Analytica Chimica Acta 745 (2012) 149–155

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

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

Determination of nitrocellulose by capillary electrophoresis with laser-induced fluorescence detection

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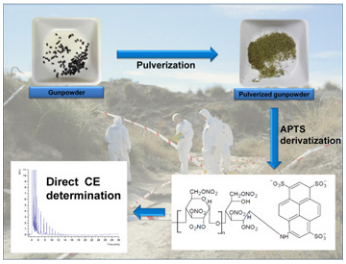
HIGHLIGHTS

- ► Development of the first method to determine nitrocellulose by capillary electrophoresis.
- ► Application of the method to the determination of nitrocellulose contained in gunpowder and collodion samples.
- ► Visual discrimination of highly and lowly nitrated nitrocellulose samples on the basis of the electrophoretic profiles.
- ► An in-capillary preconcentration strategy allowed to determine nitrocellulose contained in ~15 μg of gunpowder.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 March 2012
Received in revised form 14 July 2012
Accepted 20 July 2012
Available online 27 July 2012

Keywords:
Nitrocellulose
APTS
Smokeless Gunpowder
Collodion
Explosives
Capillary electrophoresis

ABSTRACT

The industrial application of nitrocellulose depends on its nitrogen content. When nitrocellulose presents high nitrogen content is used in the manufacture of explosives whereas nitrocellulose with low nitrogen content is used to make a wide range of daily and non-explosive products (e.g. cigarettes, paints, lacquers). This fact makes really important to develop a method for the determination and discrimination of nitrocellulose samples. This work reports, for the first time, the qualitative determination of nitrocellulose previously derivatized with 8-aminopyrene-1,3,6-trisulfonic acid (APTS) by capillary electrophoresis (CE-LIF) with laser-induced fluorescence detection (CE-LIF). APTS-labeled nitrocellulose was determined in lowly and highly nitrated nitrocellulose samples present in collodions and smokeless gunpowders, respectively, after their pulverization in liquid nitrogen. The method described enables the visual discrimination of different nitrocelluloses on the basis of the different electrophoretic profiles obtained, and provides a useful tool to determine nitrocellulose. Additionally, the use of field-amplified sample injection (FASI) enabled enhanced sample detection, which made it possible to determine nitrocellulose contained in ~15 μg of gunpowder.

1. Introduction

Nitrocellulose is a nitrated carbohydrate and low explosive [1], which was discovered in the mid-nineteenth century by Schönbein [2,3]. Nitrocellulose presents a polysaccharide structure formed by linked β-glucopyranose units substituted on carbons C2, C3 and C6, by nitro groups [3–5]. The number of nitro groups present in each glucopyranose unit depends on the synthesis conditions and

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http://dx.doi.org/10.1016/j.aca.2012.07.032

determines the nitrogen content of nitrocellulose. Nitrogen content affects the properties of nitrocellulose and determines its applications. Nitrocellulose with nitrogen content below 12% is component of a wide range of daily products such as paints, nail lacquers, cigarettes, varnishes, etc. while nitrocellulose with nitrogen content above 12% has explosive properties and is mainly employed as a component of various explosives [2].

Nitrocellulose as nitrated carbohydrate presents related characteristics with carbohydrates. These similarities could allow its determination by several analytical techniques. Carbohydrates have been widely studied, essentially by chromatographic and electrophoretic techniques [6–8]. One of the more extensively applied methodologies to study carbohydrates by capillary electrophoresis (CE) is the use of a derivatization agent. Specifically, 8-aminopyrene-1,3,6-trisulfonic acid (APTS) is one of the most frequently used derivatization agents [9] instead of other common and suitable derivatization agents for carbohydrates as 8-aminonaphthalene-1,3,6-trisulfonic acid (ANTS), 2-aminoacridone (2-AA), 7-aminonaphthalene-1,3-disulfonic acid (ANDSA), and many other [9,10]. This fact can be explained due to APTS is the only derivatization agent which yielding permanently charged carbohydrate derivatives [10] and appropriate with Argon-ion laser, used in most commercially available CE-LIF (laser-induced fluorescence detection) instruments. APTS takes part in a reductive amination reaction that provides fluorescent and anionic properties to carbohydrates, which in turn allow their selective separation by CE and sensitive detection with LIF. As a result, many studies have appeared in the literature using this derivatization agent [9–11]. However, APTS has never been applied to study nitrocellulose. In fact, the nitrocellulose study has never been performed by CE in spite of the high performance of this separation technique for carbohydrates.

On the other hand, nitrocellulose as low explosive is part of some explosive materials. This paper focuses on the study of homogeneous gunpowders (also called smokeless gunpowders due to their clean-burning nature and, hence, lack of smoke properties). Smokeless gunpowders are classified according to the number of their active/energetic components. Hence, smokeless gunpowders with one active component are designated as single-base gunpowders, with two active components as double-base gunpowders, and triple-base gunpowders are those having three active components (see Table 1) [2,3]. As can been seen from Table 2, nitrocellulose is found in large quantities in smokeless gunpowders. However, most works published in literature are focused on the determination of other gunpowders components [1,13]. In particular, CE has been used in the analysis of organic and inorganic constituents of smokeless gunpowders [14]. However, nitrocellulose was not included in these studies. In fact, there are few studies on nitrocellulose and most works are focused on the measurement of its polymer properties (molar mass, viscosity and refractive index) and the study of nitrocellulose degradation due to different processes (thermal, biological or mechanical). The high molar mass and chemical and structural complexity presented by this molecule make very challenging to identify it [2]. As has been reported in Table 3, mass spectrometry [15,16], ion-mobility spectrometry [17–20], high-performance liquid chromatography [21,22], ion chromatography [23–25], infrared [26–29] and Raman spectroscopy [27,30], thin-layer chromatography and size-exclusion chromatography [1] have been employed for nitrocellulose determination. Nevertheless, standard nitrocellulose (also known as collodion), isolated nitrocellulose or the decompositions products of nitrocellulose (nitrite and nitrate ions) were required in all of these techniques.

Thus, the aim of this work was to develop a CE-LIF method to determine nitrocellulose polymer in collodion samples and in much more complex samples as smokeless gunpowders. This method was designed to avoid the previous nitrocellulose solvent extraction processes and/or nitrocellulose decomposition procedures, which are complex and time- and solvent-consuming.

2. Experimental

2.1. Materials and chemicals

Propellant samples (Table 2) were kindly provided by Acuartelamiento San Juan del Viso (Madrid, Spain). Two nitrocellulose standards, 4–8% collodion solution in ethanol/diethyl ether and collodion flexible in diethyl ether, were purchased through Panreac (Barcelona, Spain) and Prolabo S.A. (Barcelona, Spain), respectively. Trisodium APTS was purchased from Fluka (St. Louis, USA) and 1.0 M sodium cyanoborohydride solution in tetrahydrofurane was obtained from Aldrich (Milwaukee, USA). Amicon Ultra-4 centrifugal filters of 10, 30, and 50 kDa from Millipore (Bedford, USA) were used. All buffers were filtered prior to use through a 0.45 μm pore size nylon membrane filters obtained from Filter-Lab (Barcelona, Spain). All solutions were prepared with ultrapure water from a Milli-Q system.

2.2. Instrumentation

A Beckman P/ACE MDQ capillary electrophoresis system (Beckman Coulter, Inc., Fullerton, USA) equipped with LIF detection using a 4 mW argon-ion laser (excitation wavelength of 488 nm and emission band-pass filter of 520 nm) was used. Control equipment and data acquisition were carried out using 32 Karat software (Beckman Coulter, Inc.).

2.3. Capillary electrophoresis conditions

CE was performed with uncoated fused-silica capillaries (Polymicro Technologies, Phoenix, USA) of 50 μm internal diameter, 50.2 cm total length, and 40.0 cm effective length, thermostatted at 25 °C. Moreover, for Normal Stacking Mode (NSM) experiments, capillaries of 75 μm internal diameter, 75.2 cm total length, and 65.0 cm effective length were employed. Before first use, all capillaries were preconditioned with methanol (5 min), Milli-Q water (2 min), 1.0 M NaOH (30 min), Milli-Q water (2 min), 0.1 M HCl (10 min), Milli-Q water (2 min) and separation buffer (15 min) at 20 psi. A 1.0 M formate buffer at pH 2.0 was used as separation buffer. Samples inside the CE system were kept at 15 °C and injected into the capillary by hydrodynamic injection at 0.5 psi during 5 s (or 15 s for filtered samples). Separation within the capillary was carried out with reverse polarity at 20 kV. After each separation step, the capillary was flushed with 0.1 M HCl for 2 min; then Milli-Q water during 2 min and, finally, separation buffer during 4 min.

2.4. Sample preparation

Smokeless gunpowders (see Table 2) and collodion samples were prepared by pulverization in a ceramic mortar previously freezing with 5 mL of liquid nitrogen. Approximately 2.00 g of gunpowder and the film formed after to dry 2–3 mL of collodion during 24 h at room temperature were used. Pulverization was performed in order to achieve optimal derivatization with APTS before CE-LIF separation (Fig. 1). The freezing process prior to pulverization is critical for handling smokeless gunpowders because at room temperature they may ignite due to pressure changes or shocks.

Pulverized samples were derivatized by a derivatization process that was developed based on a procedure designed to analyze carbohydrate samples [11]. Derivatization was performed by adding 2 μL of 1×10^{-4} mg mL^{-1} APTS in 15% (v/v) glacial acetic acid and 2 μL of 1.0 M sodium cyanoborohydride in tetrahydrofuran to 0.30 mg of gunpowder sample or 0.50 mg of collodion sample and