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Discrimination of non-explosive and explosive samples through nitrocellulose fingerprints obtained by capillary electrophoresis

Mª Ángeles Fernández de la Ossa, Fernando Ortega-Ojeda, Carmen García-Ruiz*

Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering and University Institute of Research in Police Sciences (IUICP), University of Alcalá, Ctra. Madrid-Barcelona km 33.600, 28871 Alcalá de Henares (Madrid), Spain

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ABSTRACT

This work is focused on a novel procedure to discriminate nitrocellulose-based samples with nonexplosive and explosive properties. The nitrocellulose study has been scarcely approached in the literature due to its special polymeric properties such as its high molar mass and complex chemical and structural characteristics. These properties require the nitrocellulose analysis to be performed by using a few organic solvents and in consequence, they limit the number of adequate analytical techniques for its study. In terms of identification of pre-blast explosives, mass spectrometry is one of the most preferred technique because it allows to obtain structural information. However, it has never been used to analyze polymeric nitrocellulose. In this study, the differentiation of non-explosive and explosive samples through nitrocellulose fingerprints obtained by capillary electrophoresis was investigated. A batch of 30 different smokeless gunpowders and 23 different everyday products were pulverized, derivatized with a fluorescent agent and analyzed by capillary electrophoresis with laser-induced fluorescence detection. Since this methodology is specific to D-glucopyranose derivatives (cellulosic and related compounds), and paper samples could be easily found in explosion scenes, 11 different paper samples were also included in the study as potential interference samples. In order to discriminate among samples, multivariate analysis (principal component analysis and soft independent modeling of class analogy) was applied to the obtained electrophoretic profiles. To the best of our knowledge, this represents the first study that achieve a successful discrimination between non-explosive and explosive nitrocellulose-based samples, as well as potential cellulose interference samples, and posterior classification of unknown samples into their corresponding groups using CE-LIF and chemometric tools.

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1. Introduction

Nitrocellulose is a nitrated carbohydrate based on the nitration of the cellulose. Specifically, from one to three hydroxyl groups of the D-glucopyranose unit can be substituted by nitro groups, producing in this way different types of nitrocellulose. These compounds are present in smokeless gunpowders as well as in a wide range of everyday products. The difference of application relies on the nitrogen content. Low nitrogen content gives mainly covering and protection properties to the nitrocellulose molecule while a high nitrogen content provides explosive properties to this compound becoming it an energetic material. In practice, lowly nitrated nitrocellulose is found in common products such as cigarettes, nail polishes and varnishes while highly nitrated nitrocellulose is part of some explosive compounds such as smokeless gunpowders or dynamites [1].

The identification and discrimination of evidence taken from crime scenes is a common practice in forensic investigations. To this aim, forensic chemistry has been strongly assisted by analytical chemistry tools [2-4]. Nitrocellulose characterization and identification have been mainly performed by chromatographic and spectrometric techniques. Some of these studies have been collected in a recent review article which shows that a complete study of nitrocellulose polymer characteristics (especially focused on molar mass investigation) has been performed by size-exclusion chromatography (SEC), whereas its thermal and morphological properties have been deeply studied by several thermal and spectroscopic techniques [1]. The identification of nitrocellulose with explosive properties has been mostly approached by vibrational spectroscopy, mass spectrometry and liquid chromatography and, in all cases, after the performance of a degradation or isolation process. However, the determination and discrimination of lowly nitrated nitrocellulose from highly nitrated nitrocellulose

^{*} Corresponding author at: Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Multipurpose Building of Chemistry, University of Alcalá, Ctra. Madrid-Barcelona km 33.600, 28871 Alcalá de Henares (Madrid), Spain. Tel.: +34 91 885 6431.

E-mail address: carmen.gruiz@uah.es (C. García-Ruiz).

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Table 1

Samples analyzed by CE-LIF and consecutive multivariate analysis. %NC, nitrocellulose content (m/m percentage) of sample; %N of NC, nitrogen content (m/m percentage) in nitrocellulose.^{a,b,c,d,e}

Press - - P1 Start Wile paper - - P2 Multiellie wile paper - - P3 Lagk Wile paper - - P4 Lagk Wile paper - - P5 Und recycled paper - - P6 Under system - - P7 Under system - - P6 Under system - - P7 Under system - - P7 Under system - - P7 Under system - - P8 Under system - - P8 Under system - - P10 Tatan paper nore - - Cage Multime - - - Cage Patrice - - - Cage Patrice - - - Cage Patrice <td< th=""><th>Name</th><th>Sample</th><th>%NC</th><th>%N of NC</th></td<>	Name	Sample	%NC	%N of NC
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DB17 Double-base 17 85.00 13.20 TB1 Triple-base 1 19.00 n.i. TB2 Triple-base 2 19.00 n.i.	DB16	Double-base 16	85.00	13.20
TB1 Triple-base 1 19.00 n.i. TB2 Triple-base 2 19.00 n.i.	DB17	Double-base 17	85.00	13.20
TB2 Triple-base 2 19.00 n.i.	TB1	Triple-base 1	19.00	n.i.
	TB2	Triple-base 2	19.00	n.i.

n.i., not indicated.

a ≈6-10% (m/m) of nitrocellulose with ≈10-11.5% of nitrogen content [13].
b Nitrocellulose concentration from the product label and nitrogen content determined by ionic chromatography [14].

 $c \approx 10-16\% (m/m)$ of nitrocellulose with $\approx 10-11.5\%$ of nitrogen content [15-17]. $d \approx 30-40\% (m/m)$ of nitrocellulose with $\approx 10-11.5\%$ of nitrogen content [18-20]. e Nitrocellulose concentration from the official label of this ammunition and nitrogen content determined by an official procedure [21].

(as polymer, avoiding degradation processes) is still a challenging issue due to their polymeric characteristics such as its high molar mass and complex chemical and structural characteristics [1,5]. Most commercial nitrocellulose samples present a high degree of polymerization (referred to the number of units in the polymer) from 70 to 850 corresponding to molecular weights from 20,000 to 250,000 kDa. Additionally, the molecular structure of nitrocellulose provides a high polarity to the polymer (caused by the extensive network of nitro and hydroxyl groups) restricting its solubility to high dielectric solvents such as esters, ketones and ether-alcohol mixtures, and excluding aromatic and aliphatic hydrocarbons. As well as cellulose, nitrocellulose is insoluble in water solutions [6]. In 1984 a SEC methodology with electrochemical detection by pendant mercury was proposed to address the problem of nitrocellulose differentiation [5,7]. However, the discrimination (where less than 10 different nitrocellulose samples were analyzed) based on the visual comparison of size-exclusion chromatograms from non-explosive and explosive nitrocellulose samples was ineffective. Similar profiles were registered for both types of samples, making difficult and inaccurate the proposed differentiation. Additionally, this methodology has two drawbacks, it required a previous dispersion, filtration and dissolution of the samples in organic eluents, and it used electrochemical techniques based on mercury electrodes which are being disused in favor of nontoxic detection alternatives.

For the identification of pre-blast explosives the use of techniques which provide structural or elemental information, such as mass spectrometry (MS), are recommended. When these techniques are inadequate, highly selective techniques, as capillary electrophoresis (CE), are proposed by Forensic Laboratories Guidelines [8]. MS is one of the most powerful identification techniques, but it has never been used to analyze polymeric nitrocellulose [1]. Nevertheless, CE has been recently presented as appropriate, nontoxic, with a minimal solvent consumption and highly sensitive and selective technique for the analysis of polymeric nitrocellulose. In fact, a novel CE-LIF method to detect polymeric nitrocellulose in pulverized samples derivatized with 8-aminopyrene-1,3,6trisulfonic acid (APTS) has been reported in the literature [9].

Additionally, chemometric methods allow to achieve objective, quick and effective comparisons of the comprehensive electrophoretic patterns [10]. Principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA) of the separation profiles are powerful metabolomics instruments for the developing of numerous metabolites fingerprints [11,12]. In spite of that, these chemometric tools have never been used to discriminate between non-explosive and explosive samples. In consequence, the objective of this work was to develop the first methodology to discriminate between non-explosive and explosive nitrocellulose-based samples analyzing nitrocellulose fingerprints by means of PCA and SIMCA multivariate techniques. For this purpose, several everyday materials such as cigarettes, nail polishes and varnishes were selected as nonexplosive nitrocellulose-based samples. Smokeless gunpowders were used as samples containing explosive nitrocellulose. Due to the specificity of APTS reaction to D-glucopyranose derivatives, different paper samples were also included in this investigation as potential interferences in a crime scene.

2. Materials and methods

2.1. Samples

A batch of different non-explosive and explosive materials were used (listed in Table 1).

Non-explosive materials: papers, cigarette filter papers, nail polishes and varnishes commercial-available in Spanish market (Madrid, Spain) were used. Standards of low-nitrogen content nitrocellulose (called collodions) were purchased from Fluka (St. Louis, USA) (C1 and C2), BDH (London, UK) (C3) and Panreac (Buchs, Switzerland) (C4 and C5).

Explosive materials: smokeless gunpowders of single-, doubleand triple-base containing highly nitrated nitrocellulose were kindly provided by Acuartelamiento San Juan del Viso (Madrid, Spain).

2.2. Sample preparation

Smokeless gunpowder, collodion, nail polish and varnish samples were prepared using a pulverization process [9]. This process briefly consisted of freezing 2.00 g of each sample with 5 mL of liquid nitrogen and a posterior pulverization on a ceramic mortar. The freezing process was indispensable for handling the smokeless gunpowder samples because they may ignite due to pressure changes or shocks at room temperature. In this study none of the samples were modified (or decomposed) by ignition during or after the pulverization process. Then, pulverization of paper and cigarette filter paper samples were performed through a different pulverization process which was based on the use of a scalpel to produce paper powder by scratching [22]. Approximately 0.30 mg of each type of pulverized sample were weighted and subjected to an APTS (Fluka, St. Louis, USA) derivatization reaction. To this aim, $2 \,\mu$ L of 1×10^{-4} mg mL⁻¹ APTS solution in glacial acetic acid



Fig. 1. Example of (a) a correct and (b) an incorrect peak matching using SpecAlign software.

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Fig. 2. Methodology process scheme.

(15%, v/v) and 2 μ L of 1.0 M cyanoborohydride in tetrahydrofuran were added to the sample contained in different vials [9]. Then, vials were incubated in a thermostatic bath at 65 °C and during 4 h for collodion, nail polish, varnish and smokeless gunpowder pulverized samples and, 6 h for paper and cigarette filter paper pulverized samples. Finally, all vials were filled with 46 μ L of Milli-Q water.

2.3. Instrumentation

All CE experiments were performed on a Beckman P/ACE MDQ capillary electrophoresis system (Beckman Coulter Inc., Fullerton, USA) equipped with LIF detection using a 4 mW argon-ion laser with an excitation wavelength of 488 nm and emission band-pass filter of 520 nm. Sampling rate of the LIF detector was established



Fig. 3. Mean and standard deviation for APTS-labeled single-base gunpowder electropherograms obtained for (a) five independently prepared samples injected in triplicate (*n* = 15) and (b) successively injection (*n* = 5) of the sample.

at 4Hz for all analysis. Control equipment and data acquisition were carried out using 32 Karat software (Beckman Coulter Inc., USA). The analysis of all APTS-labeled samples was performed following the CE-LIF method and conditions previously described in literature [9] which employ a 1.0 M formate buffer at pH 2.0 as separation buffer, an hydrodynamic injection at 0.5 psi during 5 s and a electrophoretic separation at -20 kV. Samples were analyzed in duplicate.

Pulverized samples were weighted on a Discovery DV215CD analytical balance (Ohaus, USA) with a precision value of ± 0.01 mg.

2.4. Data analysis

The CE electropherograms were processed to allow their correct comparison. The complete electrophoretic profile of every sample was exported as text files from the CE equipment. Initially, baseline correction and alignment of CE profiles were performed with SpecAlignv2.4.1 [23]. The profiles were multialigned using the correlation and peak matching combined method provided in the software. Since the pre-treatment parameters (e.g., window size for the baseline correction, range and max shift for the multialignment) are sample dependent, they were modified sequentially until obtaining the best visible (see Fig. 1) and mathematical (minimum standard deviation) results. Subsequently, the CE profiles data were carefully checked and organized into samples (rows) and variables (columns) within an Excel 2010 (Microsoft, USA) transposed matrix. The transposed matrix was later imported into The Unscrambler X 10.2 (Camo, Norway) for the last pre-treatment. i.e., normalization by range [24,25], and its posterior multivariate data analysis. In the Unscrambler data matrix, the sample classes (row groups or families) consisted of the non-explosive and explosive nitrocellulose-based samples (electropherograms) were grouped by type, and each one categorized with its specific categorical variable (i.e. single-base gunpowder, nail polish, varnish, etc.). On the other hand, the variables (columns) comprised every data point (electrophoretic-signal) collected in a specific time. Together, all the samples classes were identified as the calibration (training) set.

Since this work only deals with a qualitative discrimination between non-explosive and explosive nitrocellulose-based samples, a quantitative/regression modeling of the data was unnecessary and only the PCA overview and SIMCA classification were explored.

2.4.1. PCA modeling

In order to obtain the relevant information from the CE pretreated data, and distinguish between non-explosive and explosive samples present in the system, PCA models were generated for every sample class and for the training set. For this purpose, prior to the PCA analysis, the data were mean centered by subtraction of the column means from every variable and weighted using the 1/(StdDev) equation. The weighting by 1/(StdDev) was selected since it assured the variables were representative compared to each other. Additionally, cross validation and non-linear iterative partial least squares algorithm (NIPALS) were used for PCA analysis. NIPALS algorithm was used as it handled missing values and was suitable to compute only the first few factors of a dataset. No auto-pre-treatment for further samples classification was used.

2.4.2. SIMCA classification

To test whether the PCA models were adequate to perform a classification of a group of randomly chosen unknown samples (testing samples), a SIMCA classification procedure with the



Fig. 4. Selected view of the training PCA 3D scores plot for PC-1 vs. PC-2 vs. PC-3.

previously calculated PCA models was used. All testing samples were aligned to a visually and suitable similar reference-class electropherogram, and normalized by range. In addition, all available PCs were used for every chosen class PCA, their values were mean centered, and no other pre-treatments were applied prior to the classification. In order to maximize the confidence of the designed procedure to classify unknown samples, a 95% confidence level was set for the classification process.

Fig. 2 shows a brief scheme containing one example from each type of electropherogram according to its corresponding sample, and all the stages used for the mathematical pre-treatments and the multivariate analysis performed on the CE electrophoretic data.

3. Results and discussion

In order to discriminate non-explosive and explosive nitrocellulose-based samples using multivariate data analysis, appropriate signals patterns were pursued. CE was selected as technique to obtain the profiles of the different nitrocellulose samples because a recently published CE-LIF methodology [9] had been able to analyze nitrocellulose contained in smokeless gunpowders. The proposed methodology (described in Section 2) was based on the APTS derivatization of nitrocellulose which, in terms of time of derivatization, was adapted to each type of nitrocellulose-sample and applied in this work. The discrimination between non-explosive and explosive nitrocellulose samples capability of the CE-LIF method combined with PCA and SIMCA analysis was evaluated through the analysis of other nitrocellulose-based substances that commonly appear in an explosion scene such as cigarettes, nail polishes or varnishes residues. This differentiation was important because both highly and lowly nitrated nitrocellulose compounds are D-glucopyranose derivatives and the developed CE-LIF methodology is highly selective to these compounds. In addition, since this methodology is specific to D-glucopyranose derivatives (including cellulosic compounds), and paper samples could be easily found in explosion scenes, different paper samples were also included in the study as potential interference samples.

In order to assure the correct comparison of the data and determine the influence of the sample rate of the detector and the replicate analysis on the variability of electrophoretic profiles, different experiments were performed. First, one sample of singlebase gunpowder (prepared and APTS derivatized by following the sample preparation procedure described in Section 2) was analyzed in triplicate at different frequencies of sampling rate from 2 to 16 Hz (2, 4, 8 and 16 Hz). The variation of sampling rate value did not affect to the signal features (results not shown). In consequence, an intermediate frequency of sampling rate at 4 Hz was established to perform all subsequent analysis. Next, the potential variability introduced by replicate analysis was also evaluated. For this



Fig. 5. Close-up of the 3D scores plot for PC-1 vs. PC-2 vs. PC-3.

purpose, two different experiments were performed. Five different samples of APTS-labeled single-base gunpowder, independently prepared according to Section 2, were analyzed in triplicate to determine the variability introduced in the electrophoretic profiles. Subsequently, one sample of APTS-labeled single-base gunpowder was injected in quintuplicate in order to define the instrumental variance. Fig. 3 shows the mean and standard deviation obtained for both experiments. Additionally, values of the standard deviation were calculated for the first three peaks since these nitrocellulose signals were always the most intense in all samples and, in consequence, were registered for all samples and patterns for the alignment process. As result, the variance between samples (reproducibility) was of 6% of the mean signal and the instrumental variance (repeatability) corresponded to the 3% of the mean signal. Being both values, acceptable for CE protocols.

Although some electropherograms were differentiated visually (cellulose from nitrocellulose samples), the discrimination among nitrocellulose-based samples was difficult by direct visualization of the electrophoretic profiles (see Fig. 1). Consequently, PCA and SIMCA analysis were performed to test, in practice, if the different nitrocellulose-based samples could be distinguished by statistical comparison of the corresponding electropherograms.

3.1. PCA analysis

PCA is a bilinear modeling method that offers an interpretable overview of the core information enclosed in a multidimensional table. This projection technique takes information from the original variables and projects them onto a smaller number of latent variables called Principal Components (PC) [26]. Each PC clarifies a portion of all the information contained in the original data, where PC-1 explains most of the information in the data set and the following PC contains, subsequently, less information than the previous one [24]. In addition, plotting PCs reveals significant sample and variable interrelationships, which leads to the interpretation of some sample similarities, differences or clusterings [27]. In this PCA analysis, the score plots for PC-1 and PC-2 were initially used for the study of the class separation since they summarize more variation in the data than any other group of components, i.e., 40 and 19%, respectively. The training PCA scores plot for PC-1 vs. PC-2 (not shown) proved that the explosive classes appeared together in a rather close bunch, while the non-explosive classes were located apart from the explosives. As a result, it is remarkable that the discrimination between non-explosive and explosive nitrocellulose-based samples was achieved only considering a 2D model. Despite these good results, and in order to increase the sample discrimination among classes and since PC-3 considered the 13% of the data variation, the third component was included in the analysis. The 3D scores plot was performed and this plot view showed (see Fig. 4) a clearer separation of the classes with no entanglements. All smokeless gunpowders were located apart from other classes. Additionally, cellulose class (P) was projected compactly and apart from the rest classes. Similar behavior was shown for the nail polish class (NP) which was located in other compact and separate group. On the other hand, cigarette (Cig), collodion (C) and varnish (V) classes were projected rather dispersed, but still did not entangle with other sample groups.

This 3D score plot (Fig. 4) also proved a successful discrimination between non-explosive and explosive samples. In addition, a good classification was shown in the 3D plot for nitrocellulosebased non-explosive samples, being possible to clearly differentiate among the 6 classes studied in this work: smokeless gunpowders, nail polishes, collodions, cigarettes, varnishes and papers. Nail polish samples (NP1–NP8) were the most compact nitrocellulosebased non-explosive class while cigarettes (Cig1–Cig5), collodions (C1–C5) and varnishes (V1–V5) appeared as lightly dispersed

Table 2

SIMCA classifications percentage (%) table (rows, testing samples marked with x and y in their names and columns, PCA classes) for the testing class containing non-explosive and explosive samples.

	Paper	Nail polish	Collodion	Cigarette	Varnish	SB gunpowder	DB gunpowder
Vx	0.00	0.00	0.00	0.00	85.9	0.00	0.00
Px	100.0	0.00	0.00	0.00	0.00	0.00	0.00
NPx	0.00	99.9	0.00	0.00	0.00	0.00	0.00
Cx	0.00	0.00	99.9	0.00	0.00	0.00	0.00
Cigx	0.00	0.00	0.00	99.1	0.21	0.00	0.00
SBx	0.00	0.00	0.00	0.00	0.00	99.9	0.00
DBx	0.00	0.00	0.00	0.00	0.00	0.00	100.0
Vy	0.00	0.00	0.00	0.00	99.9	0.00	0.00
Ру	95.8	0.00	0.00	0.00	0.00	0.00	0.00
NPy	0.00	49.8	0.00	0.00	0.00	0.00	0.00
Су	0.00	0.00	99.1	0.00	0.00	0.00	0.00
Cigy	0.00	0.00	0.00	99.1	0.21	0.00	0.00
SBy	0.00	0.00	0.00	0.00	0.00	100.0	0.00
DBy	0.00	0.00	0.00	0.00	0.00	0.00	99.9



Fig. 6. Coomans plot for nail polish vs. varnish classes (NPy sample circled in red to clarify).

classes. This dispersion could be explained through the sample composition and manufacturing procedure of each class. In such a way that nail polish samples are mass-produced following standard and tight manufacturing procedures, usually more homogeneous than those used for collodions and varnishes, both manufactured under heterogeneous conditions. This fact could explain that nail polishes scarcely have differences among sample compositions and appeared as a compact class and collodions and varnishes as more dispersed classes.

Since cigarettes are also commercial and standard samples manufactured under strict conditions, a completely compact group in the same trend as nail polishes was also expected. However, cigarettes formed a compact class with the exception of the sample Cig2. Since cigarettes presented cellulose and nitrocellulose in their composition the further position for Cig2 regarding its class was attributed to a variation of cellulose/nitrocellulose percentage in the powder sample in contrast to the rest of cigarette samples.

Interestingly, paper samples appear perfectly classified and inside a compact and completely separate group (see Fig. 4). Hence, we can conclude that paper samples, despite being Dglucopyranose derivatives, which may act as interferences in this study, were successfully distinguished from any nitrocellulosebased samples. Finally, a closer examination of the 3D plot (Fig. 5) revealed that different compact groups were defined for each type of smokeless gunpowder, single- and double-base gunpowders. Therefore, the possibility to discriminate single-base gunpowders from double-base gunpowders was also possible. Despite triple-base gunpowders samples were projected outside of the single- and double-base smokeless gunpowder group (see Fig. 5), more samples of triple-base gunpowder would be necessary to improve and make representative the already successful discrimination. An insufficient number of triple-base gunpowder samples were analyzed in this work due to their limited availability.

3.2. SIMCA classification

Next, data were also explored through a SIMCA classification. SIMCA classification is a supervised pattern recognition method based on making a PCA model for each class in a defined training set where classification rules are defined by the individual PCA models [24,25]. Unknown samples are then compared to those class modes. For this study, Table 2 showed that 12 of the 14 unknown samples investigated were automatically (by software) recognized by their rightful class models with probabilities higher than 96%. In other words, they were within the mathematical limits on sample-to-model distance and leverage, and thus, they were automatically recognized as members of their corresponding class. Therefore, these results confirmed those found with the PCA training model.

Vx and NPy were the two samples that showed lower automatic mathematical classification to their proper classes than the rest of samples (86% and 50%, respectively). However, both unknown samples did not presented probabilities of being classified in any other classes. Since NPy sample had the lowest probability of correct classification in the Table 2 (50% to belong to nail polish class), a graphical verification was proposed. The Coomans plot (see Fig. 6), which shows the distance from sample to the corresponding model, clearly indicated that NPy belonged to the nail polish class, being far from the rest of the classes. Additionally, even though unknown cigarette samples (Cigx and Cigy) were also classified as varnish class, (probability <1%), the inherent dispersion found for the varnish samples class could explain this fact and subsequently, a large influence on the entire model.

Finally, through the examination of the misclassification table (not shown) the data obtained in the SIMCA classification table were confirmed. All samples were correctly classified into their corresponding groups without the existence of false negative or positive errors, and consequently, sensitivity and selectivity values corresponding to the SIMCA classification were the maximum (100%).

4. Conclusions

The discrimination and classification of non-explosive and explosive nitrocellulose-based samples has been successfully performed by studying their CE-LIF electropherograms together with two multivariate approaches (PCA and SIMCA).

First, the PCA multivariate analysis was suitable for the differentiation between nitrocellulose-based explosive samples (smokeless gunpowders) and other everyday nitrocellulose-based samples (cigarettes, nail polishes and varnishes). Additionally, a clear discrimination of nitrocellulose-based samples from potential interference samples such as those containing cellulose, has been demonstrated.

Subsequently, the exploration of data using the SIMCA classification approach has confirmed the PCA results previously obtained, and also has determined probabilities higher than 96% for the correct classification of 12 from the 14 unknown samples studied into their corresponding group.

In summary, this work has revealed a novel approach to discriminate, by first time, nitrocellulose-based non-explosive and explosive samples, and also from their potential interferences, through the analysis of nitrocellulose fingerprints by CE-LIF-PCA and CE-LIF-SIMCA. The proposed methodology opens a new approach to differentiate intact non-explosive and pre-blast explosive, all nitrocellulose-based samples, using the entire CE-LIF profiles. However, future studies considering the analysis of exploded nitrocellulose-based samples would be highly relevant to investigate the real potential of this approach for the identification of nitrocellulose-based explosives in post-blast residues.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2013. 06.034.

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