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New protocol for the isolation of nitrocellulose from gunpowders: Utility in their identification

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ABSTRACT

In this work, a new approach for the isolation of nitrocellulose from smokeless gunpowders has been developed. A multistep solvent extraction method was needed to purify nitrocellulose contained in gunpowders. For single-base or double-base gunpowders six consecutive solvent extractions were selected: three extractions with methanol (to remove nitroglycerin, 2,4-dinitrotoluene, ethyl-centralite, diphenylamine, and diphenylamine derivatives); one extraction with dichloromethane (to remove colorants and plasticizers of organic nature); one extraction with methanol (to facilitate a final polar extraction); and one extraction with water (to remove ionic components) were necessary at 35 °C. For the triple-base gunpowder studied, eight solvent extractions were needed due to a high concentration of the water-soluble nitroguanidine was present. In addition to the same five initial phases used for the single-base and double-base gunpowders, three water extraction phases at a higher temperature (75 °C instead of 35 °C) were also needed. A final step to solubilize nitrocellulose in methyl ethyl ketone was used to remove inert components (mainly graphite). Nitrocellulose isolated from these propellants was characterized by Fourier-Transformed Infrared Spectroscopy (FTIR spectroscopy). The same FTIR spectra were observed for nitrocelluloses isolated from different types of gunpowders. A comparison of FTIR spectra of nitrocellulose samples of different nitration degree evidenced that the bands regions most affected by this factor were: 3600–3400 $\mathrm{cm^{-1}}$, corresponding to the stretching vibrations of residual hydroxyl groups; 1200–1000 $\mathrm{cm^{-1}}$, attributed to the valence vibrations νCO of the glucopyranose cycle; and 750–690 $\mathrm{cm^{-1}}$, assigned to vibrations of the nitrate group. In both cases, the bands appearing in these regions were more pronounced in the spectra of nitrocellulose samples of low nitration degree.

1. Introduction

Nitrocellulose, discovered in 1846 by Christian Friedrich Schönbein [1], is a nitrated cellulose ester polymer where the different monomer units are joined by β-1,4 bonds. Its chemical formula is $[C_6H_7O_2(OH)_{3-x}(ONO_2)_x]_n$, where x is the number of hydroxyl groups substituted by nitrate groups, also known as degree of substitution (D.S.) [2,3]. The D.S. can be calculated according to Eq. (1) [4]:

$$\text{D.S.} = \frac{3.6 \times \text{nitrogen content (\%)}}{31.13 - \text{nitrogen content (\%)}} \tag{1}$$

When one of the hydroxyl groups is replaced (D.S. = 1), a 6.76% of the monomer of nitrocellulose is nitrogen, while percentages of nitrogen may reach theoretical values of 11.11% or 14.15% for D.S. of 2 and 3, respectively. As an example, Fig. 1 shows the chemical structure of a nitrocellulose with a D.S. of 2.3 and with a nitrogen content of 12.2%. This figure also takes into account the carbons reactivity (C6 > C3 > C2) and the ignorance of the real distribution of nitrate ester along the polymer. For the nitrocellulose shown in Fig. 1 the polymer would contain 50% trinitrated rings, 34% dinitrated rings, 16% mononitrated rings, and, essentially no rings without nitrate esters [2].

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Table 1
List of commercially available products of nitrocellulose (CAS number: 9004-70-0) for laboratory utilization [23–32].

Supplier	Nitrocellulose product	Nitrogen (%, m/v)	Alcohol content
Electron Microscopy Sciences [23]	Collodion 2% in amyl acetate	n.s.	98%
Fluka [24]	Collodion 2% in amyl acetate	n.s.	98%
Fluka [24]	Collodion solution 4–8% in ethanol/diethyl ether	n.s.	n.s.
Fluka [24]	Collodion solution approximately 7% in ethanol/diethyl ether	n.s.	n.s. (total impurities: approximately 5% castor oil)
Electron Microscopy Sciences [25]	Collodion 5% solution	n.s.	25% alcohol and 75% diethyl ether
J.T. Baker [25]	Collodion, U.S.P. grade	>5	n.s.
J.T. Baker [25]	Collodion, U.S.P. grade	>5.25	n.s.
EMD Chemicals [26]	Collodion	>5	25% ethanol and 70% ether
Spectrum Chemical MFG Corp. [27]	Collodion, U.S.P. grade	5	22.0–26.0%
Panreac [28]	Collodion solution 4–8% in ethanol/diethyl ether	n.s.	n.s.
Prolabo S.A. [29]	Collodion flexible in diethyl ether	n.s.	n.s.
Fisher Scientific [30]	Collodion flexible methylated	n.s.	n.s.
SP^2 Scientific Polymer Products, Inc. [31]	Cellulose nitrate	10.9–11.2	n.s.
SP^2 Scientific Polymer Products, Inc. [31]	Cellulose nitrate	11.8–12.2	n.s.
Island Pyrochemical Industries [32][a]	Nitrocellulose	12.5–12.7	Wetted with 28% ethyl alcohol (denaturated with 2% of ethyl acetate)

The characteristics specified are given by suppliers solely with informational purposes. n.s.: Not specified. D.S.: Degree of substitution (mol nitrogen per mol cellulose).

[a] Only available for the international military community.

The applications of nitrocellulose depend on its nitrogen content. Low-nitrogen content nitrocellulose (less than 12%) is used in varnishes, clothes, films, etc. whereas high-nitrogen content nitrocellulose (more than 12%) is used in the manufacture of explosive materials [5,6].

Nitrocellulose can take part of strong explosives, such as dynamites, or propellants such as smokeless gunpowders. Nitrocellulose-based gunpowders are grouped in three different types: single-base gunpowders (containing mainly nitrocellulose), double-base gunpowders (composed of nitrocellulose and other explosive substances like nitroglycerin or dinitrotoluene), and triple-base gunpowders (consisting of nitrocellulose, nitroglycerin or dinitroethylenglycol, and a third energetic material: nitroguanidine) [7–10]. These gunpowders also contain stabilizers (diphenylamine, ethyl-centralite, and methyl centralite), plasticizers, and inert material (mainly graphite), among other components.

In the last decades, an increasing interest on the development of new energetic materials, avoiding the technological and chemical difficulties inherent in their production has been revealed [11]. In addition, the need for unequivocal identification of the new explosives [12], the proper storage of them to avoid risks of accidents, and the employment of some of these materials in terrorist acts have promoted the development of reliable analytical methods to accomplish the analysis of explosives.

While numerous publications on the analysis of other components of nitrocellulose-based gunpowders, i.e. nitroglycerin, dinitrotoluene, diphenylamine, nitroguanidine etc., may be found in the literature [13–16], there are few studies on the analytical determination of intact nitrocellulose. This may be due to several factors: (i) the high chemical and structural complexity of this polymer, (ii) its high molar mass, and (iii) the inherent complexity of nitrocellulose based explosives. In fact, in the “Workshop on Explosives Trace Analysis Methods” that was held in Kent (United Kingdom) in 1999 [17], it was highlighted the lack of analytical methods for nitrocellulose quantitation as well as for quality control of explosives and propellants containing it.

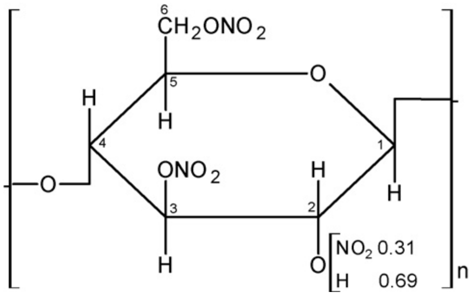

Fig. 1. Chemical structure of a nitrocellulose with a nitrogen content of 12.2% (D.S. of 2.31) [2].

In the few works studying nitrocellulose in gunpowders, the first step consists of the separation of this compound from the sample matrix by means of a solvent extraction procedure with dichloromethane [18,19], followed by its precipitation in water [19]. However, after the solvent extraction and precipitation it was not possible to quantitatively isolate the nitrocellulose, since a colloidal precipitate, of difficult manipulation, was obtained. Other works focused on removing nitrocellulose prior to the determination of other components present in the gunpowders, by precipitation in water [20] or water containing 2% of calcium chloride, before solubilization of nitrocellulose with acetone [21]. Although these methods are fast, they lead to an incomplete isolation of nitrocellulose, mainly due to the existence of coprecipitates.

On the other hand, the determination of hydrolyzed nitrocellulose in soil, based on the elimination of co-contaminants by means of the extraction with water and ethanol, followed by the acetone extraction of nitrocellulose, has been recently described by MacMillan et al. [22]. In this work a basic hydrolysis of nitrocellulose was carried out previous to the ion-chromatographic determination of nitrates and nitrites formed in this process.

When studying nitrocellulose from explosive materials another drawback is the lack of commercial standards or reference materials with a comparable degree of nitration to that of explosives (>12%). Table 1 shows the standards commercially available nowadays. In spite of the very few standards showing its nitrogen content, it can be noticed that most of them have less than 12% nitrogen, being not appropriate to be used as reference materials for explosives.

As consequence, the aim of this work has been to develop a new protocol for the effective isolation of nitrocellulose from propellants, specifically smokeless gunpowders of single-, double-, and triple-base, for its use in the identification and characterization of these materials.

2. Experimental

2.1. Instrumentation

A fully equipped Agilent liquid chromatography series 1100 (Agilent Technologies, Palo Alto, CA) with diode-array (DAD) and

Table 2
Smokeless gupowders studied in this work. The composition, the nitrocellulose content (%, m/m), and the nitrogen content (%, m/m) of the nitrocellulose were obtained from the official label of this ammunition [19].

Gunpowders	Composition		Name	Nitrocellulose content (%, m/m)	Nitrogen content (%, m/m) in nitrocellulose[a]
	Major components (explosives)	Minor components (<5%)			
Single-base	Nitrocelullose	Diphenylamine and potassium sulfate	A	100	13.2
	Nitrocelullose	Diphenylamine, potassium sulfate, superficial agents, and graphite	B	98.3	13.1
	Nitrocelullose	Diphenylamine, centralite, graphite, and flame retardant	C	95.7	13.0
	Nitrocelullose	Ethyl-centralite, diphenylamine, dibutyl phthalate, sodium oxalate, potassium sulfate, graphite, and residual solvent	D	63.7	11.8
Double-base	Nitrocelullose, nitroglycerin	Dibutyl phthalate, diphenylamine, sodium sulphate, potassium nitrate, dinitrotoluene, graphite, and residual solvent	E	82.0	>13.0
	Nitrocelullose, nitroglycerin	Dibutyl phthalate, diphenylamine, sodium sulphate, potassium nitrate, dinitrotoluene, calcium carbonate, graphite, and residual solvent	F	82.0	>13.0
	Nitrocelullose, nitroglycerin	Potassium nitrate, ethyl-centralite, and graphite	G	57.7	13.2
	Nitrocelullose, dinitrotoluene	Diphenylamine, graphite and solvent	H	89.3	12.0
	Nitrocelullose, dinitrotoluene	Diphenylamine, graphite, potassium sulfate, and dibutyl phthalate	I	87.0	13.1
Triple-base	Nitrocelullose, nitroglycerin, nitroguanidine	Centralite and potassium sulfate	J	19.0	Unknown

[a] Determined by a digestion/titration method based on a potentiometric titration of the nitric nitrogen obtained from isolated nitrocellulose with concentrated sulfuric acid at low temperature [19].

mass spectrometry (MS) detectors was employed. The LC/MS software ChemStation® (Agilent Technologies, Palo Alto, CA) was used for instrument control and data analysis. The separation was performed with a ProntoSIL column (C18, 250 mm × 6 mm, 5 μm particle size) from Scharlau (Barcelona, Spain). The column temperature was set at 40 °C. Mobile phases were water (mobile phase A) and methanol (mobile phase B). A four-step gradient, routinely used in the Criminalistic Service Laboratory of the Guardia Civil (Madrid, Spain), was employed at a flow-rate of 1 mL min^{-1}. The different gradient steps were: from 25 to 40% B in 10 min, from 40 to 55% B in 10 min, from 55 to 70% B in 10 min, and from 70 to 95% B in 7.5 min. Sample injection volume was 5 μL. DAD detection at 210 ± 2 nm (reference at 450 ± 40 nm) and at 230 ± 2 nm (reference at 550 ± 50 nm) was used. MS detection was performed using APCI ionization and a quadrupole analyzer. The nebulizer and drying gas (N_2) conditions were: 40 psi and 9 L min^{-1} at 350 °C and a potential of 3000 V.

FTIR sample analyses were performed using a Thermo Nicolet Nexus 670 FTIR instrument, equipped with a DGTS KBr detector and XT-KBr beam splitter (Thermo Nicolet Analytical Instruments, Madison, WI). An Omnic® version 6.0 software of Thermo Nicolet was used for instrument control and spectra acquisition. An Avatar Single-Bounce Smart accessory for attenuated total reflectance (ATR) with a ZnSe crystal was used. FTIR analysis with an ATR accessory was used for obtaining the spectra of the isolated nitrocellulose and the gunpowder solutions in the mid-infrared region (wave numbers from 4000 to 650 cm^{-1}). An air background was collected before every sample and subtracted from the sample spectrum prior to the analysis. A total of 32 scans at 4 cm^{-1} resolution were registered for each spectrum.

A Mettler-Toledo (Spain) Delta Rage Electronic Analytical SemiMicro Balance (model AX205), with a readability of 0.1 mg, an ultrasonic bath (Ultrasons-H de J.P. Selecta, Barcelona, Spain), and a centrifuge (Hettich EBA 20 Centrifuge, Tuttlingen, Germany) were used.

2.2. Reagents and samples

Methanol (UV-IR-HPLC-HPLC isocratic), and sodium hydroxide pellets (PA-ACS-ISO) were purchased from Panreac (Barcelona, Spain). Different collodion (pyroxylin) solutions were used: collodion solution in ethanol/diethylether 4–8% QP, from Panreac (Barcelona, Spain); collodion solution 4–8% in ethanol/diethylether, from Fluka (Buchs SG, Switzerland); collodion flexible in diethylether, from Prolabo S.A. (Barcelona, Spain); and collodion flexible methylated, from Fisher Scientific (Madrid, Spain). Dichloromethane (HPLC grade) was supplied from Lab-Scan (Stillorgan, Dublin, Ireland). Methyl ethyl ketone (ACS) and methyl isobutyl ketone (ACS) were obtained from Scharlau (Barcelona, Spain). Acetone (GC grade) was purchased from Merck (Darmstadt, Germany). Different standards were used: ethyl-centralite (99% purity), from Sigma–Aldrich Química, S.A. (Madrid, Spain), diphenylamine (ACS), from Fluka (Buchs SG, Switzerland), and nitroguanidine (100 μg mL^{-1} in methanol), nitroglycerin (1000 μg mL^{-1} in methanol), and 2,4-dinitrotoluene (1000 μg mL^{-1} in acetonitrile), all of them supplied from Restek Corporation (Bellefonte PA, USA). Ultrapure water was produced with a Millipore Milli-Q gradient A10 water purification system (Millipore, Bedford, MA, USA).

The gunpowder samples were kindly gifted by the *Acuartelamiento San Juan del Viso* (Madrid, Spain). Ten different smokeless gunpowders were studied: 4 of single-base, 5 of double-base, and 1 of triple-base (see further details in Table 2). All the studied gunpowders were used in their original formats, with the exception of the triple-base gunpowder that was provided ground.

2.3. Sample preparation

Nitrocellulose isolation was carried out starting from about 0.03 g of gunpowder, which were weighed and introduced into glass centrifuge tubes with screw-on cap. Then, different volumes of methanol (3 mL), dichloromethane (3 mL), and water (3 or 8 mL) were added to extract other components different from nitrocellulose. The extraction process was assisted with an ultrasonic bath, for a certain time and at a given temperature (both variables were studied). Finally, the nitrocellulose was dissolved in 5 mL of methyl ethyl ketone, using the ultrasonic bath during 30 min at 35 °C. The separation of the two existing phases (solid–liquid) was performed by centrifugation at 3450 × *g* for 5 min.

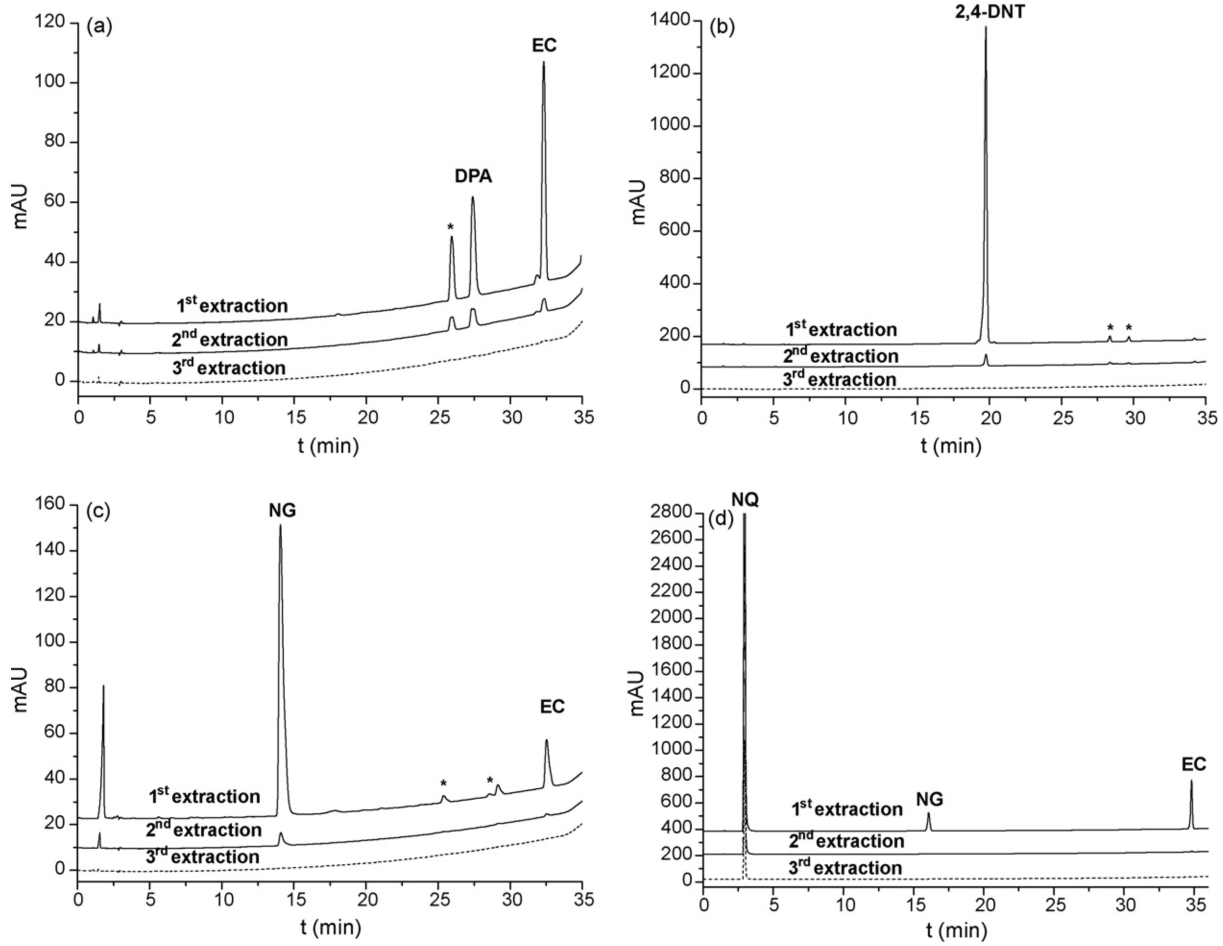

Fig. 2. HPLC-DAD chromatograms of the three first methanol extractions for the single-base gunpowder C (a), the double-base gunpowders H (b) and G (c), and triple-base gunpowder J (d). The extraction was performed with 3 mL of methanol at 45 °C, with sonication for 10 min. The supernatant obtained after centrifugation (3450 × g for 5 min) was injected into a HPLC-DAD-MS system. HPLC conditions: ProntoSIL column (C18, 250 mm × 6 mm, 5 μm particle size); mobile phase A: water and mobile phase B: methanol; gradient elution: from 25 to 40% B in 10 min, from 40 to 55% B in 10 min, from 55 to 70% B in 10 min, and from 70 to 95% B in 7.5 min; flow-rate, 1 mL min^{-1}; column temperature, 40 °C. DAD detection: 230 ± 2 nm with reference at 550 ± 50 nm. MS detection: nebulizer and drying gas (N_2) at 40 psi and 9 L min^{-1}, 350 °C, and 3000 V. Abbreviations: DPA (diphenylamine), EC (ethyl-centralite), NG (nitroglycerin), NQ (nitroguanidine), 2,4-DNT (2,4-dinitrotoluene). (*) Unknown peaks.

HPLC-MS analyses of the different extracts obtained during the procedure for nitrocellulose isolation from gunpowder samples were carried out in order to assure the quantitative extraction of the different components of these samples. In addition, a drop of the nitrocellulose solution in methyl ethyl ketone was left for complete solvent evaporation prior to the characterization of nitrocellulose by FTIR spectroscopy. Once the solvent was evaporated, the analysis was repeated until the solvent signal disappeared completely.

2.4. Data treatment

The limits of detection (LODs) obtained by HPLC for the different components of the studied gunpowders were calculated as the minimum analyte concentration detectable with DAD detection at 230 ± 2 nm (reference at 550 ± 50 nm), since, at this wavelength, less change of the baseline was observed in comparison with 210 ± 2 nm (reference at 450 ± 40 nm). With this aim, different standard solutions in methanol containing both nitroguanidine and ethyl-centralite at decreasing concentrations close to the LOD of these compounds (5.00, 3.00, 1.00, 0.25, and 0.10 μg mL^{-1}) were injected in the HPLC-DAD-MS system. The same procedure was followed with 2,4-dinitrotoluene and nitroglycerin mixtures, which were injected at the low and decreasing concentrations of 5.00, 2.50, 1.00, 0.50, 0.25 and 0.10 μg mL^{-1} in the chromatographic system. Taking into account the lowest detectable concentrations (S/N = 3), the LODs determined were: 0.10 μg mL^{-1} for nitroguanidine, 0.25 μg mL^{-1} for ethyl-centralite, 1.00 μg mL^{-1} for diphenylamine, 0.50 μg mL^{-1} for 2,4-dinitrotoluene, and 1.00 μg mL^{-1} for nitroglycerin.

HPLC chromatograms and FTIR spectra were composed in Origin® version 7.0 software.

3. Results and discussion

3.1. Optimization of a method for the isolation of the nitrocellulose contained in gunpowders

In this work, a multistep solvent extraction process was selected to isolate nitrocellulose from gunpowders. This is one of the simplest and easiest procedures to be applied to this kind of sample in routine laboratories such as Forensic Chemistry laboratories, owing to their explosive nature.

Different solvents that do not solubilize significantly the nitrocellulose contained in the gunpowders were selected: methanol, dichloromethane, and water [2]. The number of extractive phases, the order of the solvents employed, and the volume of solvent needed to ensure the isolation of nitrocellulose, by removing the other components initially present in the gunpowders, were carefully studied. To be sure of the minimum number of phases necessary to clean nitrocellulose from the other components, the extracted phases were analyzed by HPLC-MS, as commented in Section 2.

Methanol was first used since this solvent penetrated into the polymeric structure of nitrocellulose and facilitates the extraction of the polar components of the studied propellants: diphenylamine or its derivatives (e.g. N-nitrosodiphenylamine, 2-nitrodiphenylamine, and 4-nitrodiphenylamine), centralite (ethyl- or methyl-centralite), dinitrotoluene, and nitroglycerin. Fig. 2 shows, as an example, the chromatograms of the extracts obtained after the first, second, and third treatment with methanol of one single-base gunpowder (sample C), two double-base gunpowders (sample H, containing nitrocellulose and dinitrotoluene, and sample G, containing nitrocellulose and nitroglycerin), and one triple-base gunpowder (sample J). As seen in Fig. 2a–c, for single-base and double-base gunpowders, 3 consecutive methanol extractions (3 mL, sonication for 10 min at 35 °C) were needed to remove diphenylamine or its derivatives, ethyl-centralite, nitroglycerin, and 2,4-dinitrotoluene, to concentrations lower than their LODs (see them in Section 2.4).

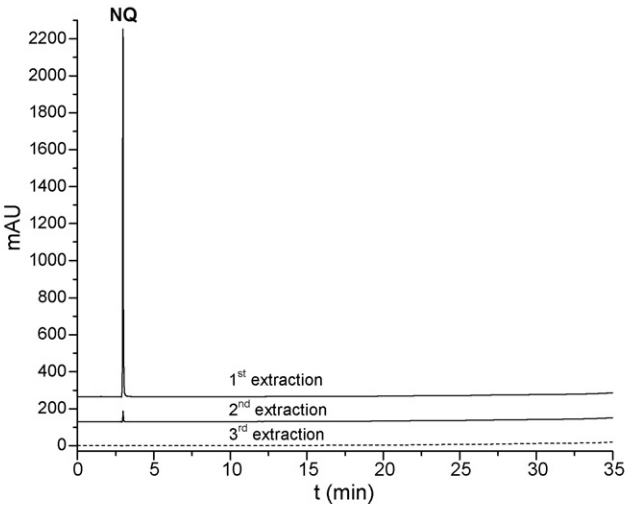

Fig. 3. HPLC-DAD chromatograms obtained for the triple-base gunpowder (sample J) extracted with water. Water extractions were performed with 8 mL of water at 75 °C for 15 min with sonication. Experimental conditions as in Fig. 2. Abbreviations: NQ (nitroguanidine).

After the three extractions with methanol in single- and double-base gunpowders an extraction step with dichloromethane (3 mL), which was employed to extract the organic compounds of gunpowders (colorants or plasticizers), was applied. Then, another extraction step with methanol (in the same experimental conditions), was used in order to facilitate a final extraction step with water (3 mL), necessary to accomplish the solubilization of those ionic compounds (mainly sulfate, nitrate, and oxalate salts), which are only partially soluble in methanol. All of these extractions were carried out by sonication at 35 °C (since dichloromethane has a boiling point at 40 °C) during 10 min. No chromatographic peaks corresponding to the different components accompanying the nitrocellulose in these gunpowders were observed in the extracts analyzed by HPLC-MS.

As seen in Fig. 2d, nitroguanidine present in triple-base gunpowder could not be extracted with the three methanol extractions, although nitroglycerin and ethyl-centralite concentrations in the third methanol extract were lower than 1.00 μg mL^{-1} and

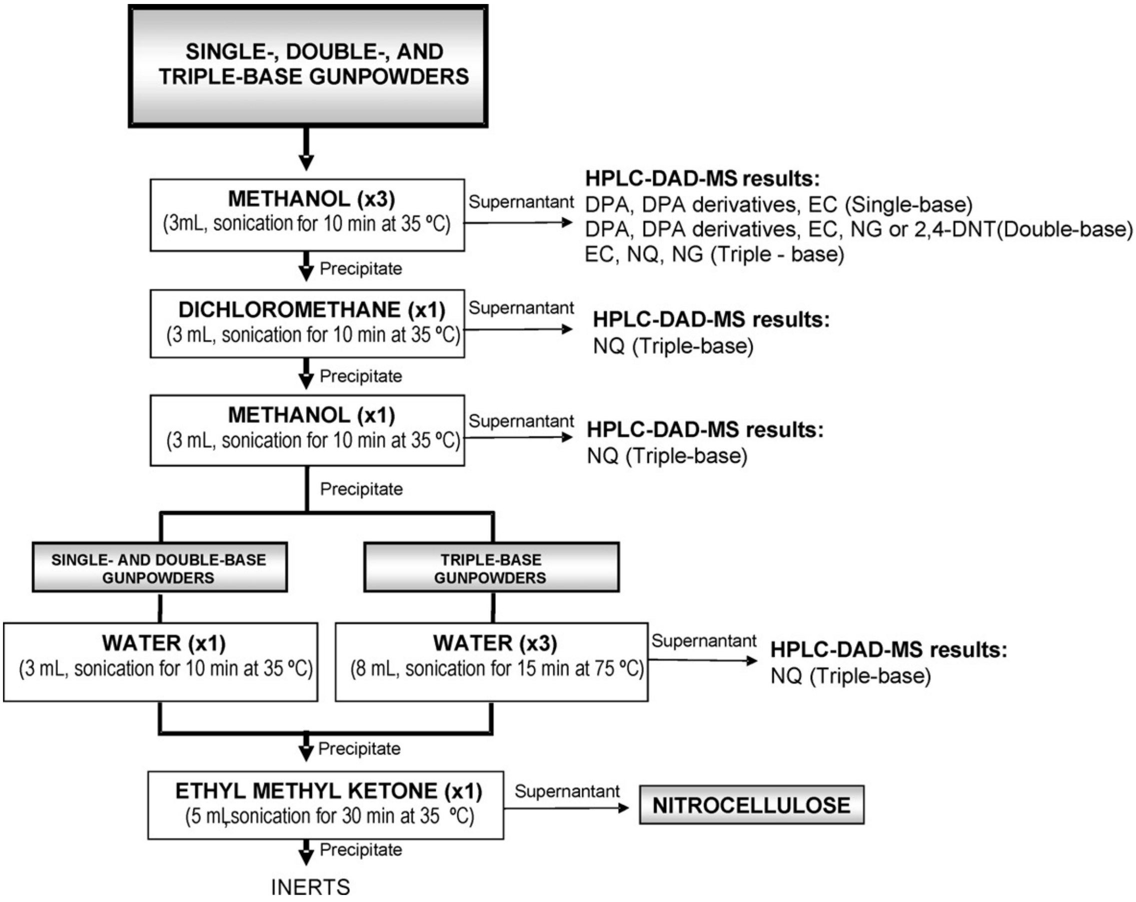

Fig. 4. Diagram indicating the different steps of the optimized protocol to isolate nitrocellulose from single-, double-, and triple-base gunpowders.

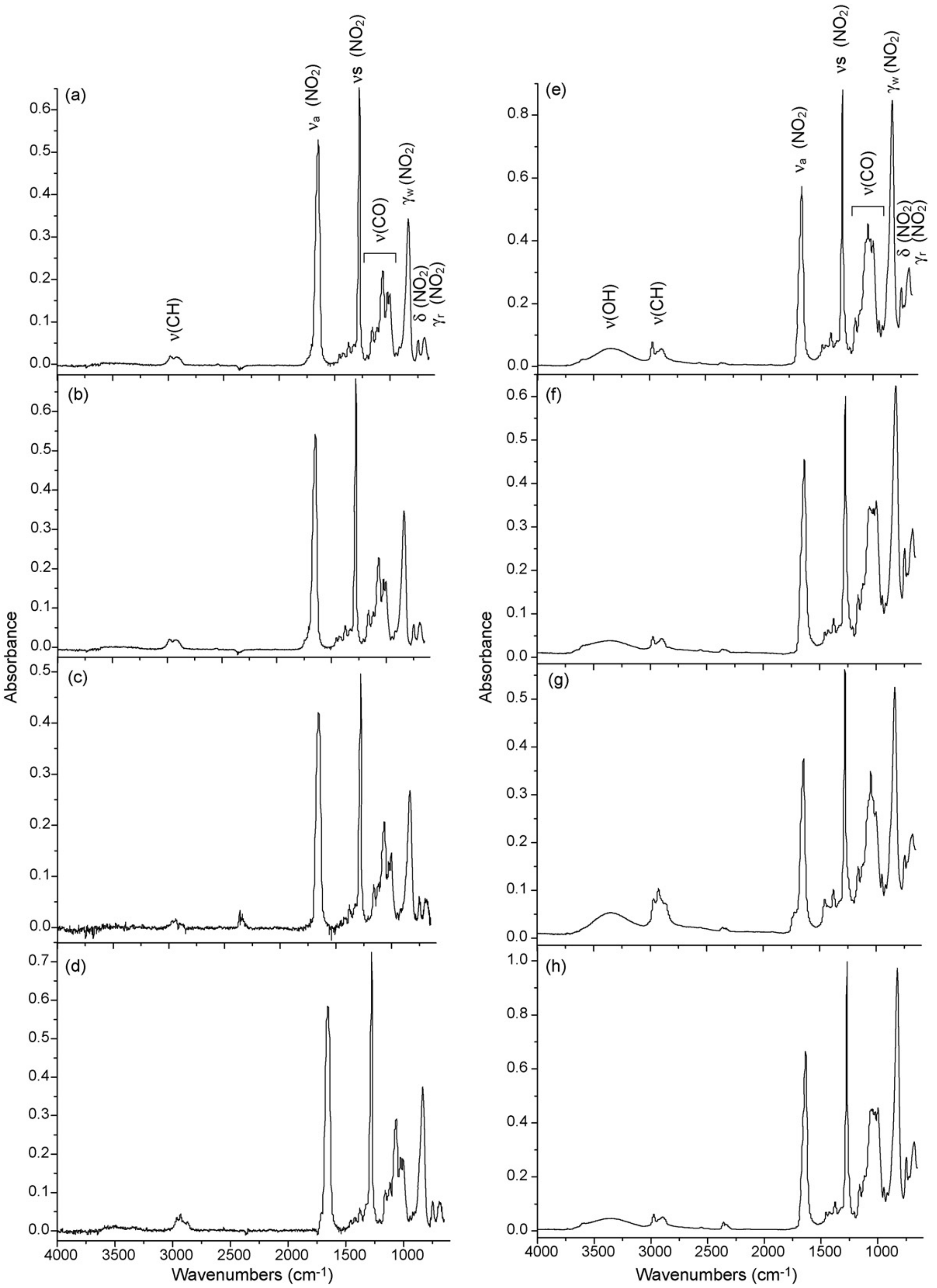

Fig. 5. FTIR spectra obtained for the nitrocellulose isolated from four different gunpowders (a–d), compared with those corresponding to four different nitrocellulose standards, collodion products (e–h). Isolated nitrocellulose from single-base gunpowder D (a), double-base gunpowders H (b) and G (c), and triple-base gunpowder J (d); collodion solution 4–8% in ethanol/diethylether, Fluka (e); collodion flexible in diethylether, Prolabo S.A. (f); collodion flexible methylated, Fisher Scientific (g); and collodion solution 4% in ethanol/diethylether, Panreac (h). A total of 32 scans at 4 cm^{-1} resolution were registered for each spectrum. Band assignments are shown above appropriate wave numbers. Notation: ν, stretching; δ, scissoring; γ_r, rock; γ_w, wag; subscript s, symmetric; subscript a, antisymmetric.

0.25 μg mL^{-1}, respectively. It should be noted that the triple-base gunpowder studied consists of a mixture of three explosive compounds, with nitroguanidine the major one (55% of the gunpowder composition). Based on the high solubility of nitroguanidine in water and alkalis [33], the efficiency in nitroguanidine extraction with water and that obtained with a sodium hydroxide solution in water (0.5%, m/v) was compared. The analysis of the HPLC-MS chromatograms obtained for these extracts (results not shown), evidenced that the sodium hydroxide solution produced the partial alkaline hydrolysis of nitrocellulose, as it has been previously reported in the bibliography [6]. For this reason, water was selected as the best solvent for nitroguanidine extraction from nitrocellulose. Then, the influence of other water extraction variables such as the volume of water added, the sonication times, and the temperature, were optimized. According to the results obtained (not shown), the most important parameter in nitroguanidine extraction was the temperature, since an increment from 35 to 75 °C led to a fast decrease in the chromatographic peak obtained for this compound, which is in agreement with the increase in solubility of nitroguanidine in water with temperature [34]. Then, three extractions with water at 75 °C during 15 min were enough to remove nitroguanidine from the triple-base gunpowder studied to concentrations below 0.10 μg mL^{-1} (Fig. 3).

Finally, with the aim to remove inert compounds (mainly graphite) from the remaining solution of nitrocellulose, different appropriate solvents for nitrocellulose [2] were tested: acetone, methyl isobutyl ketone, methyl ethyl ketone, a methyl ethyl ketone:methyl isobutyl ketone mixture (1:1, v/v), and a acetone:dichloroethanol mixture (1:1, v/v). Among them, methyl ethyl ketone (5 mL) was chosen due to its capability to dissolve nitrocellulose more rapidly. The temperature and time selected for a fast dissolution of nitrocellulose by sonication were 35 °C and 30 min, respectively. Inert compounds remained insoluble with this solvent and were separated by centrifugation.

As a consequence of the above-mentioned experiments, the different steps needed to purify nitrocellulose, depending on the type of gunpowder studied, are compiled in Fig. 4. For single- and double-base gunpowders, six consecutive solvent extractions (3 mL, sonication for 10 min at 35 °C) were enough: three extractions with methanol; one extraction with dichloromethane; one extraction with methanol; and one extraction with water. For triple-base gunpowders eight consecutive solvent extraction were needed: the five initial steps used for the single-base and double-base gunpowders, and then, three water extraction phases (8 mL, sonication for 15 min at 75 °C).

Since the protocol developed in this work requires the previous knowledge of which type of propellant is going to be analyzed, a novel and fast way to discriminate between single-/double- and triple-base gunpowders is proposed in this work. Briefly, methyl ethyl ketone is added to the propellant, solubilizing all its components except nitroguanidine (partially insoluble in this solvent) and inerts (i.e., graphite). Since nitroguanidine is characteristic of the formulation of triple-base gunpowders, its precipitation allow the identification of this type of propellants. In addition, nitroguanidine may be easily confirmed in the precipitate by FTIR spectroscopy.

By means of this protocol, two goals can be achieved: (i) the differentiation among types of propellants by means of the identification of the components accompanying the nitrocellulose in the gunpowders and (ii) the purification of nitrocellulose, which is ready to be used as standard or for the quantitation of its nitrogen content.

It is important to note that although the optimized multistep procedure require about 2 h in practice, a very important reduction in time (about 35 times) with respect to the method routinely used to isolate nitrocellulose in gunpowders [19] (based on a dichloromethane extraction, nitrocellulose solubilization in acetone and precipitation in water, filtration, washing of the precipitate with water and methanol, and drying), has been achieved. Furthermore, to perform this new protocol, no special laboratory conditions, equipment nor personal training are necessary.

3.2. Characterization by FTIR spectroscopy of nitrocellulose isolated from gunpowders

The optimized method proposed in this work allows isolating nitrocellulose contained in explosives. In order to test the efficiency in the nitrocellulose isolation procedure, a study by means of FTIR spectroscopy was performed. In Fig. 5 the FTIR spectra of nitrocellulose isolated from single-, double-, and triple-base gunpowders are compared with the spectra obtained for different collodion solutions. Interestingly, the spectra obtained for the different gunpowder samples studied in this work are practically identical, which confirms the quality of the new optimized protocol to isolate nitrocellulose from gunpowders. Regarding to the band assignment, in the region of high frequencies of the spectra, only alkane CH stretching absorptions (just below 3000 cm^{-1}) from the carbons of the glucose structure, are found. In contrast, the right half of the spectrum, below 1700 m^{-1}, contains many peaks of varying intensities. Three intense bands due to the different vibrations of the nitrate group were observed at around 1660 cm^{-1} (antisymmetric NO_2 stretching), 1280 cm^{-1} (symmetric NO_2 stretching), and 840 cm^{-1} (the valence NO stretching). In the region of 1200–950 cm^{-1} there are few peaks with medium intensity, corresponding to the different vibrations of the CO group [35].

Direct comparison between the two groups of spectra (nitrocellulose isolated from gunpowders and collodion samples) allowed us to observe differences in some FTIR bands, which may be attributed to the different nitration degree of these samples. As expected, the band corresponding to residual hydroxyl groups of nitrocellulose (3600–3400 cm^{-1}), practically negligible in the nitrocellulose from gunpowders, is much more clear for collodion samples, characterized for a small nitration degree. According to Kovalenko et al. [35], the contour of this band depends on the nitration conditions even for nitrocellulose with the same degree of substitution. There are also clear differences between both groups of spectra in the regions of 1200–1000 cm^{-1} (attributed to the valence vibrations νCO of the glucopyranose cycle) and 750–690 cm^{-1}, assigned to vibrations of the nitrate group. The bands appearing in these regions were more pronounced in the spectra of collodion samples than in those corresponding to the nitrocellulose isolated from gunpowder samples.

4. Conclusions

A new protocol to isolate nitrocellulose from gunpowders has been developed in this work. A multistep protocol using an extraction with methanol, diclorometháne, and water, followed by a solubilization of nitrocellulose in methyl ethyl ketone has allowed, first, removing and unequivocally identifying (according to the monitorization performed by HPLC-DAD-MS) the different components present in nitrocellulose base gunpowders of single-, double-, and triple-base. Besides, with a maximum number of seven or nine extraction steps, nitrocellulose contained in these gunpowders is isolated, being the remaining components below the μg mL^{-1} level.

FTIR analysis of the samples reflected the validity of the isolation process optimized in this work, given the similarity of spectra corresponding to the nitrocellulose isolated from different types of gunpowders. A comparison of FTIR spectra of the isolated nitrocellulose (of high nitration degree) with those corresponding to nitrocellulose of low nitration degree (collodion samples) evidenced the band regions most affected by this factor: 3600–3400 cm^{-1}, corresponding to the stretching vibrations of residual hydroxyl groups; 1200–1000 cm^{-1}, attributed to the valence vibrations νCO of the glucopyranose cycle, and 750–690 cm^{-1}, assigned to vibrations of the nitrate group. All these bands were more pronounced for the low nitrated nitrocellulose samples.

Although this multistep protocol require about 2 h, it is much faster than the method currently used by the forensic laboratories to isolate nitrocellulose, which requires about three days. In addition, the solvent extraction method developed in this work is cheap and easy to be used in routine laboratories of forensic chemistry.

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