase [16], ion [17–20] and size exclusion chromatography [20,21], without omitting functional properties (stability, ignition, heat of explosion, fiber quality) for civilian and military purposes [22]. Moreover, analysis of NC in formulated explosive products normally requires a proper extraction and purification procedure. Recently, López-López et al. [3] developed a new protocol for the extraction of NC contained in smokeless single-, double-, and triple-base gunpowders. Although acidic hydrolysis was considered as the reference first step for the determination of nitrogen content [22], it does not behave fully satisfactory, and alkaline hydrolysis at 150 °C, followed by ion chromatography to monitor released nitrite and nitrate ions, was recently preferred by López-López et al. [18]. Mainly for forensic purposes, which needs miniaturized and more sensitive methods, the same group also developed a method for the discrimination of explosive and non-explosive NCs from NC fingerprints obtained by capillary electrophoresis (CE) with laser induced fluorescence detection after derivatization with 8-aminopyrene-1,3,6-trisulfonate [23], and use of chemometric tools (principal component analysis and soft independent modeling of class analogy) [24]. Unfortunately, no assignment of the fingerprint was proposed.

Apart from being a preliminary step to NC analysis, alkaline hydrolysis has also been used to convert waste NCs from civilian and military industries into non-energetic materials that can be removed by biological processes. This strategy has been the subject of a number of investigations [18,19,25–27]. The reaction between NC and strong alkalis is not a simple saponification reaction leading only to the formation of cellulose and nitrate ions. A lot of decomposition products (nitrite, nitrate, ammonia, cyanide, nitrogen oxides, carbon dioxide, acids, sugars, modified cellulose, and partially denitrated NC) are formed [28]. The effects of temperature [26–28], reaction time [17,18,26,28], types and concentrations of bases [17,18,26–28] were considered. It was generally observed that the time required to denitrate a given weight of NC decreased with increasing temperature and sodium hydroxide concentration. In no case, nevertheless, the denitration yield has been reported to reach 100%.

In this work, the influence on the alkaline hydrolysis of NCs of sodium hydroxide concentration, temperature, reaction time, and their interactions, was studied using an experimental design within reasonable ranges of these parameters in an attempt to maximize the yield of this first analytical step. To the best of our knowledge, this has never been undertaken before. Because of the very pronounced differences in NC physico-chemical behaviors according to their nitrogen contents, explosive and non-explosive NCs were studied separately. The experiments were conducted with six non-explosive and three explosive NC standards of known nitrogen content and weight-averaged molar mass to investigate the influence of NC characteristics on denitration yields. The possible interfering effect of dinitrotoluene (DNT), diphenylamine (DPA) and centralite on denitration reaction was also considered. For the first time, CE was applied to quantify the nitrite and nitrate ions released after the alkaline hydrolysis of NCs, using a purposely developed method [29]. Desirability functions were employed for finding the conditions leading to maximum denitration yields for non-explosive and explosive NCs, separately. For practical purposes, correction factors based on this maximal denitration yield can be proposed for the determination of nitrogen content, based on preliminary alkaline denitration. The optimized conditions of hydrolysis were next applied to determine the nitrogen content of highly nitrated NCs extracted from smokeless gunpowders, applying a correction factor based on this maximum denitration yield.

2. Materials and methods

2.1. Standards and electrolytes

NC standards (Table 1) with a nitrogen content of 11.20 (NC2, NC3), 12.00 (NC4) and 12.20 (NC6) were purchased just at the beginning of this study from Dow Chemical Company (Dow Wolff Cellulosics, Bomlitz, Germany). Their manufacturing date was not available. NC standards with a nitrogen content of 11.14 (NC1) and 12.09 (NC5), 12.55 (NC7), and 13.42 (NC8, NC9) were provided by the Central Laboratory of Police Prefecture (LCPP, Paris, France). At the time of the experiments, they were less than one-year old. NCs were received with ethanol (NC1 to NC6) or water (NC7 to NC9) as damping agent, at a content of approximately 30%. Dinitrotoluenes (2,4-DNT and 2,6-DNT), diphenylamine, and centralite, all of analytical grade, were from Interchim (Montluçon, France). Single-base gunpowders (containing NC, DPA, dibutylphthalate, DNT, potassium sulfate, calcium carbonate, and graphite; the quantitative composition cannot be disclosed) were provided by the Central Laboratory of Police Prefecture. 1 M volumetric solutions (ConvoL Normadose®) of sodium hydroxide used as base for NC hydrolysis were supplied by VWR (Fontenay-sous-Bois, France). Sodium nitrite (>97%), sodium nitrate (>99%), sodium molybdate dihydrate (≥99.5%) used as internal standard and hexadimethrine bromide (HDMB, >94%) used as electroosmotic flow (EOF) reversal agent were supplied by Sigma (Saint-Quentin-Fallavier, France). Sodium phosphate monobasic (>99%) and sodium phosphate dibasic (>99%) from Sigma were employed for electrolyte preparations. All standard solutions and electrolytes were

Table 1
Nitrogen content, substitution degree, and weight-averaged molar masses of the nine studied non-explosive and explosive NC standards.

Identification code	Nitrogen content (%)	Substitution degree	M_w (g/mol)	Damping agent	Explosive (E)/ non-explosive (NE)
NC1	11.14	2.0	20,000	Ethanol	NE
NC2	11.20	2.0	35,500	Ethanol	NE
NC3	11.20	2.0	137,600	Ethanol	NE
NC4	12.00	2.3	312,100	Ethanol	NE
NC5	12.09	2.3	95,000	Ethanol	NE
NC6	12.20	2.3	28,700	Ethanol	NE
NC7	12.55	2.4	200,000	Water	E
NC8	13.42	2.8	69,000	Water	E
NC9	13.42	2.8	110,000	Water	E