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# **CHEMICAL CLASSIFICATION OF EXPLOSIVES**

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## **KEYWORDS**

Classification of explosives; chemical classification; individual explosive molecules; oxidizer-fuel explosive mixtures; analytical chemical determination

## **ABSTRACT**

This work comprehensively reviews some fundamental concepts about explosives and their two commonly used classifications based on either their velocity of detonation or their application. These classifications are highly useful in the military/legal field, but completely useless for the chemical determination of explosives. Because of this reason, a classification of explosives based on their chemical composition is comprehensively revised, discussed and updated. This classification seeks to merge those dispersed chemical classifications of explosives found in literature into a unique general classification, which might be useful for every researcher dealing with the analytical chemical identification of explosives. In the knowledge of the chemical composition of explosives, the most adequate analytical techniques to determine them are finally discussed.

## **Chemical explosives and explosions**

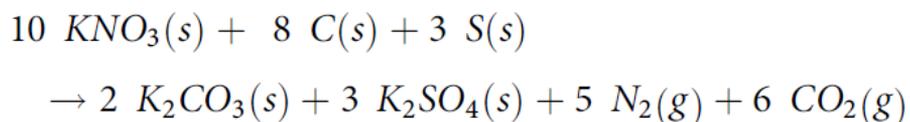
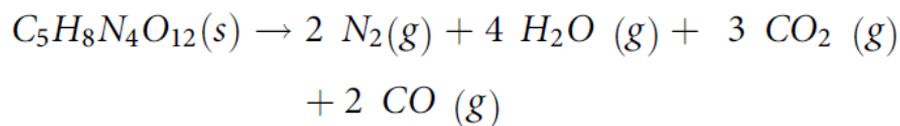
An explosive may be simply defined as a substance that is capable of producing an explosion, which means that is capable of producing a large volume of expanding gas in an extremely brief period.<sup>[1-3]</sup>

When talking about explosives and explosions, the term explosion usually refers to chemical detonations, i.e., explosions produced as a consequence of a chemical reaction in which the chemical energy of a substance, or mixture of substances, is rapidly released causing a sudden expansion of the air (expansive shock wave). The velocity at which the shock wave front travels through the detonating explosive is called velocity of detonation.<sup>[1-9]</sup> When the velocity of detonation is faster than the speed of sound, a detonation occurs regardless of whether the explosive is confined or not. On the contrary, a deflagration occurs when the velocity of detonation is lower than the speed of sound, being necessary the confinement of the explosive to ultimately produce an explosion.<sup>[1-9]</sup>

Despite the large number of ultra-fast chemical reactions that may ultimately cause an explosion, most of them can be classified in two main groups: unimolecular decomposition reactions and multi-molecular redox (reduction-oxidation) reactions.<sup>[9-13]</sup> As main requirement, the reaction has to proceed fast enough to generate an expansive shock wave, either because the velocity of reaction is supersonic, or because the generation/accumulation of gas products from a subsonic deflagration is faster than their release when inside a container.<sup>[1-9]</sup>

In this respect, an explosive can be either a pure individual substance or a mixture of substances depending on the type of chemical reaction that produces the explosion.<sup>[1-11]</sup> An individual compound is required for unimolecular decomposition reactions, while two compounds (at least) are required for multi-molecular redox reactions. For instance, the former case is exemplified, below, by PETN decomposition<sup>[12]</sup> while the latter is explained through the redox reaction of black powder.<sup>[8]</sup>

Although the precise chemical reactions occurring during detonations are notably complex (as later discussed), simplified equations are provided below to show chemical transformations of these explosives.



As observed in both reactions, a solid compound (or mixture of solid compounds) transforms into a large number of gaseous molecules (11 moles in both cases).

Regarding those explosives whose detonation is based on unimolecular decomposition reactions, they necessarily have to be molecules big enough to decompose into smaller molecules. In this respect, nitromethane, (which has 61 u of molecular weight), is one of the smallest molecules that may suffer an explosive decomposition; and nitromethane is liquid (at atmospheric pressure). Thus, the state of the matter (at atmospheric pressure) of any other explosive molecule that is bigger than nitromethane will be still liquid

Table 1. Velocities of detonation of some explosives. The highest value found in literature for each explosive is provided, since the velocity of detonation is affected by some other factors besides the chemical composition such as the particle size or the density of the explosive.<sup>[2-6,15-20]</sup>

Explosive	RD	PET	TNT	TATP	HMT	ANF	Dyna	Flash	Black
	X	N			D	O	mite	powder	powder
Velocity of	87	840	690	530	510	420	3800	1000	400
detonation/deflagratio	00	0	0	0	0	0			
n (m/s)									

(like nitro-ethane or nitroglycerin (NG)) or solid (most explosives like TNT, RDX, PETN, TATP, HMTD, etc.).<sup>[1-9]</sup>

On the contrary, for those explosive mixtures, whose detonation is caused by the redox reaction between an oxidizer and a fuel, there exists a wider variety of oxidizer-fuel combinations, in different states of matter each.<sup>[2-8]</sup> Most of these explosives are also solid due to the most common oxidizers, which are solid inorganic oxidizing salts (mainly nitrates, chlorates and perchlorates):

- Solid oxidizing salt – Solid fuel. Those explosive mixtures in which both oxidizer and fuel are solid substances (such as black powder).
- Solid oxidizing salt – Liquid fuel. Those explosives in which a solid oxidizing salt is mixed with a liquid fuel (such as ANFO).

However, liquid/gas oxidizing agents (such as nitric acid or oxygen) might be also used to produce explosives.<sup>[3-5]</sup>

- Nitric acid – Solid/liquid fuel. Those explosives in which nitric acid is mixed with a solid/liquid fuel (such as nitric acid-nitrobenzene).
- Oxygen Gas – Solid fuel. Those explosive mixtures in which oxygen is mixed with a solid fuel dispersed into a dust cloud (such as flour dust suspended in the air). Such explosions are known as dust explosions.
- Oxygen Gas – Liquid fuel. Those explosive mixtures in which oxygen is mixed with a liquid fuel (such as hydrazine-oxygen mixture).
- Oxygen Gas – Gas fuel. Those explosive mixtures in which both oxidizer and fuel are gas substances (such as hydrogen-oxygen mixture).

Due to the complicate manipulation of gas substances, their use in the manufacture of explosives is unusual. In addition, those explosions caused by oxygen-fuel mixtures are typically unexpected or negligent accidents rather than malicious bombings.<sup>[8]</sup> In fact, they are usually produced because of an uncontrolled combustion. The term “combustion” typically refers to the oxidation of a combustible substance with the oxygen present in air by means of a flame.<sup>[9-13]</sup> Nevertheless, depending on the velocity of detonation and confinement, the transition from deflagration (flame) to detonation (explosion) may occur.<sup>[12]</sup> For instance, a butane gas cylinder maliciously prepared to explode can provoke an explosion, which is chemically based on a rapid combustion of butane.

Nevertheless, the individual components are not explosives on their own, but only the mixture is properly classified as an explosive. Neither potassium nitrate, sulfur, butane nor hydrogen are explosives alone. The explosives are black powder, the butane-oxygen mixture or the hydrogen-oxygen mixture. In this respect, although oxygen from

air is an always present constant, the chemical reaction that provokes an explosion is so fast that surrounding air has no time to reach and participate in the reaction.<sup>[7]</sup> Thus, a butane gas cylinder is not an explosive but a fuel. Therefore, explosives are those substances whose detonation do not require the presence of air to explode.

### **Current classifications of explosives**

Different criteria may be considered when classifying explosives, thus there exist multiple forms of classification. Perhaps, the classification most usually found in literature is the one based on the velocity of detonation, which has been traditionally used in the military field.<sup>[1-9]</sup> In addition, it is becoming prevalent in the forensic field the classification of explosives based on their source or use/application.<sup>[1-8]</sup>

#### *Based on the velocity of detonation*

The velocity of detonation influences the destructive power of the explosive's deflagration/detonation, in such a way that "detonations traveling at supersonic speeds will be more destructive".<sup>[14]</sup> This classification based on the velocity of detonation of explosives is highly relevant in certain fields such as military, mining industry or building demolition in which knowing the destructive power of explosives associated to their velocity of detonation is mandatory. This is the reason why infinite resources from these influencing and economically gifted fields have been allocated to study the velocity of detonation of explosives in such detail. As an example, Table 1 summarizes the velocities of detonation of some common explosives. For further information regarding the velocity of detonation of pure energetic materials, the reader is referred to Klapötke's encyclopedia.<sup>[15]</sup>

Detonation occurs when velocity of detonation exceeds the speed of sound in the unreacted material.<sup>[2-8]</sup> It should be reminded that the speed of sound in air medium

at room temperature is around 340 m/s.<sup>[4-8]</sup> However, the speed of sound increases when propagated through liquid or solid media because of the higher proximity of atoms/molecules in liquid/solid state (*e.g.*, 1500 m/s in water, 3000 m/s in wood or 6400 m/s in aluminum<sup>[21,22]</sup>). Regarding explosives (normally prepared in powdered forms), the speed of sound in most of them is expected to range from 1000 to 3000 m/s;<sup>[6-8]</sup> noticeably lower than the speed of sound in densely packed aluminum metal. Thus, a tentative velocity of detonation range of 1000–3000 m/s is usually established to discriminate between high and low velocity of detonation explosives.<sup>[2-8]</sup>

- *High energy explosives.* High energy explosives detonate creating a supersonic shock wave that propagates usually exceeding 4000 m/s. Three classes are typically subdivided for high explosives according to their sensitivity to explode: primary, secondary and tertiary explosives.<sup>[1-8,16-19,23-26]</sup>
- *Primary explosives* are extremely sensitive to different weak stimuli (such as heat, spark or friction) by which detonation initiates. In general, primary explosives are not particularly powerful. Because of these properties, they are usually used in little amounts as detonators of secondary high explosives. Some typical primary explosives are mercury fulminate, silver fulminate, lead azide, cuprous acetylide, lead picrate, lead styphnate, diazodinitrophenol, tetrazoles, NG, TATP and HMTD.<sup>[1-4,19,25,26]</sup>
- *Secondary explosives* are practically insensitive to weak stimuli and they usually require the input of a strong shock to detonate. Most secondary explosives are exceptionally powerful (with velocities of detonation that exceed 6000 m/s). Secondary explosives include the most common explosives used in the military field such as RDX, PETN, HMX, TNT, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), tetryl, picric acid, CL-20 and NC.<sup>[1-13,16-20,23-26]</sup>

- *Tertiary explosives* is an extra group, sometimes added in the classification, to include and separate those insensitive explosives widely used for mining and demolition purposes, which have lower velocities of detonation than military secondary explosives. ANFO, ANAI and dynamite compositions are common examples of tertiary explosives.[3,4,11,24,26]

- *Low energy explosives*

Unlike high energy explosives, low energy explosives deflagrate creating a subsonic wave front that does not reach the speed of sound. The explosion that low explosives may produce is a consequence of the overpressure generated inside a container by the accumulation of gas products from deflagration. Because of the progressive production of these gas products during their deflagration, low explosives are mostly used as propellants, either in pyrotechnics, space rockets or ammunition for firearms. Smokeless powder, black powder and flash powder are typical examples of low explosives.[1-13,24-26]

*Based on the source, use or application*

The classification of explosives based on the source, use or application is based on the categorization of explosives according to the easy/complicated, legal/illegal obtaining of each explosive. Such particular interest comes from police, forensic and intelligence investigations, which focus on solving, facing and preventing the criminal use of explosives in terrorist attacks.[6-8] Therefore, depending on how explosives are obtained, explosives may be classified into three different categories: military, commercial and homemade explosives.[2-8]

- *Military explosives*

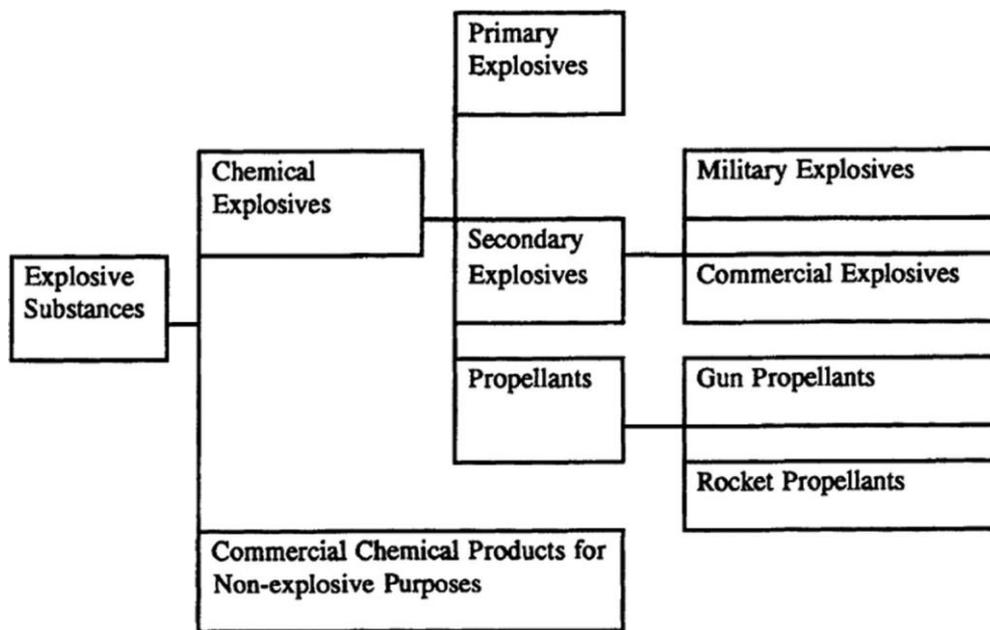
Military explosives are high explosives meeting strict requirements in terms of performance, functionality and safe handle, storage and transport. They have to be powerful while insensitive to weak/medium intense stimuli, requiring the use of detonators to detonate.<sup>[1-4]</sup> Military explosives are generally organic molecules containing only carbon, hydrogen, oxygen and nitrogen atoms. Particularly, oxygen and nitrogen atoms are typically found as nitro-groups (-NO<sub>2</sub>) in these molecules. The explosive nature of these molecules is due to those nitro-groups, thus military explosives are usually referred as nitro-explosives.<sup>[1-8,23-26]</sup> Common military explosives are RDX, PETN, HMX and TNT. However, the use of individual “powdered” explosives is uncommon. Today, most military explosives are plasticized using inert flexible binders with the aim of making moldable and easy-to handle explosive compositions. Such compositions are known as plastic explosives and may contain one or more individual explosives combined with the plasticizer. Since plasticizers are non-explosive compounds, their addition reduce the explosive power of the mixture. For this reason, the mass proportion of plasticizers in plastic explosives does not usually exceed 10%.<sup>[4-8]</sup> Common plastic explosives are C-4, PG-2, Composition B and Semtex. For instance, PG-2 explosive is composed of 91% RDX (explosive), 5.3% bis(2-ethylhexyl) phthalate (plasticizer), 2.1% polyisobutylene (binder) and 1.6% motor oil; while Composition B is composed of 59.5% RDX (explosive1), 39.5% TNT (explosive2) and 1% paraffin wax (plasticizer).<sup>[5-8]</sup> Military explosives are strictly controlled in most countries, only having access to them military personnel.

- *Commercial explosives*

Commercial explosives include those explosives that are legally used for nonmilitary purposes including the explosives used in mining industry, demolitions, and firearms/rocket/ pyrotechnic propellants.<sup>[3-8]</sup> Dynamite and ANFO compositions

are the most common commercial explosives used today for mining and demolition purposes. They are high explosives with relatively small velocities of detonation (in comparison with military explosives), which enable a more precise control about the required power to move and fragment rocks and buildings.<sup>[4-8]</sup> Regarding firearm ammunition, the explosive propellants currently used for shooting are smokeless gun-powders based on NC.<sup>[1-8]</sup> Either dynamite, ANFO or smokeless gunpowders are particularly safe to handle and transport since they are insensitive to weak stimuli and require detonators to explode. On the contrary, the propellants used in pyrotechnics mostly consist of black powder and/or flash powder, which are particularly sensitive and may accidentally deflagrate and explode.<sup>[1-8,27-29]</sup> All these explosives are commercially available for nonmilitary citizens. Thus, their acquisition and ultimate usage (either legal or criminal) is particularly easy since they are not as controlled as military explosives. Because of these reasons, commercial explosives are frequently used in terrorist attacks.

- *Homemade explosives*



Scheme 1. Classification of explosives proposed by Akhavan in 2004 (reproduced from<sup>[2]</sup> with permissions).

Homemade explosives include all “do-it-yourself” explosives. With the arrival of Internet last century, it is no longer necessary to be a chemist to produce or synthesize explosives. Freely accessible recipes guiding step by step about how to obtain, produce and synthesize different explosives are available online. These recipes typically include oxidizer-fuel explosive mixtures such as ANFO.<sup>[5]</sup>

In addition to these explosive mixtures that you can either purchase or do-it-yourself, there exist homemade explosives that are not commercially available because their instability and sensitivity is extreme. However, they are high energy explosives whose synthesis is simple and from easy attainable reagents such as TATP or HMTD peroxide explosives. In fact, TATP is widely known because of having been used in many recent terrorist attacks.<sup>[3-8,19]</sup> TATP is easily synthesized through the reaction between hydrogen peroxide and acetone,<sup>[19]</sup> whose recipe is also available on Internet.

As previously indicated, TATP does not require a detonator to explode, increasing the

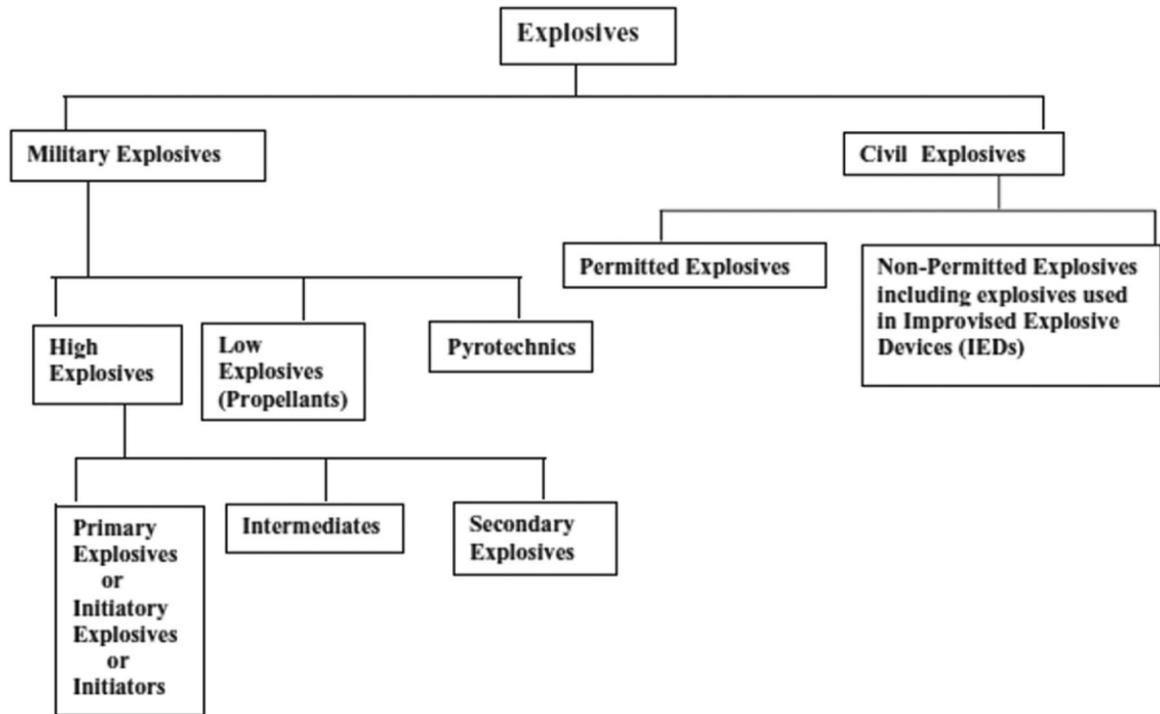
danger and ease of use of TATP, in spite of the frequent accidents associated to their synthesis.<sup>[19]</sup>

*Intermediate classifications (combining velocity of detonation and use)*

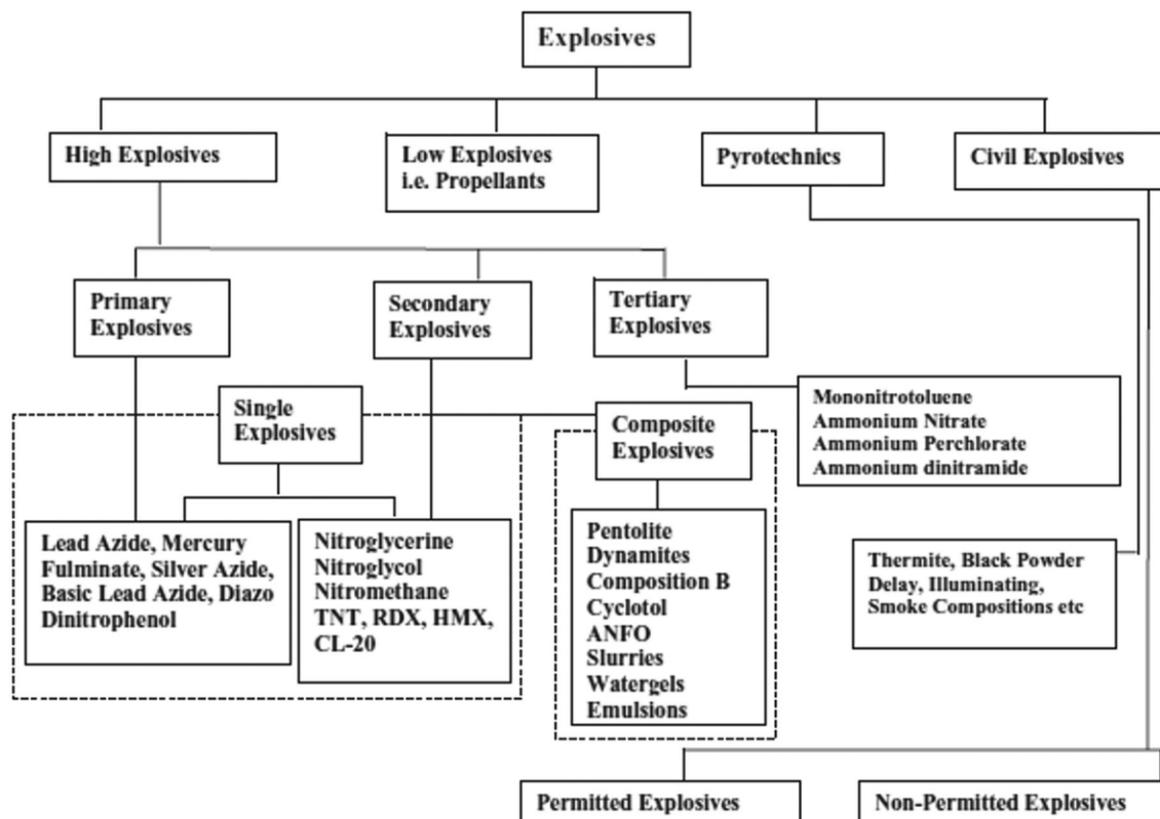
Some classifications combining both velocity of detonation and use/application have been also proposed in literature. In most of them explosive substances are classified as primary explosives, secondary explosives, propellants (or low explosives) for guns or rockets, and pyrotechnics. In this respect, four relevant classifications of explosives found in literature are displayed below as examples (Schemes 1–4).

## Classification of explosives based on their chemical composition

The knowledge about the chemical composition of explosives may provide useful information not only to predict the chemical reaction by which such explosive may cause a detonation, but also, and more important, to properly focus the subsequent determination of explosive traces toward the correct analytes. This involves selecting the appropriate methodology and analytical instrumentation depending on the chemical compound that is aimed to be determined. For instance, gas/liquid chromatography coupled to mass spectrometry is suitable to determine organic explosives such as TNT or TATP, but completely useless for black powder. Similarly, ion chromatography or capillary electrophoresis is adequate to determine the ionic components of flash powder or black powder, but very ineffective for TNT. Therefore, from the point of view of chemical identification, the classification of explosives according to their chemical composition is essential. Significant approaches for a chemical classification of explosives have been made up to now, which are summarized in Table 2. Most of these approaches have been manually extracted from the index headings with which different authors decided to structure their books/ manuscripts. The first attempt for a chemical classification of explosives, which was proposed by van't Hoff in 1909, was based on the seven types of chemical bonds that usually provide explosive properties to molecules, including: N O (nitro-compounds, nitric esters and salts), N N (diazo-compounds), O-Cl (chlorates and perchlorates), N C (fulminates), N-Cl (nitrogen chloride), O-O (peroxides and ozonides) and C C (acetylene and acetylides).<sup>[2,23]</sup> A posterior classification of explosives might be extracted from the index structure used by Davis in the book "*The chemistry of powder and explosives*",<sup>[1]</sup> a cardinal book in the field of explosives that was published in 1943. In this respect, Davis distinguished among (i) aromatic nitro-compounds,

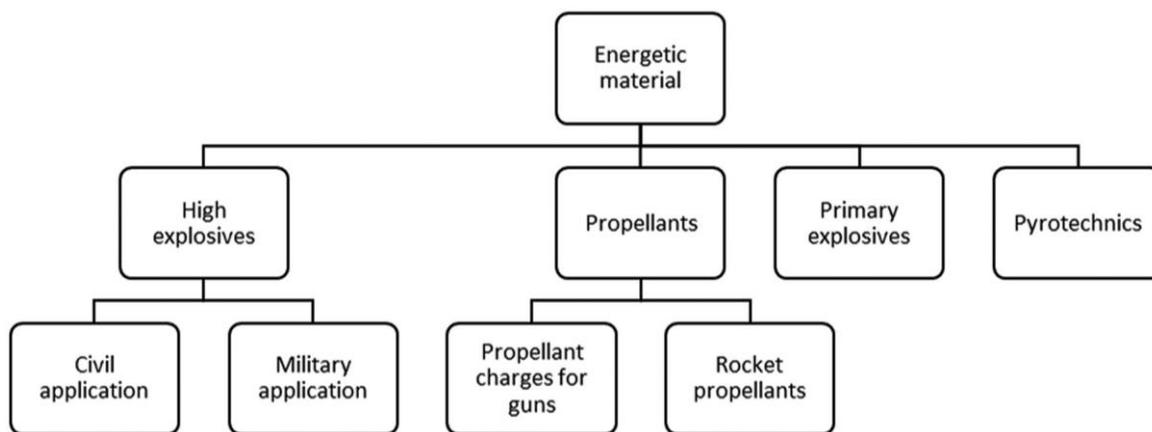


Scheme 2. Classification of explosives according to their end-use proposed by Agrawal in 2010 (reproduced from<sup>[3]</sup> with permissions).



Scheme 3. Classification of explosives according to the nature of explosive/ingredient proposed by Agrawal in 2010 (reproduced from<sup>[3]</sup> with permissions).

(ii) nitric esters, (iii) nitro-amines, (iv) chlorate and perchlorate explosives, (v) fulminating compounds (such as fulminates, azides and peroxides), (vi) smokeless powders (composed of NC), (vii) dynamites and other AN compositions, and finally, (viii) black powder and other saltpeter compositions.<sup>[1]</sup> One decade later, Plets extended the classification previously proposed by van't Hoff, by specifying the chemical groups containing the previous reported bonds (NO<sub>2</sub>/NO<sub>3</sub> for N-O bond, NF<sub>2</sub> for N-Cl bond, ClO<sub>3</sub>/ClO<sub>4</sub> for O-Cl bond) and including an eighth class for organometallic explosives containing M-C bonds.<sup>[2,3,23]</sup>



Scheme 4. Classification of explosives proposed by Klapötke in 2019 (reproduced from<sup>[30]</sup> with permissions).

In 1964, Urbanski<sup>[23]</sup> established that explosives should be first classified into chemical individual substances and explosive mixtures. The former might be further divided into six different classes: (i) nitro-compounds, (ii) nitric esters, (iii) nitro- amines, (iv) azides, (v) derivatives of chloric/perchloric acids, and (vi) other compounds capable of producing an explosion (such as fulminates, acetylides and peroxides). Explosive mixtures might be further divided into two different classes: mixtures with at least one explosive component, and mixtures where there is no explosive component.<sup>[23]</sup> Two decades later, Conkling and Mocella<sup>[28]</sup> focused on the oxidizers contained in pyrotechnic mixtures distinguishing among potassium nitrate, potassium chlorate and potassium perchlorate, amongst others. In 1994, Persson, Holmberg & Lee,<sup>[11]</sup> as Urbanski previously did, distinguished between single molecule explosives and composite explosive mixtures. But unlike Urbanski, these authors further subclassified composite explosive mixtures into three classes: (i) mixture of two single explosive substances, (ii) intermediate mixture containing one or more single explosive substances together with fuel and/or oxidizer ingredients, and (iii) mixture of a fuel and an oxidizer. Regarding pure single explosive compounds, a posterior classification distinguishing between

organic and inorganic explosives was proposed by Cooper in 1996 [9]. Within organic explosives, Cooper further differentiated between aromatic and aliphatic explosives.<sup>[9]</sup> Few years later, in 2003, Ledgard<sup>[5]</sup> differentiated, according to the chemical structure of explosives, among eleven classes of explosives (see Table 2). In a second book published in 2006,<sup>[27]</sup> Ledgard structured chapters according to their use as rocket propellants, gun propellants, pyrotechnics or fireworks. Interestingly, sections were structured based on the main component of each powder, discriminating among (i) black powder; and (ii) ammonium perchlorate, (iii) ammonium nitrate, (iv) ammonium dinitramide, (v) nitrocellulose, and (vi) miscellaneous containing propellants. Another comprehensive index structure of chapters based on the chemical composition of explosives was also presented in 2003 by Manelis,<sup>[10]</sup> who grouped explosives into thirteen different classes (as summarized in Table 2). In 2007, Kubota again highlighted the discrimination between energetic materials consisting of chemically bonded oxidizer and fuel components in the same molecule, and energetic composite materials consisting of physically mixed oxidizer and fuel components.<sup>[12]</sup> The same year, Agrawal and Hodgson offered a new grouping of organic explosives according to the index structure of their book,<sup>[20]</sup> distinguishing among six classes of explosives (see Table 2). Three years later, Agrawal published a really comprehensive reference book about high energy materials,<sup>[3]</sup> in which the classification of explosives according to their chemical structure first discriminated between single molecular explosives and composite explosives. Single explosives might be further subclassified depending on the chemical nature of their bonds (according to Plet's classification). On the other hand, composite explosives might be further sub-classified into three classes: (i) mixture of several single explosives, (ii) mixture of one or more single explosives with added fuel or oxidizer (including NG-based explosives), and (iii) mixture of fuel and oxidizer (including ANFO explosives).<sup>[3]</sup> Finally, in 2013, Matías & Pachman<sup>[19]</sup> published a book focused on primary explosives, whose chapter index structure

differentiated among eleven classes of primary explosives (see Table 2).

Additional chemical groupings of explosives, similar to previous ones, might be found in literature. However, there is no a complete chemical classification of explosives that unifies all the information previously revised. Therefore, in this work, the chemical classifications previously revised in Table 2 are joined, unified and extended into a more practical, comprehensive and diagrammatically-structured chemical classification of explosives (Scheme 5).

- *Pure individual/single explosives*

Pure individual/single explosives, also called “molecular explosives”, include every explosive compound whose unimolecular decomposition reaction may produce an explosion. This means that they are not a mixture of substances, but a pure compound. As a pure compound, it is composed of different atoms chemically bonded. Depending on the nature of the constituting atoms (i.e., elements), the chemical compound can be categorized into two classes: inorganic or organic compound.

Table 2. Chemical Classifications of explosives found in literature.[1-3,5,9-12,19,20,23,27,28]

Author	Classes										Smokeless powders (composed of NC)	Dynamites & other AN compositions	Black powder & other saltpetre compositions (also containing chlorate/perchlorate salts)
Van't Hoff (1909) [2, 23]	N=O			O-Cl	N=N	N=C	N-Cl	O-O	C≡C				
Davis (1943) [1]	Aromatic nitro compounds	Nitric esters	Nitro-amines	Chlorate & perchlorate explosives	Fulminating compounds (fulminates, azides, peroxides, etc.)								
Plets (1953) [2, 3, 23]	NO <sub>2</sub> , NO <sub>3</sub>			ClO <sub>2</sub> , ClO <sub>4</sub>	-N <sub>2</sub> , N=N	-C=N-	-NF <sub>2</sub> (F = halogen)	-O-O-	-C≡C-	M-C	Mix two exp subs		
	Nitro / nitrate			Chlorate / perchlorate	Azide/ Azo	Fulminate	Halogen amine	Peroxide	Acetylide	Organo-metallic			
Urbanski (1964) [23]	Chemical individual substances									Explosive mixtures			
	Nitro-compounds	Nitric esters	Nitramines (including aza/oxa)	Derivatives of chloric/perchloric acids Nitrates, chlorates	Azides	Others (fulminates, acetylides, peroxides, ozonides, etc.)				Those with at least 1 explosive component	Others with no explosive component		
Conkling & Mocella 1985 [28]										Oxidizer containing pyrotechnic mixtures			
										Potassium nitrate	Potassium chlorate	Potassium perchlorate	
										Strontium nitrate		Ammonium perchlorate	
Barium nitrate													

											Other oxidizers		
Persson, Holmberg & Lee (1994) [11]	Single molecule explosives / Single explosive substances												
Cooper (1996) [9]	Pure explosive compounds												
	Organic explosives					Inorganic explosives (including metal azides, metal fulminates & AN)							
	Aromatic (including mono- / poly-substituted monocyclic trinitrobenzenes & polycyclic aromatic explosives)		Aliphatic (including open chain and cyclo- aliphatic explosives)										
			Nitrate esters	Nitramines									
Ledgard 2003 2006 [5, 27]	Ledgard (2003) [5]										Ledgard (2006) [27]		
	Nitro-paraffins and their derivatives	Nitro-benzenes (including aminonitro-benzenes and polynitro-benzenes)	Nitro-triazoles									Ammonium perchlorate containing	Ammonium dinitramide containing
		Nitro phenyls and nitro phenyl salts		Nitrate esters			Azides and azo nitros	Metal azide, fulminates and nitrides	Miscellaneous (nitroguanidine, nitrourea, tetracene, acetone peroxide, etc.)	Black powder	Ammonium nitrate containing	Nitrocellulose containing	
		Nitro-tetrazoles									Miscellaneous containing		
						Onium salts, nitric & perchloric acids, & dinitramide							

Manelis (2003) [10]	Aliphatic nitro- compounds	Aromatic nitro-compounds	Nitro esters	Nitroamines	Organic azides	Organic difluoro amino compounds	Heterocyclic compounds		
					Ammonium nitrate				Ammonium dinitramide
					Ammonium perchlorate				Salts of hydrazinium, hydroxyl-ammonium & nitronium
					Metal perchlorates and nitrates, & metal salts of dinitramide				
Kubota (2007) [12]	Energetic materials consisting of chemically bonded oxidizer and fuel components in the same molecule							Energetic composite materials consisting of physically mixed oxidizer and fuel components	

(continued)

Table 2. Continued.

Agrawal & Hodgson (2007) [20]	Organic energetic compounds									
	Aliphatic C-nitro compounds (including polynitro-polycycloalkanes)	Aromatic C-nitro compounds	Nitrate esters	N-Nitro compounds		Miscellaneous explosive compounds (azides, peroxides, diazophenols, etc.)	N-heterocycles (pyrroles, pyrazoles, etc.)			
Agrawal 2010 [3]	Single explosives						Composite explosives			
	Classification of explosives based on their chemical structure according to Plets' classification						Mixture of several single explosives	Mixture of 1 or more single explosives with added fuel or oxidizer (including NG-based explosives)	Mixture of fuel and oxidizer (including ANFO explosives)	
Matías & Pachman 2013 [19]	Focused on primary explosives									
	Salts of polynitrophenols			Others (Salts of nitramines, organophosphates & hydrazine complexes)	Tetrazoles	Azides	Fulminates	Nitrogen halides		
		Diazodinitrophenol	Salts of benzofuroxan		Tetrazole ring-containing complexes				Organic peroxides	Acetylides

- *Organic explosives*

Pure individual organic molecular explosives include those explosive molecules that contain at least one atom of carbon and no atoms of an element different to C, H, O, N or halogen in their structure. This includes, for example, TNT ( $C_7H_5N_3O_6$ ), TATP ( $C_9H_{18}O_6$ ) or even nitroguanidine ( $CH_4N_4O_2$ ), which only has one atom of carbon. Because of the large

number of organic explosives that exist today, organic explosives are usually sub-divided into several different classes (peroxide explosives, nitro-explosives, organic azides, halogen amino compounds, and azo/diazo compounds (including diazo- methane)). In addition, a sixth class named “other organic explosives” is also presented in which including those organic explosives that are not included in previous classes.

- *Peroxide explosives*

Peroxide explosives are organic explosives characterized by having in their structure one or more peroxide groups (-OO-). The most popular peroxide explosives are TATP and HMTD.<sup>[6,19]</sup>

- *Nitro-explosives*

Nitro-explosives are organic explosives characterized by having in their structure one or more nitro-groups (-NO<sub>2</sub>).<sup>[1-6,20,23-26]</sup> Nitro-explosives are also sub-divided into four different classes depending on the atom to which nitro-group is chemically bonded.

- *Nitro-aromatic.* Nitro-group is bonded to an aromatic carbon (C(Ar)-NO<sub>2</sub>). *E.g.* TNT, tetryl, picric acid and TATB.
- *Nitro-aliphatic.* Nitro-group is bonded to an aliphatic carbon (C-NO<sub>2</sub>). *E.g.* nitromethane, nitro-ethane, and FOX-7 (1,1-diamino-2,2-dinitroethene).
- *Nitramine.* Nitro-group is bonded to a nitrogen atom (N-NO<sub>2</sub>). *E.g.* RDX, HMX, and CL-20.
- *Nitrate ester.* Nitro-group is bonded to an oxygen atom (O-NO<sub>2</sub>). *E.g.* PETN, NG and NC.

### *Organic azides*

Organic explosive azides are characterized by having in their structure at least one carbon atom and one azide group ( $-N_3$ ). Cyanuric triazide ( $C_3N_{12}$ ) or ammonium azidotetrazolate ( $NH_4CN_7$ ) are common examples of organic triazides with explosive properties.<sup>[19,20]</sup>

### *Organic halogen amino compounds*

Halogen amino explosive compounds are organic explosives characterized by having in their structure at least one carbon atom and one halogen-amino group ( $-NX_2$ ), such as methyldichloramine ( $CH_3NCl_2$ ).

### *Azo/diazo explosive compounds*

Azo/diazo explosive compounds are organic explosives characterized by having in their structure at least one carbon atom and one or more azo/diazo groups ( $-N=N-$  or  $-N=N$ ). Diazomethane ( $CH_2N_2$ ) and diazodinitrophenol (which combines nitro and diazo groups) are common examples of azo/diazo explosives.<sup>[19,20]</sup>

### *Other organic explosives*

As previously introduced, most organic molecular explosives contain either peroxide, nitro, azide, halogen-amino or azo/diazo groups in their structure. In fact, the explosive character of organic explosives is usually due to those groups. Nevertheless, there are some exceptions. Thus, an extra group is created to include every organic explosive that does not contain neither peroxide, nitro, azide, halogen-amino nor azo/diazo groups in its structure. For this reason, a wide variety of chemically different compounds has a place in this group such as tetracene ( $C_{18}H_{12}$ ) or fulminic acid ( $HCNO$ ).<sup>[19,20]</sup>

### *- Inorganic explosives*

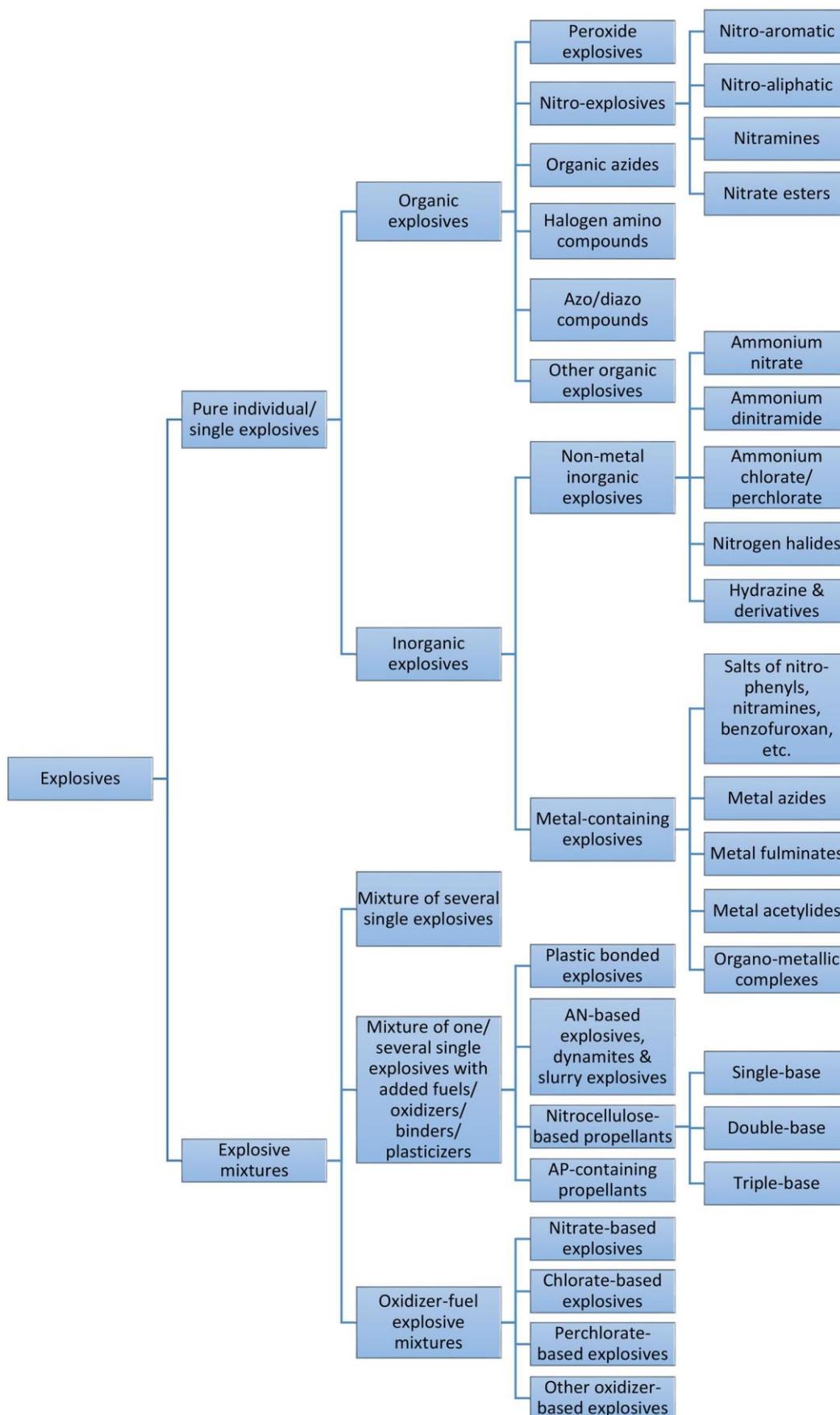
Pure individual inorganic explosives include those explosive compounds that either 1) do not contain carbon atoms in their structure or 2) contain at least one atom different to carbon, hydrogen, oxygen, nitrogen or halogen in their structure. This includes, for example, lead azide ( $Pb(N_3)_2$ ), nitrogen trichloride ( $NCl_3$ ) or

ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), which do not contain carbon atoms; but also, silver fulminate ( $\text{AgCNO}$ ), cuprous acetylide ( $\text{Cu}_2\text{C}_2$ ), lead styphnate ( $\text{PbC}_6\text{HN}_3\text{O}_8$ ) or lead picrate ( $\text{PbC}_{12}\text{H}_4\text{N}_6\text{O}_{14}$ ), which, despite containing carbon atoms, contain at least one atom different to C, H, O, N or halogen (generally a metal element).<sup>[3,19]</sup> In fact, inorganic explosives are usually sub-classified in two classes depending on this issue: those explosives containing metal elements and those explosives only composed of nonmetal elements.

- *Nonmetal inorganic explosives*

Nonmetal inorganic explosives are those explosive substances that do not contain neither carbon nor metal atoms in their structure. Concretely, most explosives included in this group are exclusively composed of nitrogen, hydrogen, oxygen and halogen (mainly chlorine). These explosives might be further subclassified into:

- Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). Ammonium nitrate is an inorganic ionic salt composed of nitrate anion (*i.e.* a nitrogen atom equally bonded to three oxygen atoms ( $\text{NO}_3^-$ )), and ammonium cation (*i.e.* a nitrogen atom equally bonded to four hydrogen atoms ( $\text{NH}_4^+$ )).<sup>[3]</sup>



Scheme 5. Classification of explosives according to their chemical composition.

Metal fulminates. Metal fulminates are characterized by containing a metal element and a fulminate group (-CNO), such as silver fulminate (AgCNO) or mercury fulminate ( $\text{Hg}(\text{CNO})_2$ ).<sup>[19]</sup>

Metal acetylides. Metal acetylides are characterized by containing a metal element and an acetylide group (-C≡C-), such as cuprous acetylide ( $\text{Cu}_2\text{C}_2$ ).<sup>[19]</sup>

Organo-metallic complexes. This class includes those organo-metallic complexes with explosive properties, such as tetrazole-ring containing cobalt perchlorate complexes.<sup>[19]</sup>

- *Explosive mixtures*

- *Mixture of several single explosives*

Two or more different single explosives can be combined to produce more harmful composite explosive mixtures such as Composition B (which is an explosive substance composed of RDX nitramine organic explosive (60%) and TNT nitroaromatic organic explosive (40%); pentolite (which is an explosive substance composed of PETN nitrate ester organic explosive (50%) and TNT (50%)); or Semtex H (which is an explosive substance composed of PETN (50%) and

[2,3]

Ammonium dinitramide ( $\text{NH}_4\text{N}(\text{NO}_2)_2$ ). Ammonium dinitramide is an inorganic ionic salt composed of dinitramide anion (*i.e.* a nitrogen atom equally bonded to two nitro groups ( $\text{N}(\text{NO}_2)_2^-$ )), and ammonium cation.<sup>[3]</sup> Ammonium chlorate/perchlorate ( $\text{NH}_4\text{ClO}_3/\text{NH}_4\text{ClO}_4$ ). Ammonium chlorate and ammonium perchlorate are inorganic ionic salts composed of chlorate/perchlorate anion (*i.e.* a chlorine atom equally bonded to three/four oxygen atoms ( $\text{ClO}_3^-/\text{ClO}_4^-$ )), and ammonium cation.<sup>[3]</sup>

RDX (50%)).

- *Mixture of one/several single explosives with added fuels/ oxidizers/binders/plasticizers*

The use of one single explosive alone or the combination of two or more single explosives alone is uncommon. Single explosives are usually combined with plasticizers/binders/ fuels and/or oxidizers to improve different properties of the explosive substance such as facilitating their malleability,

3 4

- Nitrogen halides. The nitrogen halides contain three atoms of one of the halogens bound together with one atom of nitrogen, such as nitrogen triiodide (NI<sub>3</sub>) or nitrogen trichloride (NCl<sub>3</sub>).<sup>[19]</sup>
- Hydrazine and derivatives (N<sub>2</sub>H<sub>4</sub>). Hydrazine is an inorganic molecule composed of two nitrogen atoms, bonded to two hydrogen atoms each (H<sub>2</sub>N-NH<sub>2</sub>).<sup>[19]</sup>

- *Metal-containing explosives*

Metal-containing inorganic explosives are those explosives composed of at least one metal atom. Due to the large variety of metal-containing explosives, they are usually sub-classified into different more-specific classes depending on the chemical structure of the nonmetal part:

- Nitro-phenyl salts, nitramine salts, benzofuroxan salts, etc. This class includes every explosive salt that results from the hydrogen-metal replacement in an organic explosive. This includes salts of picric acid (*e.g.* lead picrate), salts of trinitroresorcine (*e.g.* lead styphnate), salts of benzofuroxan (*e.g.* potassium 4,6-dinitrobenzofuroxan), salts of nitrotetrazole (*e.g.* cupric 5-nitrotetrazole), salts of azidotetrazole (*e.g.* silver 5-azidotetrazole), salts of nitramines (*e.g.* silver methylene-dinitramine), etc.<sup>[19]</sup>
- Metal azides. Metal azides are characterized by containing a metal element and an

azide group ( $-N_3$ ), such as sodium azide ( $NaN_3$ ) or lead azide ( $Pb(N_3)_2$ ).<sup>[19]</sup>

handling and transport; adjusting their explosive power or sensitivity; increasing their degradation to completely oxidized products; etc. For example, when used alone, PETN is always desensitized with 5% 10% paraffin wax.<sup>[3]</sup>

It should be noted that a large variety of explosive substances can be included in this group, due to the multiple combinations of single explosives with plasticizers, binders, fuels and/or oxidizers. Nonetheless, from the point of view of their composition, four main classes might be highlighted:

*Plastic bonded explosives*

Plastic bonded explosives (PBXs) are explosive mixtures that are composed of one or several high-energy secondary explosives (typically organic nitro-explosives) in a very high proportion (>80%), and other substances that act like binders and plasticizers in small proportion (<20%).<sup>[3]</sup> As an example, PG-2 plastic explosive (a variety of Composition C4 explosive) is composed of 91% RDX nitramine organic explosive as shown in Table 3.

*AN-based explosives, dynamites and slurry explosives*

Ammonium nitrate-based explosives are an extensive group of explosive mixtures all having in common the ammonium nitrate as main component (40–95%). The other components are usually fuels, binders, plasticizers, other explosives, etc. Some typical explosive mixtures based on AN are, for example, ANFO (i.e., 90% AN mixed with 10% fuel oil); ANA1 (i.e., 80–85% AN mixed with 15–20% aluminum powder), ammonal (50–70% AN mixed with 15–20%

Table 3. Chemical composition of PG2 plastic explosive (adapted from<sup>[31]</sup> with permissions).

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Main explosive:	RDX (91%)
Plasticizer (fuel):	Bis(2-ethylhexyl)phthalate (5.3%)
Binder (fuel):	Polyisobutylene (2.1%)
Absorbent (fuel):	Motor oil (1.6%)

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Table 4. Chemical composition of Goma-2 ECO dynamite (adapted from<sup>[31]</sup> with permissions).

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Main explosives:	AN (66%), EGDN (29%)
Plasticizer (fuel):	Dibutyl phthalate (2.5%)
Binder (fuel and oxidizer):	NC (1%)
Absorbents-Stabilizers (fuel):	Sawdust (1.2%), CaCO <sub>3</sub> (0.3%)

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Table 5. Chemical composition of a slurry explosive (adapted from<sup>[12]</sup> with permissions).

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Main explosive:	AN (45%)
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Gelling agent:	Monomethylamine nitrate (30%)
Water:	H <sub>2</sub> O (10%)
Oxidizer:	KNO <sub>3</sub> (10%)
Metal fuel:	Al (2%)
Others:	Others (3%)

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aluminum powder and 10–20% TNT), dynamites (whose original composition based on NG and kieselguhr was replaced in modern dynamites by AN mixed with EGDN, sawdust and plasticizers, as summarized in Table 4); or slurry explosives (water-gel explosives composed of AN, water and gelling agents, as summarized in Table 5).<sup>[3,12,31]</sup>

- *Nitrocellulose-based propellants*

Nitrocellulose-based propellants are explosive mixtures that are composed of nitrocellulose (or nitrocellulose in combination with another organic nitro-explosives) in a very high proportion (>90%), and other substances that act like binders, plasticizers, stabilizers, etc. in small proportion (<10%). Depending on the number of explosive compounds in their composition, NC-based propellants are further subclassified in three classes: single-base, double-base and triple-base NC-based propellants.<sup>[3,12]</sup>

- Single-base propellants are composed of NC.
- Double-base propellants are composed of NC and a second nitro-explosive, usually NG/DNT.
- Triple-base propellants are composed of NC and another two nitro-explosives (normally NG/DNT and NQ).

The proportion of NC in each NC-based propellant might vary, as displayed in

Table 6.

As observed in previous examples, around 5–10% of NC-based propellants are substances that act like binders, plasticizers, stabilizers, etc. Table 7 summarizes the chemical substances usually added as binders, plasticizers, etc. in the manufacture of double-base NC-based propellants.

- *AP-containing propellants*

Ammonium perchlorate containing propellants are an important group of composite propellants that are composed of a mixture of ammonium perchlorate (70%) and other substances including metal powders (such as aluminum), and polymers (such as carboxy-terminated polybutadiene) that act like fuels and binders.<sup>[3,12]</sup> Table 8 summarizes the chemical substances usually used as binders in the manufacture of AP composite propellants.

Table 6. Chemical composition of four different NC-based powders (adapted from<sup>[32]</sup> with permissions).

Single-base	Double-base	Double-base	Triple-base
NC (94%)	NC (85%)	NC (71%)	NC (19%)
Others (6%)	DNT (10%) Others (5%)	NG (25%) Others (4%)	NG (18%) NQ (55%) Others (9%)

Table 7. Chemical substances used to form double-base propellants (adapted from<sup>[12]</sup> with permissions).

Plasticizer (oxidizer and fuel): NG, TMETN, TEGDN, DNT

Plasticizer (fuel): DEP, DBP, TA, PU

Stabilizer: EC, 2NDPA, DPA

Plasticizer (energetic fuel): GAP, BAMO, AMMO

Binder (fuel and oxidizer): NC

Burning rate catalyst: PbSa, PbSt, Pb<sub>2</sub>EH, CuSa, CuSt, LiF

Burning rate catalyst modifier: C (carbon black, graphite) Combustion

instability suppressant: Al, Zr, ZrC

Opacifier: C (carbon black, graphite)

Flame suppressant:  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$

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- *Oxidizer-fuel composite explosives or Sprengel explosives* Oxidizer-fuel composite explosives include every mixture (i.e., combination of two or more non-explosive compounds) whose redox reaction may produce an explosion. As every redox reaction, one of the components in the mixture serves as oxidizing agent while the other component/s serve/s as fuel (reducing agent).<sup>[1-8,25-31]</sup> Oxidizer-fuel explosive mixtures are also known as Sprengel explosives, in memory of Hermann Sprengel, who explained that the explosiveness of these substances was due to the sudden combustion of the fuel in contact with the oxidizing agent.<sup>[33]</sup> In fact, the chemical and explosive properties of the explosive are determined by the combination of both oxidizer and fuel. Since there exist many substances that may act as fuels in contrast with the few energetic salts used as oxidizers, Sprengel explosives might be sub-categorized according to the oxidizer. Most oxidizer-fuel explosive mixtures are composed of either a nitrate, chlorate or perchlorate salt. The use of any other oxidizing agent to make explosive mixtures is uncommon, because they are more expensive compounds (such as chromate, permanganate, bromate, iodate or any organic oxidizing compound). Thus, composite explosives might be sub-divided into nitrate-, chlorate- and perchlorate-based explosives. An extra fourth class can be also considered for those oxidizer-fuel explosive mixtures containing uncommon oxidizers.

#### *Nitrate-based explosives*

Nitrate-based composite explosives are composed of an inorganic nitrate salt or nitric acid (oxidizer) mixed with one or more fuel substances. Inorganic nitrate anion ( $\text{NO}_3^-$ ) consists of a nitrogen atom equally bonded to three oxygen atoms. It is the

conjugate base of nitric acid and forms nitrate salts with most metals. It should be noted that ammonium nitrate, despite being an inorganic nitrate (oxidizer), it is also an individual molecular inorganic explosive capable of (i) producing alone an explosion by unimolecular decomposition (by which AN is transformed into water

Table 8. Chemical substances used to formulate AP

composite propellants (adapted from<sup>[12]</sup> with

permissions). Oxidizer:	AP
Binder (fuel):	HTPB, CTPB, PBAN, HTPE, HTPS, HTPA, PU, PS, PVC
Binder (energetic fuel):	GAP, BAMO, AMMO
Curing and/or crosslinking agent:	IPDI, TDI, PQD, HMDI, MAPO
Bonding agent:	MAPO, TEA, MT-4
Plasticizer:	DOA, IDP, DOP
Burning rate catalyst:	Fe <sub>2</sub> O <sub>3</sub> , FeO(OH), nBF
Burning rate negative catalyst:	LiF
Negative burning rate modifier:	OXM
Metal fuel:	Al
High energy additive:	RDX, HMX, NQ, CL-20, AND
Combustion instability suppressant:	Al, Zr, ZrC
HCl suppressant:	Mg, MgAl, NaNO <sub>3</sub>

vapor (H<sub>2</sub>O), nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>)), or (2) being mixed with other substances (binders, plasticizers, gelling agents, etc.) to produce AN-based explosive mixtures. On the contrary, nitrate salts whose cation is a metal do not easily decompose, and if so, the decomposition is slow and non- explosive. The addition of a fuel substance is required in this case to have an explosive mixture. Normally in such cases, a deflagration caused by the multi-molecular redox reaction between oxidizer and fuel produces large amounts of gaseous products, which increase the pressure (if confined) and ultimately provoke an explosion. In fact, these oxidizing-fuel deflagrating mixtures are commonly used as propellants due to the large amount of gases they produce.<sup>[1-13,25-30]</sup> In order to ensure

the complete oxidation of the fuel, oxidizer is usually added in mass percentages ranging from 50 to 75%. Potassium nitrate is the most common nitrate used in oxidizer-fuel nitrate-based propellants as evidenced by black powder (the most renowned and widely known explosive ever, which is a mixture of potassium nitrate, charcoal and sulfur). Nevertheless, other nitrates such as lithium, barium or strontium nitrates, amongst others, are also used in pyrotechnics to provide different color effects due to the characteristic emission color of the metal ion.<sup>[25-30]</sup>

- *Chlorate-based explosives*

Chlorate-based explosives are composed of an inorganic chlorate salt (oxidizer) mixed with one or more substances which act as a fuel. Chlorate anion ( $\text{ClO}_3^-$ ) consists of a chlorine atom equally bonded to three oxygen atoms. It is the conjugate base of chloric acid and forms stable chlorate salts with some metals. Like nitrates, chlorates might be sub-divided into ammonium chlorate and metal-chlorates. However, ammonium chlorate is extremely unstable, so much so that ammonium-chlorate-based explosives are not produced. In fact, most chlorate-based explosives are composed of either sodium or potassium chlorate such as chlorate (a homemade explosive composed of sodium/potassium chlorate, sulfur and sugar) and some pyrotechnic powders (in which potassium/sodium chlorate is added to black powder).<sup>[25-30]</sup>

- *Perchlorate-based explosives*

Perchlorate-based propellants are composed of an inorganic perchlorate salt (oxidizer) mixed with one or more substances which act as a fuel. Perchlorate anion ( $\text{ClO}_4^-$ ) consists of a chlorine atom equally bonded to four oxygen atoms. It is the conjugate base of perchloric acid and forms perchlorate salts with most metals. Contrarily to ammonium chlorate and

similarly to ammonium nitrate, ammonium perchlorate (AP) is relatively stable and may produce alone an explosion by unimolecular decomposition. Therefore, AP is commonly used in combination with aluminum powder and plasticizers to produce AP-containing propellants (as previously explained). On the other hand, metal-perchlorates (as metal nitrates) require the addition of a fuel substance to have an oxidizer-fuel deflagrating mixture. Perchlorate salts of metal ions (mainly potassium perchlorate) are used in pyrotechnic compositions, either forming flash powder (a propellant composed of potassium perchlorate and aluminum/magnesium powder) or in combination with black powder (KClO<sub>4</sub> KNO<sub>3</sub> charcoal sulfur).<sup>[3-6,25-30]</sup>

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#### *Other oxidizer-based explosives*

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In the few cases in which an oxidizer-fuel explosive mixture is composed of an oxidizing agent other than nitrate, chlorate or perchlorate salts, it would be included in this group. As previously introduced, oxidizing agents such as permanganate, dichromate, chromate or iodate are not usually found in explosive compositions because they are more limited and expensive than the respective nitrate or perchlorate salts. However, some homemade explosive mixtures can be prepared by mixing these oxidizing salts with fuels such as the mixtures of potassium permanganate with aluminum, antimony or glycerin.<sup>[3-5,28]</sup>

Most adequate chemical analytical techniques for determining explosives

In the knowledge of the chemical composition of explosives, the most adequate analytical technique/s for determining each explosive<sup>[34-42]</sup> might be selected, as summarized in Table 9. The summaries for each technique described below are not intended to be exhaustive reviews containing the total number of publications in which that technique is applied to identify explosives, but just seek to provide evidence about the application of each technique to the identification of certain

explosives.

In brief, analytical techniques providing elemental information such as energy dispersive X-ray spectroscopy (EDX) or inductively coupled plasma mass spectrometry (ICP-MS) are adequate to identify metal characteristic elements. Therefore, EDX/ICP-MS has been used to determine: (i) metal elements of metal-containing inorganic explosives (metal salts of nitrophenyls, nitramines, etc.; metal azides; fulminates; acetylides; and organo-metallic complexes);<sup>[43-45]</sup>



Table 9. Analytical techniques adequate to determine each type of explosive.<sup>[34-110]</sup>

Analytical techniques					
EDX / ICP-MS	LC-MS	GC-MS	IC / CE	IR / Raman	LIBS
Elemental identification	Separation & molecular	Separation & molecular	Separation & ion	Molecular identification	Elemental identification

Useful to determine characteristic metal elements identification

- Metal elements of metal-containing inorganic explosives (metal salts of nitrophenyls, nitramines, etc.; metal azides; fulminates; acetylides; and organo-metallic complexes).
- Metal elements contained in explosive mixtures.
- Metal element of the oxidizer/fuel in oxidizer-fuel mixtures.
- 

Useful to separate and determine liquid- soluble molecules identification

- Organic explosives (peroxides; nitro- aromatic, nitro- aliphatic, nitramines, nitrate esters; halogen amino compounds; etc.)
- Covalent nonmetal inorganic explosives (nitrogen halides; hydrazine and derivatives).
- Organic part of metal- containing inorganic explosives (salts of nitrophenyls, nitramines, etc.).
- Organic explosives in mixtures of single explosives.
- Organic explosives in: plastic bonded explosives; dynamites, slurry explosives and other AN-based explosives; NC-based propel. and AP- based propel.

Useful to separate and determine volatile/ volatilizable molecules (molecular/ elemental) identification

- Volatile organic explosives (peroxides; nitro-aromatic, nitro- aliphatic, nitramines, nitrate esters; halogen amino compounds; etc.)
- Covalent nonmetal inorganic explosives (nitrogen halides; hydrazine and derivatives).
- Volatile organic explosives in mixtures of several single explosives.
- Volatile organic and inorganic explosives and fuels in: plastic bonded explosives; dynamites, slurry explosives and other AN-based explosives; NC-based propel.; AP- based propel.; and nitrate-based propel.

Useful to determine ionic elements/ molecules

- Ionic nonmetal inorganic explosives (AN; ammonium dinitramide; AP).
- Ionic metal-containing inorganic explosives (salts of nitrophenyls and nitramines, etc.; metal azides; fulminates; acetylides).
- Ionic explosives (AN, AP, etc.) in explosive mixtures.
- Ionic derivatives of organic molecular explosives (including NC derivatives)
- Ionic inorganic oxidizing salts (nitrates, perchlorates, chlorates) in oxidizer- fuel mixtures.

Useful to determine organic and inorganic molecules

- Organic explosives (peroxides; nitro- aromatic, nitro- aliphatic, nitramines, nitrate esters; halogen amino compounds; etc.)
- Inorganic explosives (AN; ammonium dinitramide; AP, nitrogen halides; hydrazine and derivatives; the organic anions of metal salts of nitro- phenyls, nitramines, etc.; metal azides, fulminates and acetylides).
- Organic and inorganic explosives, oxidizers and fuels in mixtures as long as their proportion in the mixture exceeds 20-30%.

Useful to determine inorganic and organic substances

- Organic explosives (peroxides; nitro- aromatic, nitro- aliphatic, nitramines, nitrate esters; halogen amino compounds; etc.)
- Inorganic explosives (AN; ammonium dinitramide; AP, nitrogen halides; hydrazine and derivatives; metal salts of nitro-phenyls, nitramines, etc.; metal azides, fulminates and acetylides).
- Organic and inorganic explosives in mixtures as long as they are major components in the mixture.
- Metal fuels/oxidizers contained in explosive mixtures.

*EDX: Energy dispersive X-ray spectroscopy; ICP-MS: Inductively coupled plasma mass spectrometry; GC-MS: Gas chromatography coupled to mass spectrometry; LC-MS: Liquid chromatography coupled to mass spectrometry; IC: Ion chromatography; CE: Capillary electrophoresis; IR: Infrared spectroscopy; LIBS: Laser induced break- down spectroscopy.*

(ii) metal elements contained in explosive mixtures;<sup>[43,45]</sup> and (iii) metal elements of the oxidizer/fuel in oxidizer-fuel mixtures.<sup>[41,46]</sup>

On the contrary, analytical techniques providing a selective separation followed by a molecular identification such as liquid chromatography coupled to mass spectrometry (LC-MS) have been satisfactorily used to determine molecular substances including (i) single organic explosives (peroxides; nitro-aromatic, nitro-aliphatic, nitramines, nitrate esters; organic azides; halogen amino compounds; azo/diazo compounds; etc.);<sup>[36-39,42,47-53]</sup> (ii) covalent nonmetal single inorganic explosives (nitrogen halides; hydrazine and derivatives);<sup>[54]</sup> (iii) the organic part of some metal-containing single inorganic explosives (such as salts of nitrophenyls (picrate, styphnate), nitramines, etc.);<sup>[55]</sup> (iv) organic explosives in mixtures of single explosives;<sup>[38,56]</sup> and (v) organic explosives in plastic bonded explosives; dynamites, slurry explosives and other AN-based explosives; NC-based propellants and AP-based propellants.<sup>[38-42,44,57-60]</sup>

Similarly, analytical techniques providing a selective vapor separation followed by a molecular identification such as gas chromatography coupled to mass spectrometry (GC-MS) have been successfully utilized to determine volatile molecular substances including (i) volatile single organic

explosives (peroxides; nitro-aromatic, nitro-aliphatic, nitro- amines, nitrate esters; organic azides; halogen amino com- pounds; azo/diazo compounds; etc.);<sup>[34-39,43,61,62]</sup> (ii) covalent nonmetal single inorganic explosives (nitrogen hal- ides; hydrazine and derivatives);<sup>[63]</sup> (iii) volatile organic explosives in mixtures of several single explosives;<sup>[34,42,64]</sup> and (iv) volatile organic and inorganic explosives and fuels in plastic bonded explosives; dynamites, slurry explosives and AN-based explosives; NC-based propellants; AP-based propellants; and nitrate-based propellants.<sup>[42,60,64]</sup>

Analytical techniques performing a selective separation and identification of ions such as ion chromatography (IC) or capillary electrophoresis (CE) have been used to determine: (i) ionic nonmetal single inorganic explosives (AN; ammonium dinitramide; and AP);<sup>[39-42,65-68]</sup> (ii) ionic metal-containing single inorganic explosives (including salts of nitrophenyls and nitramines, etc.; metal azides; metal fulminates; and metal ace- tylides);<sup>[67-70]</sup> (iii) ionic explosives (AN, AP, etc.) in explosive mixtures;<sup>[34,41,51,65-68]</sup> (iv) ionic derivatives of organic molecu- lar explosives (including NC derivatives);<sup>[40,68,71]</sup> and (v) ionic inorganic oxidizing salts (nitrates, perchlorates, chlorates) in oxidizer-fuel mixtures.<sup>[34,41,51,72-76]</sup>

Finally, some analytical techniques such as Infrared and Raman spectroscopy enable the determination of both

organic and inorganic molecules. Their major limitation is the limit of detection in such a way that a significant amount of single explosive (and/or a significant proportion (>10–30%) of the compound in an explosive mixture) is required to be determined by IR/Raman. For instance, IR and Raman spectroscopy do not usually enable the detection of the fuel in oxidizer-fuel explosive mixtures. Positively, IR and Raman spectroscopy have been used to determine (i) organic explosive molecules (including peroxides; nitro-aromatic, nitro-aliphatic, nitramines, nitrate esters; organic azides; halogen amino compounds; azo/diazo compounds; etc.),<sup>[31,32,40,77–93]</sup> (ii) inorganic explosive molecules (including AN; ammonium dinitramide; AP, nitrogen halides; hydrazine and derivatives; the organic anions of metal salts of nitro-phenyls, nitramines, etc.; metal azides, fulminates and acetylides),<sup>[31,86–93]</sup> and (iii) oxidizers (i.e., nitrate, chlorate and perchlorate salts) as long as their amount exceeds the limit of detection.<sup>[31,32,41,76,88–94]</sup>

In addition, laser induced breakdown spectroscopy (LIBS), despite being a technique for determining the elementary chemical composition, is increasingly being used in combination with chemometric analysis for the selective identification of explosives due to the characteristic LIBS spectrum of each explosive substance. Particularly, LIBS has been used to determine: (i) single organic explosives (peroxides; nitro-aromatic, nitro-aliphatic, nitramines, nitrate esters; organic azides; halogen amino compounds; azo/diazo compounds; etc.);<sup>[88,89,95–104]</sup> (ii) single inorganic explosives (AN; ammonium dinitramide; AP, nitrogen halides; hydrazine and derivatives; metal salts of nitro-phenyls, nitramines, etc.; metal azides, metal fulminates and metal acetylides);<sup>[88,91,105–107]</sup> (iii) organic and inorganic explosives in mixtures as long as they are major components in the mixture,<sup>[95–100,108]</sup> with the exception of characteristic (iv) metal elements of fuels/oxidizers contained in explosive mixtures,<sup>[100,109,110]</sup> which can be easily determined even in low amounts.

The complex composition of explosives usually requires the combination of several of the above-mentioned analytical techniques. The most adequate analytical

instrumentation for determining Composition B (which combines TNT and RDX), would involve LC separation and MS identification. However, in the case of ammonal (which combines TNT, AN and Al powder), TNT could be detected using also LC-MS, but additional instrumentation would be required to properly detect AN and Al. Raman spectroscopy or water extraction followed by IC/CE could be used for detecting AN; while XRD/ICP-MS could be used for detecting Al. In the case of ANFO or dynamite, Raman spectroscopy or water extraction followed by IC/CE could be used for detecting AN; but GC should be used to determine diesel (in ANFO), while LC-MS/GC-MS might be used to further determine EGDN (in dynamite). In the case of black powder, potassium nitrate might be determined by IR or water extraction followed by IC/CE, whereas the determination of sulfur and carbon in black powder post-blast residues might be indirectly accomplished by the detection of sulfate, cyanate and carbonate using IC/CE.

## Conclusions

Chemical explosives are usually classified in literature according to either the velocity of detonation (high/low energy explosives) or the source/application (military/commercial/homemade explosives). However, an efficient way to classify explosives from the point of view of their posterior analytical determination is the one based on their chemical composition. This work revises and gathers the chemical classifications of explosives found in literature into an extended chemical classification in which explosives are first divided into pure single explosives and explosive mixtures. Secondly, pure single explosives might be classified into organic or inorganic explosives; whereas explosive mixtures are further classified into: (i) mixtures of several single explosives, (ii) mixtures of one/several single explosives with added fuels/oxidizers/binders/plasticizers ... , and (iii) oxidizer-fuel mixtures. Single organic explosives are further sub-classified into nitro-explosives (nitro-aromatic, nitro-aliphatic, nitramines, or nitrate esters), peroxide explosives, organic azides, halogen-amino compounds, azo/diazo compounds and others. Single inorganic explosives can contain metal atoms (such as salts of nitro-phenyls, nitramines, benzofuroxan, etc.; metal azides; metal fulminates; metal acetylides; or organo-metallic complexes), or can be free of metal elements (such as AN, ammonium dinitramide, AP, nitrogen halides, or hydrazine). Regarding mixtures of one/ several single explosives with added fuels/oxidizers/binders/ plasticizers, we may distinguish among: (i) plastic bonded explosives; (ii) dynamites, slurry explosives and other AN-based explosives; (iii) NC-based propellants (single-, double-, or triple-base); and (iv) AP-containing propellants. Finally, oxidizer-fuel explosive mixtures can be further subclassified according to the oxidizer into nitrate, chlorate or perchlorate based explosive mixtures).

This is a useful classification for selecting the most adequate analytical techniques for determining explosives and post-blast residues, according to the identification features of each analytical technique (i.e., elemental/ molecular, organic/inorganic,

volatile/non-volatile ... ), including SEM-EDX and ICP-MS, LC or GC coupled to MS, IC or CE, IR or Raman spectroscopy, and LIBS.

### **Conflicts of interest**

Authors declare no conflict of interest.

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