Journal of Hazardous Materials 286 (2014) 92–99

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

A new method for the determination of the nitrogen content of nitrocellulose based on the molar ratio of nitrite-to-nitrate ions released after alkaline hydrolysis

Elodie Alinat[a,b,c,e,1], Nathalie Delaunay[a,c,e,1], Xavier Archer[b], Jean-Maurice Mallet[d,e,f], Pierre Gareil[a,c,e,*]

[a] PSL Research University, Chimie ParisTech, Laboratory of Physicochemistry of Electrolytes, Colloids and Analytical Sciences (PECSA), 11 rue Pierre et Marie Curie, 75005 Paris, France
[b] Central Laboratory of Police Prefecture (LCPP), 39 bis rue de Dantzig, 75015 Paris, France
[c] CNRS, UMR 7195 PECSA, 11 rue Pierre et Marie Curie, 75005 Paris, France
[d] École Normale Supérieure-PSL Research University, Département de Chimie, 24 rue Lhomond, 75005 Paris, France
[e] Sorbonne Universités, UPMC Univ Paris 06, LBM, 4 place Jussieu, F-75005 Paris, France
[f] CNRS, UMR 7203 LBM, F-75005 Paris, France

HIGHLIGHTS

- New insights into the nitrocellulose alkaline denitration mechanism.
- Linear correlation for molar ratio of nitrite-to-nitrate ions and nitrogen content.
- Capillary electrophoresis monitoring of nitrite and nitrate ions.
- Applications to explosive and non-explosive nitrocellulose-containing samples.
- Improved performances (including safety) over classical methods.

ARTICLE INFO

Article history:
Received 25 September 2014
Received in revised form 9 December 2014
Accepted 17 December 2014

Keywords:
Nitrocellulose
Nitrogen content
Alkaline hydrolysis
Smokeless gunpowder

ABSTRACT

A new method was proposed to determine the nitrogen content of nitrocelluloses (NCs). It is based on the finding of a linear relationship between the nitrogen content and the molar ratio of nitrite-to-nitrate ions released after alkaline hydrolysis. Capillary electrophoresis was used to monitor the concentration of nitrite and nitrate ions. The influences of hydrolysis time and molar mass of NC on the molar ratio of nitrite-to-nitrate ions were investigated, and new insights into the understanding of the alkaline denitration mechanism of NCs, underlying this analytical strategy is provided. The method was then tested successfully with various explosive and non-explosive NC-containing samples such as various daily products and smokeless gunpowders. Inherently to its principle exploiting a concentration ratio, this method shows very good repeatability in the determination of nitrogen content in real samples with relative standard deviation ($n = 3$) inferior to 1.5%, and also provides very significant advantages with respect to sample extraction, analysis time (1 h for alkaline hydrolysis, 3 min for electrophoretic separation), which was about 5 times shorter than for the classical Devarda's method, currently used in industry, and safety conditions (no need for preliminary drying NC samples, mild hydrolysis conditions with 1 M sodium hydroxide for 1 h at 60 °C).

Abbreviation: NC, nitrocellulose; DS, degree of substitution; HDMB, hexadimethrine bromide; BGE, background electrolyte; DPA, diphenyl amine; DNT, dinitrotoluene.

* Corresponding address. Present address: LSABM, UMR 8231 CBI, CNRS-ESPCI ParisTech, 10 rue Vauquelin, 75231 Paris cedex 05, France. Tel.: +33 1 4079 4651; fax: +33 1 4079 4776.
E-mail addresses: elodie.alinat@chimie-paristech.fr (E. Alinat), nathalie.delaunay@espci.fr (N. Delaunay), xavier.archer@interieur.gouv.fr (X. Archer), jean-maurice.mallet@es.fr (J.-M. Mallet), pierre.gareil@chimie-paristech.fr (P. Gareil).
[1] Present address: LSABM, UMR 8231 CBI, CNRS-ESPCI ParisTech, 10 rue Vauquelin, 75231 Paris cedex 05, France. Tel.: +33 140794651; fax: +33 140794776.

http://dx.doi.org/10.1016/j.jhazmat.2014.12.032
0304-3894/

1. Introduction

Cellulose nitrate, also more commonly called nitrocellulose (NC), is prepared by nitration of cellulose in nitric and sulfuric acid mixtures [1]. Cellulose is a natural linear polysaccharide composed of glucose units linked by β (1 → 4) glucosidic bonds. In each of the repeating glucose units, three reactive hydroxyl groups (one primary hydroxyl group on the C6 position and two secondary hydroxyl groups on the C2 and C3 positions) are able to undergo esterification reaction, which results in the replacement of the hydroxyl groups by nitro groups in an acidic medium. The degree of substitution (DS), defined as the average number of hydroxyl groups exchanged by nitrate groups per glucose unit, depends on the synthesis conditions. In current applications, it is most often expressed as the nitrogen content. Theoretically, the highest achievable nitrogen content is close to 14.15% corresponding to fully nitrated NC, having a DS of 3. In practice, however, the maximum attainable nitrogen content is 13.8% [2]. Indeed, the synthesis of fully nitrated NC is expensive and dangerous, generating unstable compounds such as sulfuric cellulose esters [1]. The nitrogen content is one of the most important parameter determining NC applications, since it strongly affects its physical and chemical properties [2]. NC solubility decreases when the nitrogen content and the degree of polymerization (DP) increase. NCs having nitrogen content below 12.5% (DS close to 2) are widely used as raw material in daily products (lacquers, varnishes, paints, nail polish, ping pong ball, filter membranes, printing inks, and more recently liquid bandage). Highly-nitrated NCs having a nitrogen content higher than 12.5% are employed in the manufacturing of energetic materials such as propellants and dynamites.

NC-based smokeless gunpowders 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. Most smokeless gunpowders are formulated with graphite and various other chemicals (such as dinitrotoluene) to monitor burning, reduce muzzle flash, and make them more water resistant. Due to NC deterioration over time (release of nitric acid), smokeless gunpowders also contain small amounts of stabilizers (diphenylamine, diphenyl ureas such as ethyl or methyl centralite) to neutralize acidic byproducts.

NC characterization remains challenging due to its high molar mass, complex structure, lack of solubility in common organic solvents, both molar mass and functional dispersity, and consideration of safety constraints. Acido-basic titration (Devarda's method) [5], vibrational spectroscopy [6,7], mass spectrometry [8–10], gas chromatography [11–13], reversed phase [14,15], ion [16–19], and size exclusion [20,21] chromatography, and capillary electrophoresis [22–24] have been used to characterize NC. Before implementing most of them, long and tedious sample treatment, especially involving alkaline denitration in the absence [18] or in the presence of hydrogen peroxide [5], are needed. For most of them, dangerous NC drying before precise weighing is required. In addition to this, when NC is present in a formulated sample, it should be first extracted to remove potential interfering components or simply to isolate it before weighing. To this aim, a new protocol involving a multistep solvent extraction has just been developed by López-López et al. to isolate NC from smokeless gunpowders [3]. In spite of the existence of all these methods, few of them are relevant for the determination of the nitrogen content of NCs employed in smokeless gunpowders, and there is still a strong demand from analysts to reduce overall analysis time, simplify sample treatment, and improve safety of the assay.

Following our previous work on the optimization by experimental design of alkaline denitration reaction for maximum denitration yield [25], the molar ratio of nitrite-to-nitrate ions released during this reaction was investigated in depth. CE was used to monitor the released nitrite and nitrate ions by a previously developed method [24]. This study was conducted using nine NC standards of known nitrogen content (from 11.14% to 13.42%) and molar mass (from 20,000 to 312,000 g mol^{-1}). The influence of reaction time was considered and data were analyzed to gain a deeper insight into the understanding of the alkaline denitration mechanism. This work opens a new route to discriminate NCs according to their nitrogen contents, based on the molar ratio of nitrite-to-nitrate ions found in the post-hydrolysis solution. This strategy was successfully applied to as various NC-containing samples as ping pong ball, nail polish, NC membrane, liquid bandage, and smokeless gunpowder to determine their nitrogen content and demonstrate its suitability for real sample analysis, minimizing extraction steps and rendering NC drying useless, thus improving safety conditions.

2. Experimental

2.1. Standards, real samples, and electrolytes

NC standards (Table 1) with a nitrogen content of 11.20 (M_w = 35,000 g mol^{-1} and M_w = 137,000 g mol^{-1}), 12.00 (M_w = 312 g mol^{-1}), and 12.20 (M_w = 29,000 g mol^{-1}) were supplied by Dow Chemical Company (Dow Wolff Cellulosics, Bomlitz, Germany). NC samples with a nitrogen content of 11.14 (M_w = 20,000 g mol^{-1}), 12.09 (M_w = 95,000 g mol^{-1}), 12.55 (M_w = 200,000 g mol^{-1}), and 13.42 (M_w = 69,000 g mol^{-1} and M_w = 110,000 g mol^{-1}) were given by the Central Laboratory of Police Prefecture (LCPP, Paris, France). NCs were stored with a damping agent (water or ethanol) content of approximately 30%. Additional NC standards with nitrogen contents of 11.7 and 12.9%, which were not commercially available to us, were prepared by precisely mixing the appropriate amounts of NC2 with NC6 in 50:50 (w/w) proportions, and NC6 with NC8 in 43:57 (w/w) proportions, respectively, Samples of single-base smokeless gunpowders with and without graphite (mixtures of NC, diphenylamine (DPA), dibutylphtalate, dinitrotoluene (DNT), potassium sulphate, and calcium carbonate) were provided by LCPP. Ping pong balls, nail polish, and liquid bandage were purchased from a local store.

Table 1
Nitrogen content, substitution degree, and molar mass of the nine studied commercially available NC standards.

Identification code	Nitrogen content (%)	Substitution degree	M_w (g mol^{-1})	Explosives properties	Damping agent
NC1	11.14	2.0	20,000	No	Ethanol
NC2	11.20	2.0	35,000	No	Ethanol
NC3	11.20	2.0	137,000	No	Ethanol
NC4	12.00	2.3	312,000	No	Ethanol
NC5	12.09	2.3	95,000	No	Ethanol
NC6	12.20	2.3	29,000	No	Ethanol
NC7	12.55	2.4	200,000	Yes	Water
NC8	13.42	2.8	69,000	Yes	Water
NC9	13.42	2.8	110,000	Yes	Water