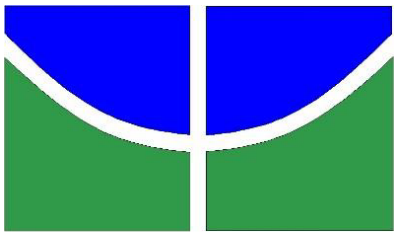

UNIVERSIDADE DE BRASÍLIA

INSTITUTO DE QUÍMICA

PROGRAMA DE PÓS-GRADUAÇÃO EM QUÍMICA

TESE DE DOUTORADO

ANÁLISE DE EXPLOSIVOS E RESÍDUOS PÓS-EXPLOSÃO: PERFIL QUÍMICO, INTERFERENTES E ESTABILIDADE POR CROMATOGRAFIA IÔNICA, CROMATOGRAFIA GASOSA COM DETECÇÃO POR ESPECTROMETRIA DE MASSAS E QUIMIOMETRIA

ANALYSIS OF EXPLOSIVES AND POST-EXPLOSION RESIDUES: CHEMICAL PROFILE, INTERFERENTS AND STABILITY BY ION CHROMATOGRAPHY, GAS CHROMATOGRAPHY WITH MASS SPECTROMETRY DETECTION AND CHEMOMETRICS

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"A ignorância é um vazio, uma ausência capaz de ser contornada, em especial pela educação, a estupidez é o contrário: é uma suficiência intelectual que não precisa ser preenchida, pois já é plena por natureza."

'A Psicologia da Estupidez' (2014)

RESUMO

A análise de resíduos pós-explosão é de grande importância na química forense, pois pode ajudar a elucidar aspectos cruciais de certos crimes. Nesse contexto, este trabalho visa contribuir para o aprimoramento da análise destes resíduos estudando dificuldades reais identificadas na rotina de análises do INC. Inicialmente, é apresentada uma contextualização na análise química de resíduos pós-explosão por meio de uma revisão de literatura e observações práticas da química forense. Casos reais de Laudos Periciais são utilizados para ilustrar cada situação, com destaque para as dificuldades mais significantes. Após essa contextualização, um estudo retrospectivo de casos de pós-explosão apresenta o primeiro perfil dos tipos de explosivos mais utilizados em ações criminosas no Brasil. Este estudo demonstra que misturas a base de cloratos e/ou percloratos, pólvora negra e emulsão explosiva são amplamente utilizados nessas atividades criminosas. Este levantamento serviu de suporte à conceptualização e ao desenho experimental desenvolvido neste trabalho e poderá também servir de apoio a estudos futuros nesta área. Posteriormente é apresentado um estudo avaliando o uso de cédulas de papel-moeda para detecção de resíduos pós-explosão. Essa matriz apresentou analitos de interesse em quantidades relevantes mesmo não havendo contato com explosivos, tornando a interpretação visual dos resultados difícil ou mesmo inviável. Contudo, após uso de PCA os resultados foram promissores na discriminação entre amostras provenientes de uma cena de crime e cédulas de uso diário. Ainda com relação a possíveis fontes de interferência, o estudo seguinte avaliou materiais de laboratório na análise de resíduos pós-explosão, principalmente relacionados à emulsão explosiva/ANFO por GC/MS. Foi demonstrado que materiais como êmbolos de seringas, luvas e filmes plásticos possuem potencial de contaminação com consequências indesejáveis nos resultados/conclusões de laudos, podendo gerar resultados inconclusivos ou falsos negativos/positivos. Por fim, avaliou-se a viabilidade de se manter contraprovas de extratos aquosos e orgânicos de resíduos pós-explosão. Os resultados indicaram que o único analito preocupante foi o íon cianato, que degrada consideravelmente nas temperaturas estudadas (-20.0, 4.5 e 18.0 °C). Apesar disso, o estudo demonstra que é possível preservar os extratos aquosos e orgânicos por pelo menos 24 e 12 meses, respectivamente, já que os outros analitos cruciais para a conclusão permanecem estáveis.

Palavras-chave: Resíduos pós-explosão, Explosivos, Misturas Explosivas Combustível-Oxidante, Amostragem, Interferentes, CG/EM, Cromatografia Iônica (CI).

ABSTRACT

The analysis of post-explosion residues is of great importance in forensic chemistry as it can help elucidate crucial aspects of certain crimes. In this context, this work aims to contribute to the improvement of these residues analysis by studying real difficulties identified in the routine analyses of the INC. Initially, a contextualization of the chemical analysis of post-explosion residues is presented through a review of the literature and observations from forensic chemistry practice. Real cases from Forensic Reports are used to illustrate each situation, highlighting the most significant challenges faced. Following this contextualization, a retrospective study of post-explosion cases presents the first profile of the most commonly used types of explosives in criminal actions in Brazil. This study demonstrates that mixtures based on chlorates and/or perchlorates, black powder, and explosive emulsion are widely used in these criminal activities. This survey supported the conceptualization and experimental design developed in this work and may also serve as valuable support for future studies in this area. Subsequently, a study evaluating the use of banknotes for detecting post-explosion residues is presented. This matrix exhibited analytes of interest in significant quantities even without direct contact with explosives, making visual interpretation of the results difficult or even impossible. However, after the use of PCA, the results were promising in discriminating between samples from a crime scene and everyday use banknotes. Still related to possible sources of interference, the next study evaluates sampling materials in the analysis of post-explosion residues, specifically focusing on the explosive emulsion/ANFO analyzed by GC/MS. It has been demonstrated that materials such as syringe plungers, gloves and plastic films have potential for contamination with undesirable consequences on the results/conclusions as inconclusive results or false negatives/positives. Finally, an evaluation study examined the viability of long-term storage for aqueous and organic extracts from post-explosion residues. The results indicated that the only concerning analyte was the cyanate ion, which degrades considerably at the studied temperatures (-20.0, 4.5, and 18.0 °C). Despite this, the study demonstrates that it is possible to preserve the aqueous and organics extracts for at least 24 and 12 months, respectively, as the other analytes crucial for the conclusion remain stable.

Keywords: Post-explosion Residues, Explosives, Fuel-oxidizer Explosive Mixtures, Sampling, Interferents, GC/MS, Ion Chromatography (IC).

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LIST OF ABBREVIATIONS AND ACRONYMS

ANAL	Ammonium nitrate/Aluminum
ANFO	Ammonium nitrate/Fuel oil
ANMAL	Ammonium nitrate /Nitromethane/Aluminum
ANNIE	Ammonium nitrate/Nitrobenzene
ANNM	Ammonium nitrate/Nitromethane
ANS	Ammonium nitrate/Sugar
ATM	Automated teller machines
CD	Conductivity detector
CE	Capillary electrophoresis
CONTRASP	Confederation of Private Security Workers
EDX	Energy-dispersive X-ray spectroscopy
EGDN	Ethylene glycol dinitrate
EOD	Explosive ordnance disposal
FINEX	Forensic International Network for Explosives Investigation
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
HME	Homemade explosive
HMTD	Hexamethylene triperoxide diamine
HMX	Octogen
HNS	Hexanitrostilbene
HPLC	High performance liquid chromatography
IC	Ion chromatography
IED	Improvised explosive device
ISADE	International symposium on the analysis and detection of explosives
NIC	National Institute of Criminalistics
LC/MS/MS	Liquid chromatography coupled to tandem mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantitation
MS	Mass spectrometry
MSA	Methane sulfonic acid
NG	Nitroglycerine

NTO	3-Nitio-l,2,4-triazol-5-one
PC	Principal component
PCA	Principal component analysis
PETN	Pentaerythritol tetranitrate
PF	Federal police
PLM	Polarizing Light Microscopy
RDX	Hexogen
SD	Standard deviation
SEM	Scanning electron microscope
SISCRIM	Federal police's criminalistics system
SLM	Stereo Light Microscopy
SVD	Singular value decomposition
TATP	Triacetone triperoxide
TNB	Trinitrobenzene
TNT	2,4,6-trinitrotoluene
TWGFEX	Technical Working Group for Fire and Explosives
USBDC	United States Bomb Data Center
XRD	X-ray diffraction
XRF	X-ray Fluorescence

INTRODUCTION

Forensic chemistry is the application of chemical knowledge in the solution of crimes and encompasses the analysis of diverse substances, including but not limited to drugs, fuels, anabolic steroids, pharmaceuticals, pesticides, toxins, accelerants in fire debris, paints, inks, documents, environmental and biological samples, explosives, post-explosion residues, and chemicals in general.

The analysis of explosives and post-explosion residues is conducted to achieve the chemical identification of the explosives involved in criminal activities or accidents, across a wide range of matrices. It is considered one of the most demanding areas within forensic chemistry, encompassing challenges at multiple stages of the process, from sample collection to the interpretation of the results.

Considering this context, the overall objective of this work was to enhance the methodology employed by the Federal Police for the analysis of post-explosion residues, taking into account the common challenges faced during routine analyses of real cases. To achieve this goal, a comprehensive literature review was initially conducted on general aspects related to the analysis of explosives and post-explosion residues. This review includes illustrations of real cases obtained from Forensic Reports and other relevant publications to highlight the common challenges encountered in this type of analysis. After this contextualization, the following specific objectives were established:

- To perform a retrospective study by analyzing the results obtained from various cases handled by the Federal Police. This study aims to establish a profile of the most frequently used types of explosives in criminal activities in Brazil through the chemical identification of explosives and/or post-explosion residues.
- To evaluate different types of banknotes, including uncirculated, circulated, and seized samples, using ion chromatography (IC) to obtain their ionic profiles. This analysis contributes to a better understanding of the background levels of ions present in banknote samples and apply exploratory chemometric analysis to the obtained data.
- To assess various materials commonly used in forensic laboratories and crime scenes. The objective is to identify potential interferents in the analysis of explosive emulsion/ANFO post-explosion residues using gas chromatography coupled with mass spectrometry (GC-MS).

- To evaluate the stability of target analytes present in extracts obtained from samples of post-explosion/burning residues of the most commonly used explosives in Brazil and worldwide. This evaluation was conducted by performing monthly analyses over a period of 24 months under different temperature conditions for the aqueous extracts and 12 months for the organic extracts. The objective is to assess the long-term stability of these target analytes and investigate any potential changes or degradation over time.

The structure of this work involves chapters dedicated to both the literature review and each specific objective. The initial chapter is dedicated to providing context for the analysis of explosives and post-explosion residues. This chapter provides a comprehensive literature review and incorporates practical learning experiences to prepare the reader for subsequent chapters. Real case images sourced from Forensic Reports and other relevant sources are included to illustrate each situation, emphasizing the common challenges encountered in routine forensic chemistry laboratory analyses.

The second chapter focuses on a retrospective study that analyzes the results from various cases handled by the Federal Police. The objective is to identify and profile the most commonly used types of explosives in criminal activities in Brazil. This study serves as a valuable reference for selecting appropriate explosives and matrices in subsequent investigations. The findings of this study were published in the Journal of Forensic Sciences in 2022 (Lograd o et al., 2022).

The third chapter focuses on a study that evaluates various banknotes, including uncirculated, circulated, and sized ones. The objective is to obtain the ionic profiles of these banknotes and enhance the understanding of the background levels of target ions commonly found in this type of matrix during the analysis of post-explosion residues using ion chromatography (IC). Furthermore, the collected data undergo exploratory chemometric analysis, which shows promising results and suggests the potential development of classification models.

In the fourth chapter, a study is conducted to evaluate various materials frequently utilized in forensic laboratories for sample collection, processing, storage, as well as in crime scene processing such as collection and transportation. The objective is to identify potential interferents in the analysis of explosive emulsion/ANFO post-explosion residues using gas chromatography coupled with mass spectrometry (GC/MS). By

examining these materials, the study aims to enhance the understanding of potential interferences and improve the accuracy of the analysis.

The fifth chapter of the thesis focuses on a study that investigates the stability of target analytes present in extracts obtained from samples of post-explosion/burning residues. The study specifically examines the effects of different temperature conditions over a period of 24/12 months, utilizing monthly/bimonthly analyses for aqueous and organic extracts, respectively. By monitoring the stability of these target analytes, valuable insights are gained regarding their degradation or preservation under varying temperature conditions. This research contributes to a better understanding of the long-term stability of these target analytes and its implications for the analysis of post-explosion residues.

As one of the challenges addressed in some chapters of this work is the presence of undesirable substances that can cause interferences in the results and their interpretation, it is worth noting that the terms “interference” and “interferents” was used to refer to both concomitants present in the original sample, added by uncontrolled environmental conditions, or added inadvertently during the analytical procedure [1]. The term "background levels" was also used to refer to the presence of analytes of interest originally present in the matrix, added by the environments to which they were subjected, and/or added inadvertently during the analytical procedure.

CHAPTER I - Analysis of explosives and post-explosion residues: an illustrated overview

ANALYSIS OF EXPLOSIVES AND POST-EXPLOSION RESIDUES: AN ILLUSTRATED OVERVIEW

1.1. Introduction

1.1.1. Importance of analysis of explosives and post-explosion residues

Explosives are legally used in Brazil in several activities, among which stand out: military use, police use, mining, oil prospecting, demolitions, construction of highways or railways, fireworks, industrial use (aeronautical and automotive), welding, among others. On the other hand, the illegal use of explosives in Brazil is also a reality, examples of this illegal use are terrorism, extortion, vandalism, predatory fishing, break-ins, robberies (banks, transportation of valuables, etc.) [2].

The analysis of explosives and post-explosion residues is an area of great importance in forensic chemistry and helps investigation of several crimes related to the use of explosives. Some of the questions to which this type of analysis can contribute are the following: i) Was it an explosion? ii) What caused the explosion? iii) Is it an underground facility for clandestine production of explosives or their storage? iv) Is it possible to determine authorship? and v) What are the most used explosives for criminal actions in Brazil? What are its possible origins? Is it possible to point out trends? [3,4]. Each of these questioning examples is detailed and illustrated in the next subsections.

1.1.1.1. Was it an explosion?

In some cases, the extent of destruction is so immense that it may initially resemble an explosion scene. In aircraft crashes, a typical example, there are occasionally suspicions of attacks with explosives, in addition to the degree of destruction similar to that of an explosion, due to the great violence of the impact. In such cases, the search for post-explosion residues through chemical analysis, combined with other pieces of information gathered during the crime scene investigation, can help provide answers to these question [3]. Figure 1.1 presents a photo that exemplify this situation [5].

AFP/ Khaled Desouki

Figure 1.1. Debris of Metrojet Airbus A321 in the desert in Egypt's Sinai region [5].

1.1.1.2. What caused the explosion?

In certain situations, the occurrence of an explosion is evident, whether through recorded footage, eyewitness accounts, or the observable characteristics of the scene. However, uncertainties may arise regarding the underlying causes of the explosion. In such cases, performing chemical analysis to identify post-explosion residues can provide vital insights and assist in differentiating between deliberate criminal acts and accidental incidents. To illustrate this scenario, Figure 1.2 presents two situations that exemplify the importance of chemical analysis in investigating explosive events [6,7].

Préfecture de police de Paris | Carlos Alberto Silva

Figure 1.2. Left – mechanical explosion at the Théâtre de l 'Empire due to failure of the heating system on February 13, 2005 [7]. Right – vehicle after explosion followed by fire in Vitória-ES. Vehicle exploded while moving along the road [6]. No post-explosion residues were identified.

1.1.1.3. Is it an underground facility for clandestine production of explosives or their storage?

The identification of clandestine laboratories involved in the production of illicit substances is a critical aspect of forensic investigations, where chemical analysis plays a significant role in reaching conclusive findings. While these clandestine laboratories are primarily associated with drug production, it is worth noting that there are also instances of laboratories engaged in the synthesis or preparation of homemade explosives (HME) and improvised explosive devices (IED), although less common. Differentiating between these types of laboratories at the earliest stages is crucial. When there is suspicion of an explosive laboratory, the procedures and interventions undergo significant changes. In such cases, the involvement of an explosive ordnance disposal (EOD) team becomes necessary to ensure compliance with the required safety measures for working in a laboratory containing various chemical products and explosive materials [8].

To distinguish between the different types of laboratories, the crime scene investigation team assesses the overall characteristics of the scene, which include the presence of utensils, equipment, reagents, solvents, labels, and other relevant factors. Portable equipment for chemical analysis can also be used for on-site investigations. Afterward, the collected samples are sent to the Forensic Laboratory for the identification of explosives and/or related compounds [8]. Figure 1.3 provides two images as examples of clandestine explosives production laboratories [9,10].

Devon and Cornwall Police San Diego Sheriff's Department

Figure 1.3. Left - clandestine explosives laboratory in Devon, England [9]. Right - clandestine explosives laboratory in Escondido, California. The presence of the grenade mold facilitates the inference regarding the type of laboratory [10].

In Brazil, illegal storage of explosives is also very common, as a significant portion of improvised explosive devices are made from commercial products such as

explosive emulsions, detonating cords, fuses, primers, and fireworks. This storage can occur in various locations, ranging from residences in urban areas to more remote areas in rural zones. The observations made in the previous paragraph regarding the distinction between different types of clandestine laboratories are equally applicable in these cases. Figure 1.4 illustrates one of these cases [11].

Figure 1.4. Residence storing items commonly used in criminal activities involving explosives in Brazil [11]. Left - fragments of fuse and detonating cord on the kitchen table along with other tools. Center - box with explosive material under a piece of furniture in one of the bedrooms of the residence. Right - Nº 8 primers found in a drawer of a cabinet in one of the bedrooms of the residence.

For the purpose of making this distinction between drugs (or other substances) and hazardous materials such as explosives, it is ideal to have a chemist knowledgeable in explosives as part of the crime scene investigation team. However, due to various factors, this is often not possible. Fortunately, there are several references available for consultation, providing information about various precursors, reagents, solvents, and explosives that may be involved in the preparation of explosives [8,12–15]. Moreover, this information is commonly organized in the form of cards to facilitate quick reference during crime scene investigations [16]. Table 1.1 presents examples of precursor chemicals used in the production of HMEs (homemade explosives) for IEDs (improvised explosive devices), categorized by chemical type and their role as oxidizers, fuels (including organic materials, energetic organic compounds, food products, or inorganic materials), and chemicals for synthesis (including strong and weak acids) [14].

Table 1.1. List of chemical precursors sorted by chemical type and role [14].

SYNTHESIS CHEMICALS	OXIDIZERS	
Acetone	Hypochlorite salts (Ca^{2+}/Na^{+})	
Aspirin	Chlorates salts (Na^{+}/K^{+})	
Erythritol	Hydrogen peroxide, concentrated (CHP)	
Ethylene glycol	Metal peroxides (Ba^{2+}/Na^{+})	
Glycerol	Nitrate salts (Ca^{2+}/Na^{+}/K^{+}/NH_4^{+})	
Hexamine	Nitrite salts (Na^{+}/K^{+})	
Hydrazine	Perchloric acid	
Hydrogen peroxide, dilute	Perchlorates salts (Na^{+}/NH_4^{+}/K^{+})	
Mannitol	Potassium permanganate	
Methanol	FUELS	
MEK	Organic Materials	Food Products
Phenol	Diesel	Artificial creamer
Sodium azide	Kerosene	Black pepper
Urea	Mineral oil	Black seed
UAN solution	Motor oil	Cinnamon
	Sawdust	Cumin
	Vaseline	Flour
	Inorganics	Honey
Strong Acids	Aluminum (Al) (powder/paste)	Acing sugar
Sulfuric acid	Antimony trisulfide	Powdered drink milk
Hydrochloric acid	Charcoal	
Nitric acid	Magnalium powder	
	Magnesium powder	Energetics Organic Compounds
Weak acids	Red phosphorous	Nitrobenzene
Citric acid	Sulfur	Nitromethane
Acetic acid	Titanium powder	
Ascorbic acid	Zinc powder	

1.1.1.4. Is it possible to determine authorship?

The materials gathered at a post-explosion scene for analysis are diverse, including metallic and plastic fragments from Automated Teller Machines (ATMs), swabs, cotton, fragments of explosive device casings, and more. Papilloscopic and genetic profiling analyses of these materials play a vital role in the investigation of potential suspects. Furthermore, the analysis of explosives and post-explosion residues can provide valuable contributions towards this objective [3].

Occasionally, as depicted in Figure 1.5, analyses are conducted on items obtained from individuals under suspicion, including banknotes, hand swabs (cotton or swabs), clothing, adhesive tapes, explosives, vehicles, and more. The purpose of these analyses is

to determine the potential authorship of a crime by comparing the results obtained from these materials with those collected from the crime scene [3,4,17].

Figure 1.5. Examples of materials that may be linked to suspects and that may be useful in the search for the authorship of the crime through comparisons with materials collected at the crime scene.

1.1.1.5. What are the most used explosives for criminal actions in a given location? What are its possible origins? Is it possible to point out trends?

Knowledge of the explosives commonly used in specific occurrences or locations can be valuable in investigations concerning the diversion or illicit use of explosives. By establishing correlations between the prevalence of certain types of explosives and specific locations, it may be possible to identify their potential sources, such as mining industries, explosive manufacturers, or fireworks factories. This information can assist in determining the origin of explosives used for criminal purposes. The observed profile of explosives usage can also guide the selection of explosives to be studied in future research, considering the wide range of possibilities available [3,4].

For instance, in Brazil, a retrospective study (Chapter II of this thesis) presents data collected by the National Institute of Criminalistics (INC/PF) of the Federal Police,

regarding chemical analysis conducted to identify explosives used in Automated Teller Machines (ATMs) and cash safes robberies in Brazil between 2014 and 2020. The study reveals the following distribution profile: 53% of cases involved explosive mixtures based on chlorates and/or perchlorates, 22% involved explosive emulsion, 13% involved black gunpowder, 11% resulted in negative or inconclusive findings, and 1% were organic explosives, specifically pentaerythritol tetranitrate (PETN) [3,4] .This study also presents other interesting findings.

Alongside data collected from chemical analyses conducted over time at specific locations, visual documentation of explosive devices confiscated prior to their deployment also enhances our understanding of the modus operandi employed by criminals in crafting these devices. Figure 1.6 shows examples of commonly used materials for making these types of explosives, as well as examples of the actual IEDs.

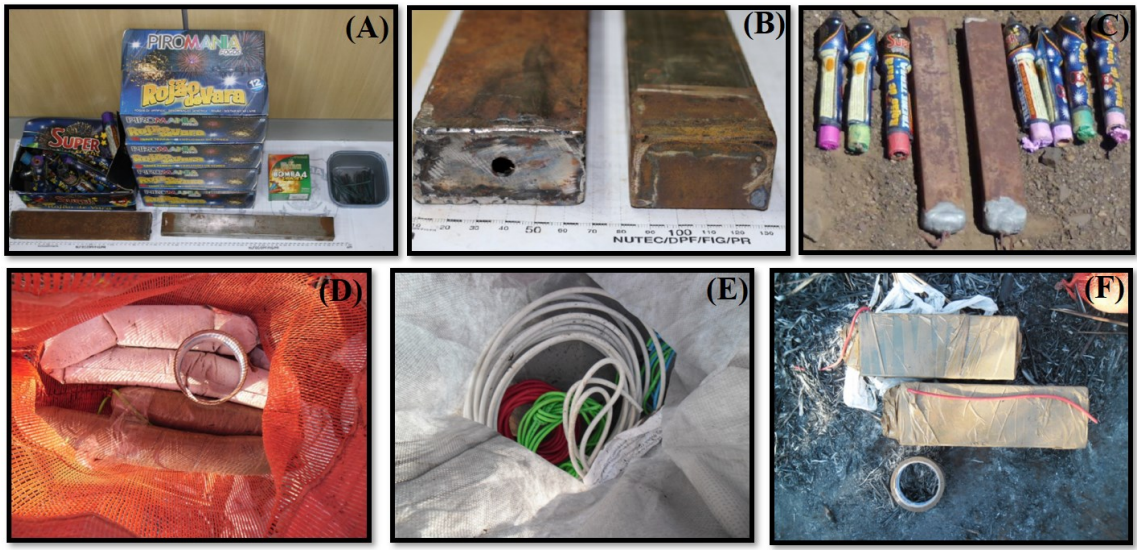

Figure 1.6. Examples of IEDs and the frequently employed materials for crafting them, commonly utilized in ATM explosions [18,19] : (A) Confiscated fireworks alongside "metalons" (carbon steel products extensively used in industry and construction), (B) Close-up of "metalons" (C) Seized IEDs found in conjunction with fireworks, (D) Explosive emulsions, (E) Detonating cord paired with fuse, and (F) IEDs seized along with the latter two components.

Regarding the types of explosives used in other countries worldwide, obtaining this kind of information with precision is challenging, as detailed information in this area is not easily available due to its inherently sensitive nature. Despite these limitations, the available data do show that commercial explosives, black powder, smokeless powder, and pyrotechnic filler were involved in a significant number of incidents in last years.

The only publicly available datasets are reported in the United States Bomb Data Center (USBDC) annual reports, which provide high-level information on all types of bombings and are currently available from 2015 to 2022 [14,20].

Additionally, personal communications with forensic experts in this field at international conferences, such as the Forensic International Network for Explosives Investigation (FINEX) conference and the International Symposium on the Analysis and Detection of Explosives (ISADE), along with other sporadic meetings featuring case study presentations, indicate that explosives based on ammonium nitrate, such as ANFO, fuel oxidizer mixtures from pyrotechnics, and other explosives like TATP are quite common in various countries worldwide.

1.2. Literature review and observations from forensic chemistry practice

1.2.1. Classifications of explosives for analytical purposes

Explosives can be classified in various ways, including their chemical nature, reaction speed, sensitivity, and applications. One particularly interesting differentiation, based on the chemical nature, is the division into two groups: i) individual explosive molecules, typically composed of organic substances such as nitroesters, nitramines, nitroaromatics, nitroaliphatics, peroxides, and their mixtures; and ii) fuel-oxidizer explosive mixtures, which consist of inorganic salts (such as nitrates, chlorates, perchlorates), serving as oxidants, combined with different fuels (such as diesel oil, vaseline, sulfur, coal, powdered metals (Al, Mg), sugars, etc.) [3,4,21,22].

This classification is particularly relevant for the analysis of explosives and post-explosion residues, as the chosen methodology for conducting the analysis largely depends on it [22,23]. Figure 1.7 provides examples of organic explosives, and Table 1.2 presents examples of fuel-oxidizer explosive mixtures [15,22,24].

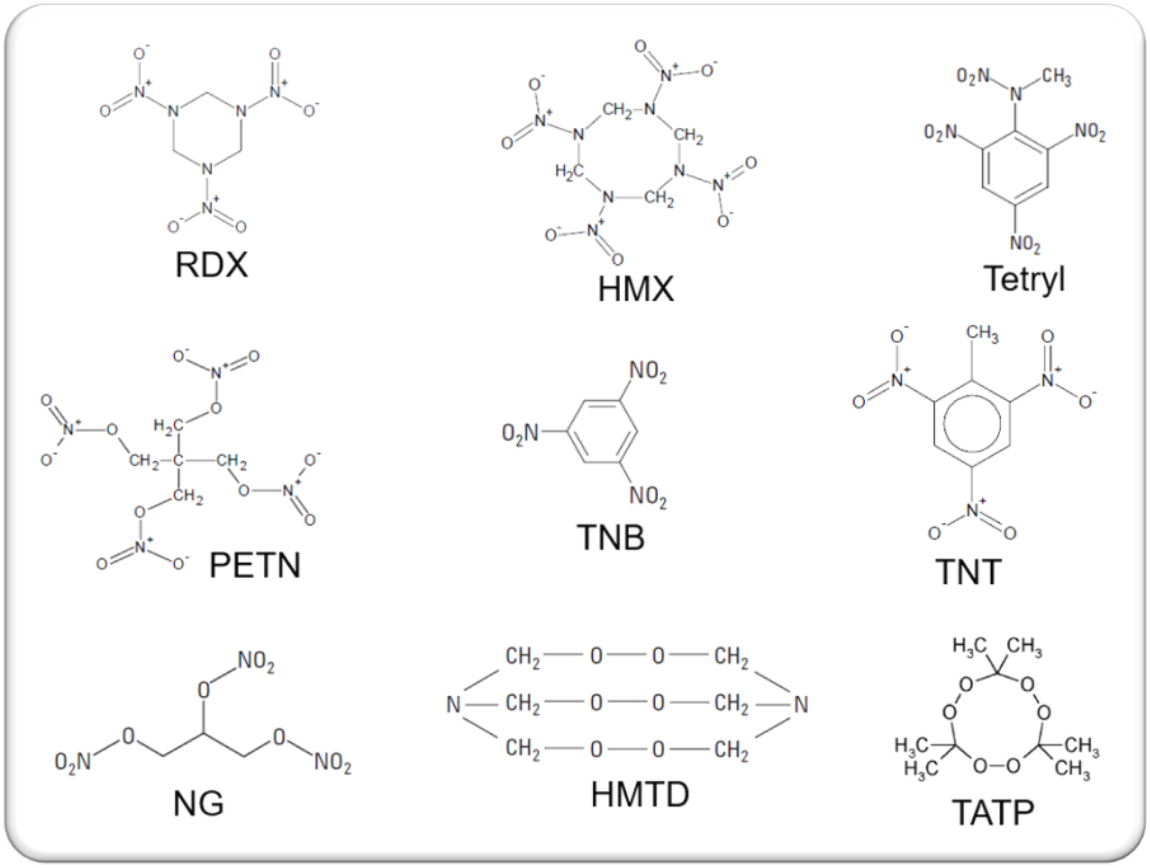

Figure 1.7. Some examples of common organic explosives.

Table 1.2. Some examples of fuel-oxidizer explosive mixtures [15,24].

Fuel-oxidizer explosive mixtures	
Oxidizer	Fuel
Ammonium nitrate	Aluminum (ANAL)
Ammonium nitrate	Carbon powder
Ammonium nitrate	Fuel oil (ANFO)
Ammonium nitrate	Magnesium powder
Ammonium nitrate	Nitrobenzene (ANNIE)
Ammonium nitrate	Nitromethane/Aluminum (ANMAL)
Ammonium nitrate	Nitromethane (ANNM)
Ammonium nitrate	Sawdust
Ammonium nitrate	Sugar (ANS)
Potassium chlorate or perchlorate	Aluminum (Flash powder)
Potassium chlorate or perchlorate	Aluminum/Sulfur (Flash powder)
Potassium chlorate or perchlorate	Nitrobenzene
Potassium chlorate or perchlorate	Paraffin
Potassium chlorate or perchlorate	Petroleum jelly
Potassium chlorate or perchlorate	Red phosphorus
Potassium chlorate or perchlorate	Sugar
Urea nitrate	Nitrobenzene
Urea nitrate	Kerosene
Urea nitrate	Aluminum
Urea nitrate	Fuel oil
Urea nitrate	Magnesium
Urea nitrate	Nitrobenzene
Urea nitrate	Nitromethane
Urea nitrate	Sawdust
Urea nitrate	Sugar
Potassium nitrate	Sulfur/Carbon (Black Powder)
Potassium nitrate	Ascorbic acid (Black canyon)

The possibilities of explosive mixtures are vast. Numerous references provide examples of the most common explosive mixtures [14,15,25–27]. In addition to scientific articles, this information can also be found in quick reference sources, such as cards provided by certain institutions involved in this field [16].

1.2.2. Explosive reactions and their residues

The target analytes for identifying the explosive at an accident or crime scene depend on the explosive reaction. In the case of organic explosives, the focus is on identifying traces of the explosive substance itself since its products do not provide relevant information for identification of the explosive. As shown in Table 1.3, the reactions of organic explosives, in general, primarily result in the formation of products

such as carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), soot (C), and water (H_2O) [21].

Table 1.3. Examples of chemical reactions in the explosion of organic substances [21].

Explosive	Explosive reaction
RDX	$C_3H_6N_6O_6 \rightarrow 3\ CO + 3\ H_2O + 3\ N_2$
HMX	$C_4H_8N_8O_8 \rightarrow 4\ CO + 4\ H_2O + 4\ N_2$
Nitrocellulose	$C_6H_7N_3O_{11} \rightarrow 4{,}5\ CO + 1{,}5\ CO_2 + 3{,}5\ H_2O + 1{,}5\ N_2$
Nitroguanidine	$CH_4N_4O_2 \rightarrow CO + H_2O + H_2 + 2\ N_2$
Nitroglycerine	$C_3H_5N_3O_9 \rightarrow 3\ CO_2 + 2{,}5\ H_2O + 1{,}5\ N_2 + 0{,}25\ O_2$
EGDN	$C_2H_4N_2O_6 \rightarrow 2\ CO_2 + 2\ H_2O + N_2$
PETN	$C_5H_8N_4O_{12} \rightarrow 2\ CO + 3\ CO_2 + 4\ H_2O + 2\ N_2$
Picric acid	$C_6H_3N_3O_7 \rightarrow 5{,}5\ CO + 0{,}5\ C + 1{,}5\ H_2O + 1{,}5\ N_2$
Tetryl	$C_7H_5N_5O_8 \rightarrow 5{,}5\ CO + 1{,}5\ C + 2{,}5\ H_2O + 2{,}5\ N_2$
NTO	$C_2H_8N_4O_3 \rightarrow 2\ CO + H_2O + 2\ N_2$
TATB	$C_6H_6N_6O_6 \rightarrow 3\ CO + 3\ C + 3\ H_2O + 3\ N_2$
Tetrazene	$C_2H_8N_{10}O \rightarrow 0{,}5\ H_2O + 2\ C + 3{,}5\ H_2 + 5\ N_2$
HNS	$C_{14}H_6N_6O_{12} \rightarrow 9\ CO + 5\ C + 3\ H_2O + 3\ N_2$
TNT	$C_7H_5N_3O_6 \rightarrow 3{,}5\ CO + 3{,}5\ C + 2{,}5\ H_2O + 1{,}5\ N_2$

In contrast, for most explosive mixtures based on inorganic salts, the analysis focuses not only on traces of the original composition but also on the products and by-products of the explosion reaction (Table 1.4). These reaction products are typically present in post-explosion residues at significantly higher concentrations compared to the residual components of the original mixture. This is because some of these reaction products are solid compounds and tend to remain in the materials. But this is not always the case. For example, in the case of ANFO, the analytes of interest are the components of the initial mixture. Similar to the organic explosives listed in Table 1.3, ANFO primarily produces gaseous products and water upon detonation, which do not provide significant information for the identification of the explosive.

Table 1.4. Examples of chemical reactions of explosive mixtures based on inorganic salts.

Explosive	Explosive reaction
Black powder [28]	$10\ KNO_3 + 8\ C + 3\ S \rightarrow 3\ K_2SO_4 + 2\ K_2CO_3 + 6\ CO_2 + 5\ N_2$
ANFO [29]	$3\ NH_4NO_3 + \text{“}CH_2\text{”} \rightarrow CO_2 + 3\ N_2 + 7\ H_2O$
Flash powder [12]	$3\ KClO_4 + 8\ Al \rightarrow 4\ Al_2O_3 + 3\ KCl$
Flash powder [30]	$KClO_3 + 2\ Al \rightarrow Al_2O_3 + KCl$
$KClO_3$ + Lactose [12]	$8\ KClO_3 + C_{12}H_{22}O_{11}.H_2O \rightarrow 8\ KCl + 12\ CO_2 + 12\ H_2O$
$KClO_4$ + C [25]	$KClO_4 + 4C \rightarrow KCl + 4\ CO$
NH_4NO_3 + C [25]	$NH_4NO_3 + C \rightarrow N_2 + CO + 2\ H_2O$
NH_4ClO_4 + C [25]	$NH_4ClO_4 + 2\ C \rightarrow 1/2\ N_2 + 1/2\ Cl_2 + 2\ H_2O + 2\ CO$
$KClO_3$ + S [12]	$2\ KClO_3 + 3\ S \rightarrow 3\ SO_2 + 2\ KCl$

The reaction products can vary depending on several factors, including the shape, size, and porosity of the components; the ratio of fuel to oxidizer; the presence of water and impurities; the charge diameter; the confinement conditions (including the type and thickness of the container material); and the influence of additives [3,15,31].

Several references are available that provide information on the main analytes and their corresponding possible original explosives [3,23,32,33]. Table 1.5 presents some analytes along with their potential source explosives [4]. Another valuable and informative resource is the publication "Recommended Guidelines for Forensic Identification of Post-Blast Explosive Residues" [23], which offers a simplified overview of the major analytes and the various applicable analytical techniques.

Table 1.5. Common analytes related to their possible original explosives [4,23].

Explosives	Target analytes in post-explosion residues
Black powder	SO_4^{2-}, NO_2^-, NO_3^-, $S_2O_3^{2-}$, SCN^-, OCN^-, K^+
Flash powder	Cl^-, ClO_4^-, ClO_3^-, K^+
Explosive emulsion/ANFO	NH_4^+, Na^+, NO_3^-, fuel oil
PETN	Parent compound
RDX	Parent compound
EGDN	Parent compound
HMTD	Parent compound
Tetryl	Parent compound

1.2.3. Explosives versus post-explosion residues

Apart from the heightened safety considerations necessary when working with explosives, the analysis of bulk explosive substances/mixtures is similar to analyzing any other common substance. A wide range of analytical identification techniques can be employed in this process. Figure 1.8 showcases seized explosive materials (pre-explosion) that were sent for chemical analysis. Some of these materials underwent countermeasures by the Federal Police EOD (Explosive Ordnance Disposal) team to ensure safer handling and obtain smaller samples, following the procedures outlined in the simplified description provided in section "1.2.7 EOD operations and interferents related to subsequent chemical analysis."

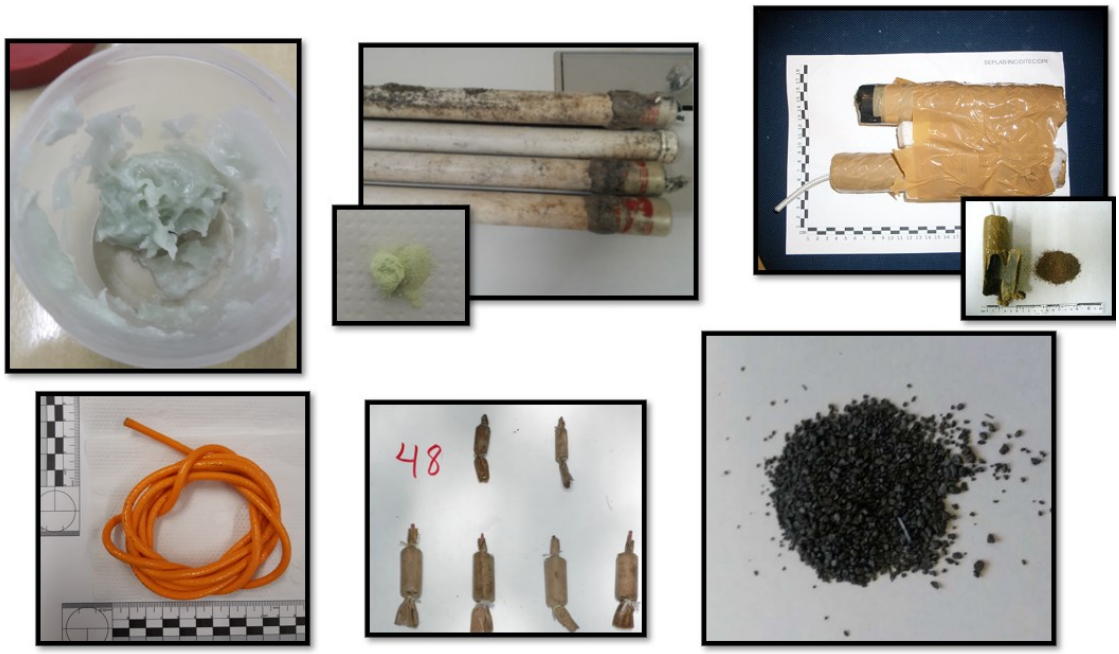

Figure 1.8. Samples of explosive materials (pre-explosion) seized and submitted to chemical analysis.

In some instances, even after an explosion, a sufficient amount of explosive material may still be present, allowing samples to be treated and analyzed using the same methods employed for pre-explosion explosive material analysis. Figure 1.9 showcases materials with bulk particles collected from post-explosion scenes, which were subsequently subjected to chemical analysis.

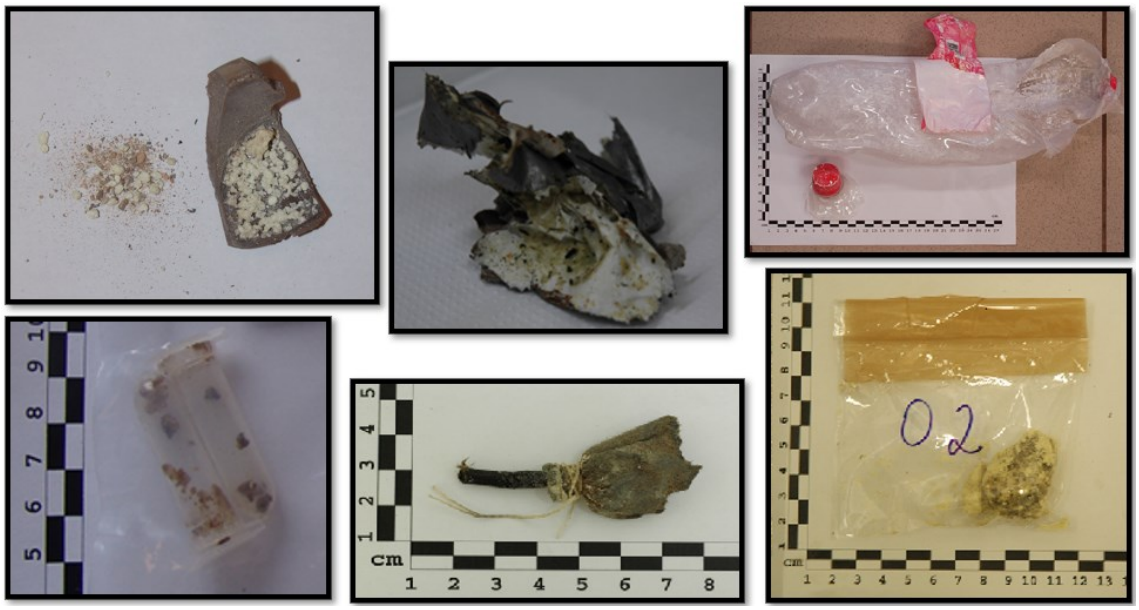

Figure 1.9. Samples of materials collected in post-explosion scenes containing bulk explosives sent for chemical analysis.

To illustrate the vast array of analytical techniques that may be required in a single case for the complete identification of each of its components, Figure 1.10 presents the results of various chemical analyses performed using FTIR spectroscopy, iodine-starch test, X-ray diffraction (XRD), gas chromatography coupled with mass spectrometry (GC/MS), and ion chromatography (IC) in a case involving an attempted explosion with a fuel-oxidizer mixture containing potassium chlorate, sulfur, and starch (with the presence of bulk material) [34]. In FTIR analysis, the key and distinctive bands are primarily associated with starch, observed in 3312 cm^{-1}, 2929 cm^{-1}, 1644 cm^{-1}, 1366 cm^{-1}, 1149 cm^{-1}, 1076 cm^{-1}, 996 cm^{-1}, 930 cm^{-1} and 861 cm^{-1} and 610 cm^{-1}. In GC/MS, the m/z signals at 256, 224, 192, 160, 128, 96, and 64 from the main GC peak are indicative of elemental sulfur. XRD analysis results were compared with the available database diffractograms, confirming the presence of $KClO_3$ and sulfur compounds. The presence of $KClO_3$ was also verified through IC analysis, while the presence of starch was confirmed via the iodine-starch test [34].

Note that the FTIR analysis identifies only one component of the mixture, which is starch. The signals of starch are prominent compared to the signals of potassium chlorate, causing the latter to be masked. It's important to note that sulfur, which is another component, does not exhibit significant signals in FTIR analysis and therefore cannot be identified using this technique alone. This result highlights the importance of employing confirmatory techniques in certain cases. The composition of these mixtures can vary widely, and relying solely on a single analytical technique may not be sufficient to identify all the components accurately. Additional techniques are necessary to ensure comprehensive identification and analysis of the mixture.

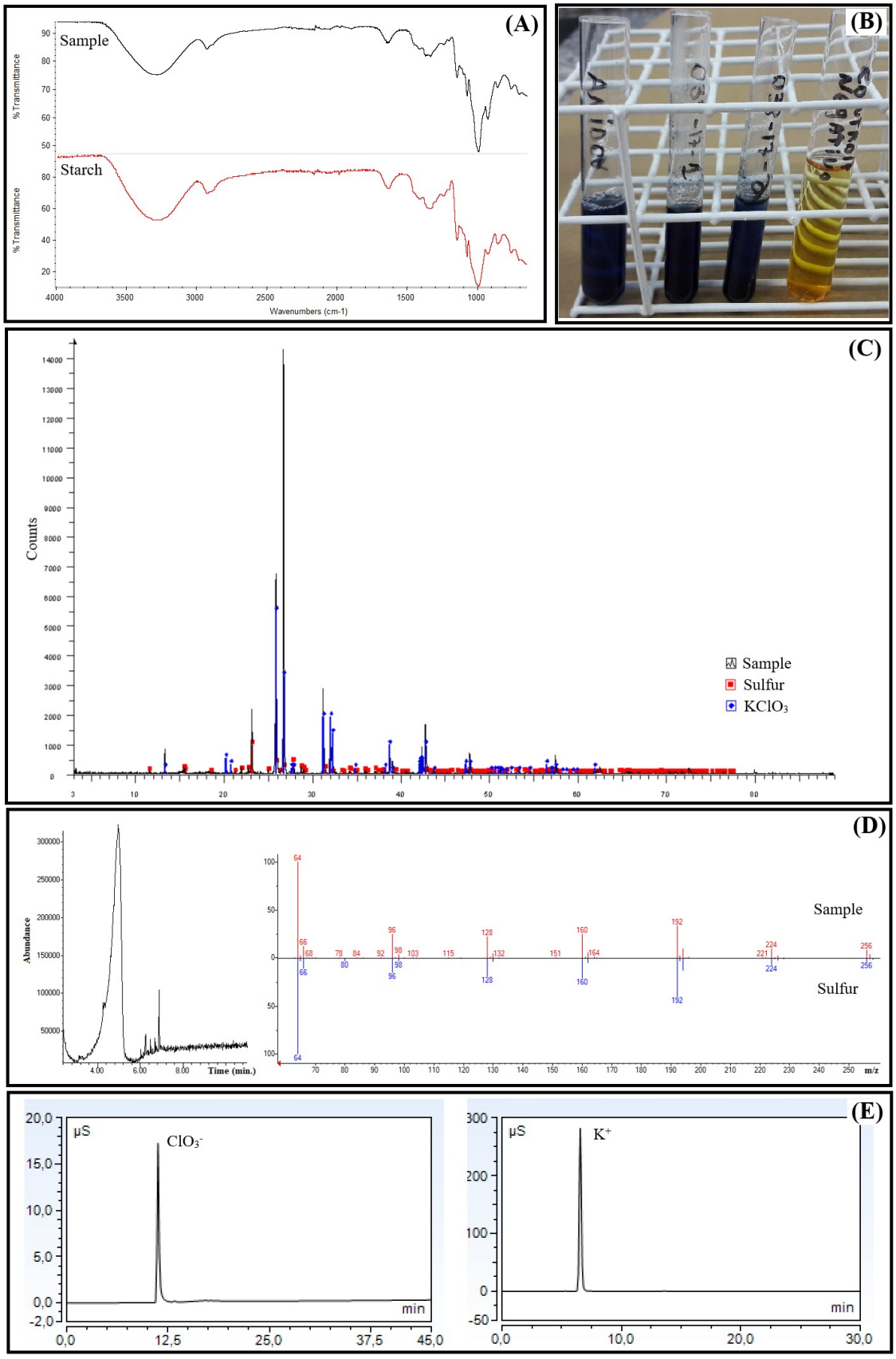

Figure 1.10. Results of analysis of an explosive mixture based on potassium chlorate, sulfur and starch from a real attempted bombing [34]. Identification of starch by FTIR (A) and iodine–starch test (B), identification of $KClO_3$ by XRD (C) and IC (E), and identification of sulfur by XRD (C) and GC-MS (D).

However, in most cases, no visible particles (bulk) remain, and therefore, post-explosion residue analyses present some additional analytical challenges due to several factors. These factors include: i) the scarcity of material; ii) the different possible matrices; and iii) the presence of environmental interference, especially when inorganic based mixtures are used as explosives, since the residues of these mixtures often contain ions that may naturally occur in the environment or in routine materials [3,4,35].

Figure 1.11 illustrates various materials collected from explosion scenes where no bulk particles were found. In such cases, the available analytical techniques for identifying analytes become limited. Typically, solvent extractions followed by analysis using chromatographic techniques or capillary electrophoresis are employed [22]. Figure 1.12 depicts typical results obtained from ion chromatography (IC) analysis [4], a widely used technique for identifying analytes in fuel-oxidizer explosive mixtures, as those listed in Table 1.2.

Figure 1.11. Examples of materials collected in post-explosion scene without the presence of bulk explosives.

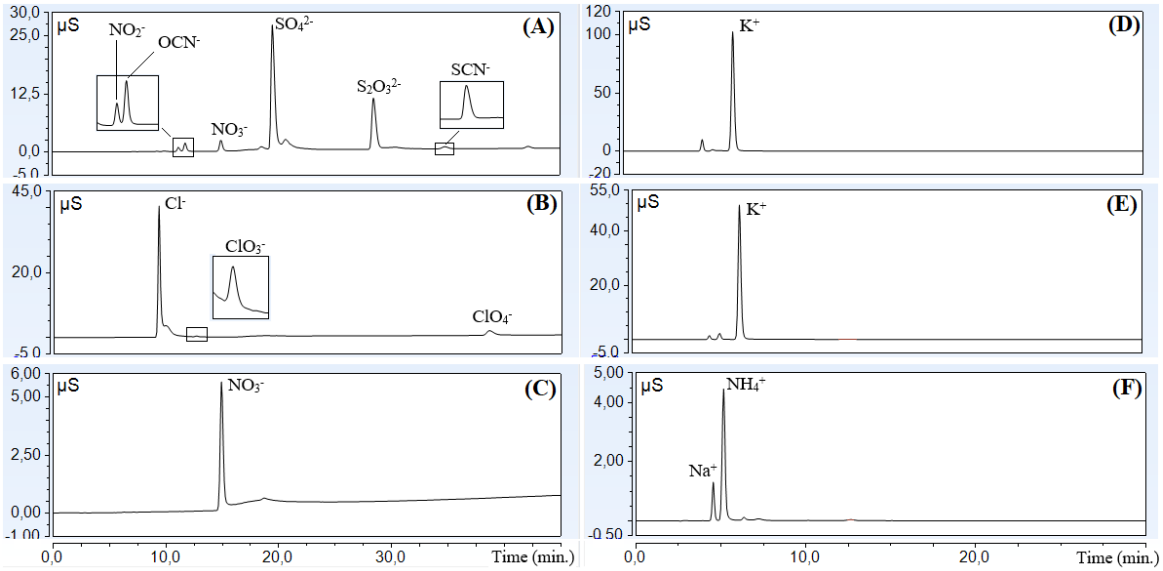

Figure 1.12. Anion exchange chromatograms of post-explosion residues from (A) black powder, (B) explosive mixture based on potassium perchlorate and (C) explosive emulsion. Cation exchange chromatograms of post-explosion residues from (D) black powder, (E) explosive mixture based on potassium perchlorate, and (F) explosive emulsion [4].

1.2.4. Extra safety precautions

Furthermore, it is important to highlight that the analysis of pre-explosion (bulk) explosives requires additional safety measures beyond the standard laboratory protocols followed by chemical professionals. This is due to the fact that certain explosives exhibit high sensitivity to shock, friction, and temperature. Therefore, analysts involved in this field should ideally possess training not only in chemistry but also in explosives, such as through EOD courses. This specialized training enables them to gain a deeper understanding of different types of explosives, their mechanisms, and common EOD procedures. By having this comprehensive knowledge, analysts can effectively handle and analyze explosives while ensuring the highest level of safety throughout the process.

Some examples of basic precautions when working with materials suspected to be explosive include: i) always work with minimal amounts of material; ii) avoid using tools that could generate sparks when handling materials; iii) exercise increased caution with analytical techniques that involve heating, pressure, and/or friction of the sample. For instance, techniques like FTIR-ATR and XRD often involve pressure during sample preparation, while RAMAN spectroscopy is capable of initiating certain types of gunpowder through heating.

Figure 1.13 illustrates one such case, showing a frame from a demonstration conducted at the Forensic Chemistry Laboratory of the National Institute of

Criminalistics. In the demonstration, a small amount of gunpowder inside a small plastic bag is initiated during Raman spectroscopy analysis using the Rigaku ResQ CQL equipment (https://youtu.be/FZFfdqn0ChI). As emphasized before, it is crucial to note that in this test, only a small amount of material was used without confinement. However, it is of utmost importance to be aware that large quantities of unknown material suspected to be explosive should never be analyzed directly, particularly when confined. Directly analyzing such materials without proper precautions can pose significant risks and should be avoided.

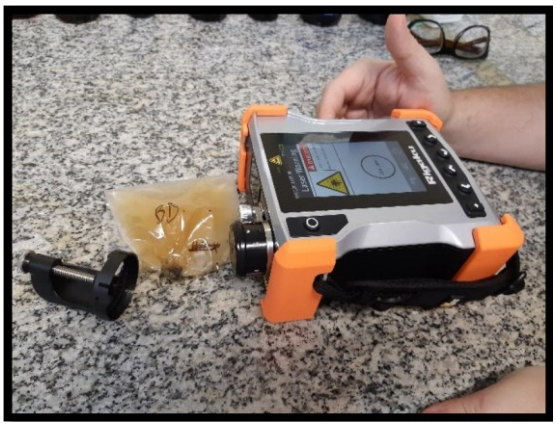

Figure 1.13. Initiation of double-base gunpowder during analysis by Raman Spectroscopy (https://youtu.be/FZFfdqn0ChI).

In the specific case of this Raman analysis equipment, additional precautions can be taken to avoid accidents, such as using the "Delay" function, reducing laser power, using samples in uncapped vials, and maintaining a safe distance when activating the laser. Another interesting precaution, when feasible, is to begin the analyses with analytical techniques that pose less risk, aiming to determine which explosive is being dealt with, and only then using techniques that are theoretically more concerning. In some cases, such as black powder, moistening a small portion of the sample to render it less sensitive can be an option in Raman analysis, as water, in this case, will not interfere with the analysis.

1.2.5. Interferents (crime scene, laboratory processing and matrices)

In the analysis of post-explosion residues for explosive mixtures based on inorganic salts (e.g., black powder, flash powders, emulsions), the presence of interferents becomes a significant concern. Unlike organic explosives, which are less commonly found in the environment, the presence of common ions (chloride, cyanate, nitrate, sulfate, thiosulfate, thiocyanate, sodium, potassium, ammonium) can pose challenges,

particularly in low concentrations of target analytes in the residues. These ions may originate from various sources, including materials used during sample collection and laboratory processing, such as cotton (swabs, discs, balls, etc.) and filters [35].

Furthermore, the wide range of potential matrices encountered in post-explosion investigations, including metallic fragments, plastic or paper casings, soil samples, fabrics, and banknotes, can introduce additional challenges in result interpretation (Figure 1.11). Therefore, having a comprehensive understanding of the materials involved and utilizing control and blank samples is of utmost importance to mitigate the risk of inconclusive or erroneous interpretation of the results [3,4].

The use of control and blank samples is crucial both during sample collection and in the subsequent analyses, as they greatly facilitate result interpretation. However, in certain situations, obtaining blanks or controls may be challenging due to failures in scene investigations or inherent difficulties related to the materials involved. For instance, it may be difficult to obtain blank swabs from suspects' hands or control samples from suspected banknotes.

Another common type of interferent in post-explosion residue samples is associated with the operations of the Explosive Ordnance Disposal (EOD) team, which is responsible for neutralizing explosive devices. Section 1.2.7 “EOD operations and interferents related to subsequent chemical analysis” will provide a more detailed discussion of these cases.

1.2.6. Unpredictable scenario and collection of post-explosion residues

The collection of materials at a post-explosion scene is a crucial stage in the overall investigation process. If not conducted properly, it can jeopardize the entire investigation, as chemical analyses performed on inadequate material can yield inconclusive or misleading results. Therefore, ensuring the quality of the collection process is of utmost importance.

The scenarios encountered at a post-explosion scene can be highly diverse and unpredictable. Explosions are uncontrolled and heterogeneous events, influenced by numerous variables including the quality and type of explosive, water content, confinement conditions, charge diameter, type and thickness of container material, presence of additives, and the expertise of the perpetrator, among others [15]. Examples of the various types of devices commonly used in criminal actions in Brazil are depicted in Figures 1.14 to 1.15.

Figure 1.14. Left – explosive device made with explosive emulsion in its original casing [36]. Right – an explosive device popularly known as “metalon”, the commercial name given to steel tubes with a rectangular profile, used in civil construction [37].

Figure 1.15. Left – explosive device made of PVC pipe [38]. Right – explosive device made with a handmade casing using plastic and string [39].

In certain scenarios, the collection of materials is straightforward and intuitive, particularly when the explosive device is not entirely consumed and leaves behind significant residues. In such cases, the identification of the material to be collected becomes easier, and the subsequent laboratory analysis with the objective of chemically identifying the explosive is facilitated, as the scarcity of material is no longer a concern.

Below are some examples of various possible scenarios extracted from Federal Police (FP) Crime Scene Reports in cases involving explosions (or attempted explosions) at ATMs. These examples aim to illustrate a range of situations, from the complete failure of the explosive device to the extensive destruction of the ATM facilities. In some cases, there may even be the presence of fatalities, further complicating the investigative work. These scenarios are depicted in Figures 1.16 to 1.20.

Figure 1.16. IED at bank branch with fuse failure preventing the initiation of the detonator and the main explosive charge [40].

Figure 1.17. Left – explosive device at bank branch with apparent failure in the main charge after initiation of the detonator. Right - detail of the failed explosive device [41].

Figure 1.18. Left – bank branch explosion with considerable part of the structure of the IED (known as "metalon") containing explosive residues. Right – details of this IED structure [42].

Figure 1.19. Bank branch destroyed by an IED [43].

Figure 1.20. Left – corpse at the crime scene after an attempted robbery at a bank branch with the use of explosives. Right – detail of two arrangements composed of fuses and detonators (known as "espoletopins"), in addition to a lighter [44].

On one hand, the partial or total failure of an explosive device can facilitate the collection process and eliminate the issue of material scarcity for chemical analysis. However, on the other hand, it introduces a new concern: the presence of a failed explosive requires the intervention of an EOD team to ensure the safety of the scene before any collection can take place. The specific procedure carried out by EOD specialists to neutralize the explosive must be taken into consideration during the collection and subsequent chemical analysis. Further details on this topic will be discussed in the next section (Section 1.2.7).

The primary objective of the crime scene team for chemical analysis purposes is to locate evidence of unreacted explosive materials. It is well-established that such evidence can persist for extended periods. For instance, oils nitroglycerine and ethylene glycol dinitrate have been recovered after being stored for five years. In the case of low explosives like black and smokeless powder, which tend to leave unreacted particles following an explosion, the evidence can remain indefinitely unless physically removed [3].

The collection of post-explosion residues involving low explosives is generally simpler and easier than high explosives. The deflagration mechanism involved in the reactions of low explosives inevitably leads to the presence of considerable amounts of unreacted particles, facilitating their collection and subsequent laboratory analysis. On the other hand, the detonation process involved in the reactions of high explosives, whose speed exceeds the speed of sound, typically leaves behind remaining unreacted particles at trace levels and invisible, making the collection and subsequent analysis more complex tasks. In this latter case, exceptions sometimes occur in low-order detonations, meaning when the explosive fails to function as intended due to failures in the firing train, inadequate mixtures, explosive quality, among other factors. This type of problem is more common in improvised explosive devices [3].

Thus, regarding the collection of samples for chemical analysis in the laboratory, in summary, the preferred materials, in order of priority, are: i) bulk explosive, ii) device casings that are in direct contact with the explosive, and iii) materials in close proximity to the explosion and hit by it. However, in many cases, it may not be feasible to send the actual material to the laboratory, particularly when dealing with large objects such as vehicles or ATMs. In such situations, swabs can be used for sampling, and it is essential to include an unused swab as a control to be sent to the laboratory.

Regarding the use of swabs, there is no single protocol used in forensic laboratories. Several studies have been conducted to achieve the best conditions for this purpose. For this, many sampling media materials and solvents (including dry swabs) have been tested for the efficient recovery of explosive residues [3,45].

As briefly discussed above, the collection of post-explosion residue depends on several factors. Effective collection is crucial to achieve accurate results in the laboratory. Given the broad scope of this field and the focus of this study on chemical analysis, it is recommended to consult the work of Alexander Beveridge for valuable insights into

collection techniques and other relevant information (Beveridge, 2011), providing a more in-depth understanding of the topic.

1.2.7. EOD operations and interferents related to subsequent chemical analysis.

In summary, EOD operations involve the detection, identification, evaluation, rendering safe, recovery, and disposal of explosive ordnance [46]. In cases where a rendering safe procedure is required, an additional concern related to the introduction of interferents into the materials must always be considered. EOD technicians often employ two main procedures to render-safe IEDs or other ordnances, which are briefly described as follows: i) countercharge, which involves using an explosive device specifically designed for destroying the suspected material, and ii) disarticulation of the device using techniques aimed at neutralizing it without detonating the explosive content. This is typically achieved using an EOD disruptor, which is a device used remotely to open or render safe a suspect item or IED, usually employing black or smokeless powder cartridges [3,47].

As both approaches involve the use of explosive materials, they have the potential to introduce interfering substances that must be taken into consideration when collecting materials for subsequent analysis [3].

Clearly, for investigative purposes, which include laboratory analysis for chemical identification, as well as fingerprinting and genetic profiling, the second approach is more advantageous. When executed successfully, it enables the collection of ample quantities of material, allowing the use of a wide range of techniques and enhancing the likelihood of identifying all components of the explosive material.

Hence, effective communication between the crime scene team and the EOD technicians is crucial to determine the most suitable approach. Even in situations where preservation of the material is not feasible and a countercharge needs to be employed, this communication remains important. The selection of an appropriate countercharge becomes significant because if the suspected explosive device and the explosive used in the countercharge are the same, the presence of this interferent can render the chemical identification conclusion infeasible.

Presented below are images depicting real examples of explosive device neutralization using a countercharge. Figure 1.21 showcases the application of explosive

emulsion as countercharge in pipe bombs, while Figure 1.22 demonstrates the use of detonating cord in a grenade.

Figure 1.21. Left – seized tube bombs. Right – same devices after positioning the countercharge (explosive emulsion) [48].

Figure 1.22. Neutralization of grenade using a detonating cord countercharge [49]. Top-left – grenade before the neutralization. Top-right – detonating cord countercharge. Bottom-left – detonating cord countercharge positioned on the grenade. Bottom-right – grenade fragments collected after neutralization.

In instances where an EOD disruptor is utilized, the primary objective is typically to disable the explosive device without triggering its detonation, with the intention of preserving evidence. However, this outcome is not always achieved. Presented below are photographs depicting real scenarios of explosive device neutralization using a disruptor. Figure 1.23 showcases a situation in which the device was successfully dismantled without detonation, thereby exposing its contents (a more favorable situation for subsequent analysis). In contrast, Figure 1.24 portrays a case in which detonation occurred (a less favorable situation for the purposes of further analysis).

Figure 1.23. Neutralization of grenades using a disruptor [50]. Left – disruptor positioned towards the grenade. Right – grenade after firing with exposure of its contents without detonation.

Figure 1.24. Neutralization of an IED using a disruptor [51]. Top-left – seized IED. Top-right – IED positioned inside a concrete shackle. Bottom-left – disruptor cannon positioned before firing. Bottom-right – shackle and device fragments subjected to chemical analysis after neutralization.

Moreover, the intervention of firefighters, particularly in situations involving post-explosion fires, can significantly alter the crime scene, posing additional challenges to evidence collection. The extensive application of water, often required in such cases, can result in material loss, further limiting the availability of residues for analysis. The use of fire extinguishers can also introduce additional complications to the scene. Consequently, these procedures can exacerbate the difficulties associated with collection, chemical analysis, and result interpretation.

The utilization of portable instruments for chemical analysis and trained explosive detection dogs can be valuable tools, particularly in more intricate cases [3].

1.2.8. Analysis methodologies

After the collection of post-explosion residues, as described in the preceding sections, the materials undergo chemical analysis in the laboratory to determine the type of explosive employed. There is no global standardization among specialized laboratories conducting such analyses. However, in general, the methodologies employed are comparable and follow a similar process, as exemplified in the flowchart provided in Figure 1.25 [3]:

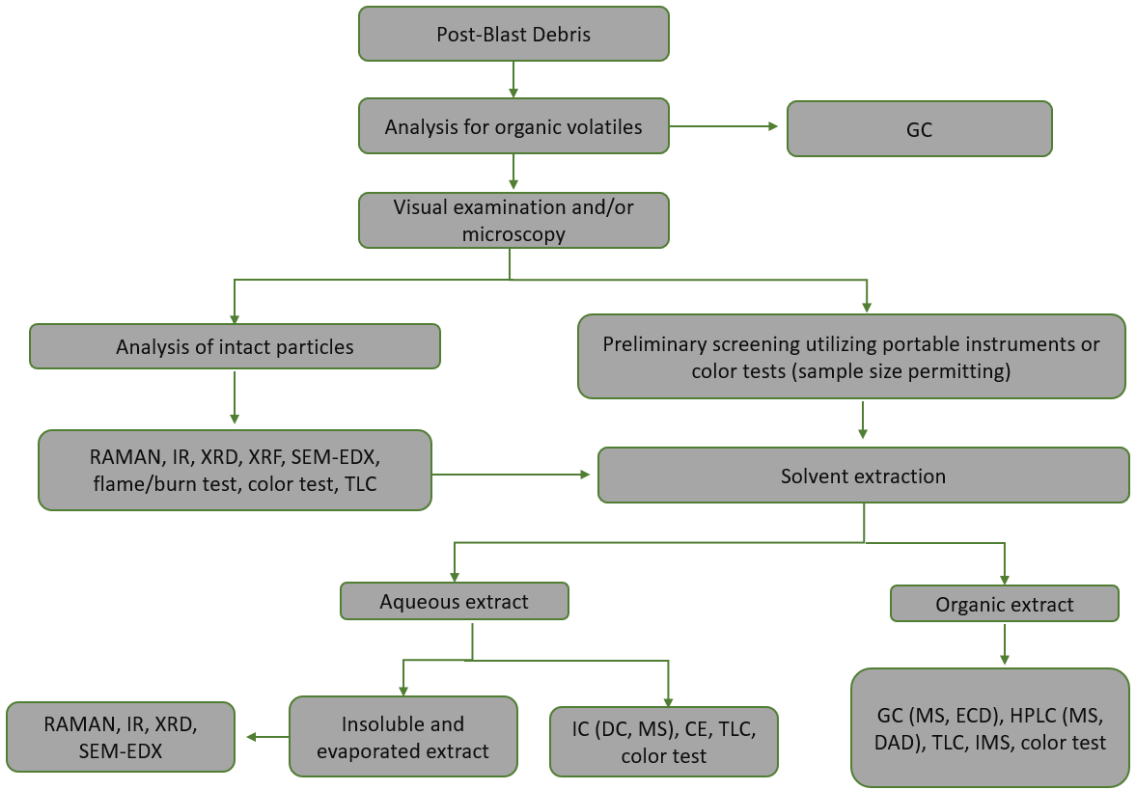

Figure 1.25. General flowchart for post-explosion residues analysis (adapted from Beveridge [3]).

As depicted in the presented flowchart, there exists a multitude of sample preparation and analytical techniques that can be applied in the analysis of explosives and post-explosion residues. The literature encompasses numerous studies utilizing this wide range of techniques, including Fourier-transform infrared spectroscopy (FTIR) [52–56], RAMAN spectroscopy [57–65], gas chromatography coupled with mass spectrometry (GC-MS) [53,56,66–69], X-ray diffraction (XRD) [70–73], scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) [53], X-ray Fluorescence (XRF) [73–78], high performance liquid chromatography (HPLC) [79–84], capillary electrophoresis (CE) [85–89] and ion chromatography (IC) [32,33,35,90–94].

Depending on the information they provide, these analytical techniques can be categorized into four groups: (1) those that provide significant structural and/or elemental information, (2) those that offer limited structural and/or elemental information, (3) those that provide a high degree of selectivity, and (4) those that are useful but do not fall into any of the other categories. Table 1.6 lists examples of these techniques provided by the Technical Working Group for Fire and Explosives (TWGFEX [24]).

Table 1.6. Categories of analytical techniques (adapted from TWGFEX [24]).

Categories 1 and 2	Category 3	Category 4
Infrared Spectroscopy (IR)	Gas Chromatography (GC)	Burn Test
Gas Chromatography/Mass Spectrometry (GC/MS)	Gas Chromatography Thermal Energy Analyzer (GC-TEA)	Flame Test
Energy Dispersive X-Ray Analyzer (EDX)	Liquid Chromatography (LC)	Spot Test
Raman Spectroscopy	Liquid Chromatography Thermal Energy Analyzer (LC-TEA)	Melting Point
X-Ray Diffraction (XRD)	Thin Layer Chromatography (TLC)	
Liquid Chromatography/ Mass Spectrometry (LC/MS)	Ion Mobility Spectrometry (IMS)	
	Polarizing Light Microscopy (PLM)	
	Stereo Light Microscopy (SLM)	

The same reference (TWGFEX [24]) also brings another interesting table in its appendix A, listing the compositions of the main explosives and the analytical techniques that can be used for the identification of each substance. This compilation is very useful because, as mentioned before, depending on the number of components in an explosive and the analytical capabilities of a laboratory, the use of more than one analytical technique is often necessary for the identification of all the analytes of interest that make up the explosive, as illustrated previously in Figure 1.10.

With the aim of providing an idea of the analytical techniques that can be used to identify the components of the most commonly used explosives in criminal actions in Brazil, Table 1.7 presents part of TWGFEX's compilation, featuring black powder, flash powder, ANFO, and explosive emulsion. The numbers presented in this table, according to TWGFEX, refer to the need or not for the use of supporting techniques for categorical identification, as follows: (1) sufficient for identification, (2) requires one more supporting technique for identification, (3) requires two more supporting techniques for identification, and (4) requires three more supporting techniques for identification.

Table 1.7. Analytical techniques for the identification of some explosive mixtures and their components (adapted from TWGFEX [24]).

Material	GC/MS	LC/MS	IR	EDX	RAMAN	XRD	GC	IC	CE	PLM	SLM	Burn	Flame	Spots	Melting Point
Black Powder											3	4			
Potassium Nitrate			1	3	2	1		3	3	3			4	4	
Sulfur	1			1		1				3	3			4	
Carbon				2						3	3	4			
Flash Powder											3	4			
Metal Fuel				1		1				3	3			4	
Oxidizer			1	3	2	1		3	3	3			4	4	
Fillers/Binders			2		2					3	3				
Emulsions											3				
Inorganic Nitrate			1	3	2	1		3	3	3	3			4	4
Oil/Wax	1		1				1								
Emulsifiers	1		2		2										
Microbaloons			2	1						1	3				
Aluminum				1		1				3	3			4	
ANFO															
Ammonium nitrate			1	3	2	1		3	3	3	3			4	4
Fuel oil	1				2		1								

In addition to the explosives and explosive mixtures mentioned, the analysis in this field may also encompass the identification of other compounds associated with explosives or fuel-oxidizer mixtures, including various additives such as stabilizers, deterrents, plasticizers, and flash inhibitors [47,95]. The identification of these additives can contribute to establishing a chemical profile that proves valuable in forensic comparisons with materials found in a suspect's residence or in other cases, thereby broadening the range of target analytes in this field.

Among the various techniques mentioned above, IC/CD stands out, particularly in the analysis of fuel-oxidizer explosive mixtures. Since its introduction as an analytical technique in 1975, IC/CD has been extensively employed for the determination of anionic and cationic analytes in various matrices [96].

In IC analyses, typical eluents consist of diluted solutions of acids, bases, or salts. The preparation of these eluents offline used to be laborious and susceptible to errors by analysts, often leading to the introduction of contaminants. However, the introduction of an automated electrolytic eluent generator in 1998 significantly simplified the application of this technique. This device enables the on-demand production of high-purity eluents using deionized water for isocratic or gradient ion chromatographic separations. Since then, this technology has gained popularity and is widely used in current practice [97].

Presently, ion chromatography encompasses various types of detectors, with one of the most commonly used being the conductivity detector (CD). In this detection

method, an eluent suppression device, known as a suppressor, is employed. The suppressor converts the eluent into a low-conductivity form while simultaneously enhancing the conductance of the target analytes. The advancement of continuously regenerated electrolytic suppressors has significantly enhanced the reliability and sensitivity of the technique by effectively eliminating counterions associated with both the eluent and analytes. Moreover, the utilization of trap columns that are continuously and electrolytically regenerated using ion exchange resins has been implemented to further enhance the performance of the technique by eliminating ionic contaminants from the chromatographic eluents [97].

This combination of electrolytic devices enables the chromatographic separation of multiple ions using solely deionized water as the mobile phase [97]. Figure 1.26 depicts a representative configuration of a contemporary IC/CD system, as illustrated in the "Dionex ICS-5000+ Ion Chromatography System Operator's Manual" [98].

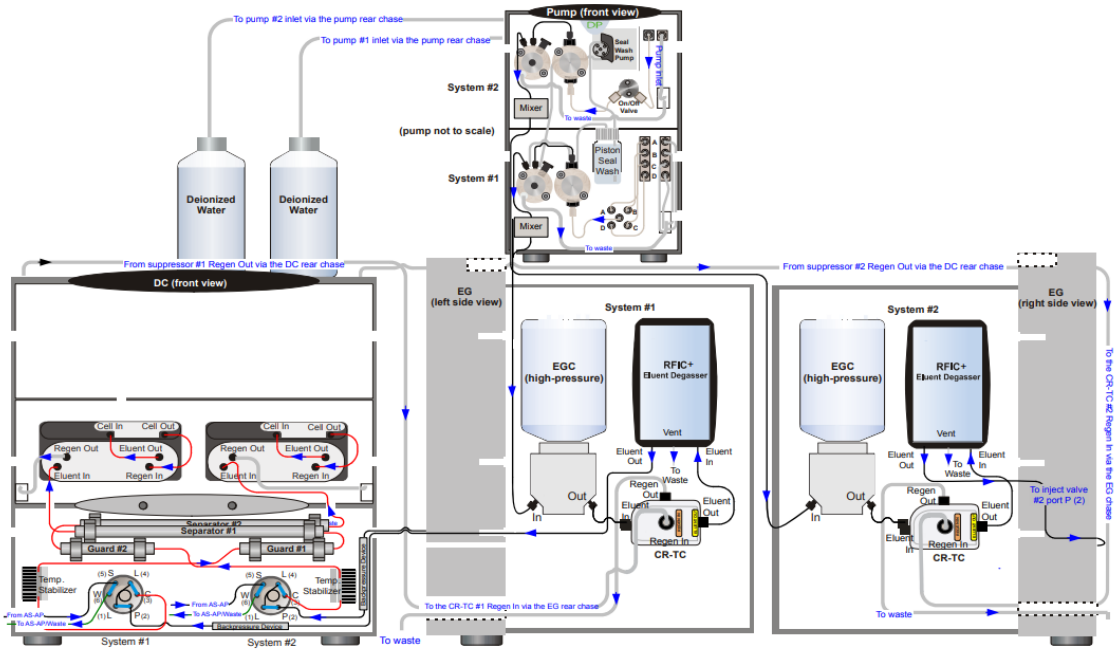

Figure 1.26. Analytical IC: Dual RFIC-EG System (CD/CD) - Dionex ICS-5000+ Ion Chromatography System Operator's Manual [98].

Another widely used technique in various areas of forensic chemistry is gas chromatography coupled with mass spectrometry (GC/MS). This versatile technique has been employed in the analysis of beverages [99–101], fingerprints [102,103], potassium cyanide [104,105], poisoning cases [106,107], food samples [108], rocks [109], pharmaceuticals [110–112], environmental samples [113], as well as in the analysis of vitreous humor for estimating

postmortem interval [114], among other applications. Therefore, it is a technique that needs no introduction as it is widely known in this field.

Specifically in the field of explosives and post-explosion residue analysis, it is also a widely used analytical technique. It is not only employed for the analysis of organic explosives, but also for the analysis of various components commonly found in fuel-oxidizer mixtures. These components include sulfur, fuel oil, vaseline, ascorbic acid, emulsifiers, among others [3,24,55,115].

All the aforementioned analytical techniques, depending on their purpose, often generate a large amount of data, as seen in the study presented in Chapter III. However, human interpretive abilities may not fully exploit this data, resulting in its underutilization or even the obscuring of hidden information instead of clarifying it [116]. Therefore, the application of chemometric methods can be beneficial for analyzing large and complex datasets, providing accurate and significant results within a shorter timeframe. There are various chemometric methods available, and each method should be chosen based on the specific type of study, such as characterization, discrimination, or model development [117].

Principal component analysis (PCA) is a fundamental and highly influential model in the field of chemometrics. It serves as a robust and versatile tool for comprehending complex multivariate data sets. PCA can be used for revealing relations between variables and relations between samples, detecting outliers, finding and quantifying patterns, generating new hypotheses and much more [118]. The primary objective of PCA is to capture the majority of the variation inherent in a given data set by reducing the dimensionality of interconnected variables into a smaller set of Principal Components (PCs) [117] . PCA has been widely employed in various forensic applications [117,119], including the analysis of post-explosion residues [120–122].

1.2.9. Conclusion

As presented, the analysis of post-explosion residues involves a wide range of explosive types, which can be prepared using substances of varied chemical natures. Additionally, it encompasses various related compounds, employs a wide variety of analytical techniques, deals with different types of matrices and environmental interferences, and faces several other challenges. Therefore, it is an area that offers great potential for studies aimed at addressing and improving the numerous difficulties encountered in routine analysis within forensic chemistry laboratories.

CHAPTER II - Profile of explosives's use in ATMs/cash safes robberies in Brazil*

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PROFILE OF EXPLOSIVES´S USE IN ATMS/CASH SAFES ROBBERIES IN BRAZIL[4]

Abstract

This retrospective study reports data obtained by the Federal Police´s National Institute of Criminalistics (INC/PF) relating to chemical analysis aimed at identifying explosives used in Automated Teller Machines (ATMs)/cash safes robberies between 2014 and 2020 in Brazil. 93 Real cases were studied and, based on the analysis carried out on the materials related to these cases, focusing on the type of explosive used, the following distribution profile was obtained: explosive mixtures based on chlorates and/or perchlorates (53%); explosive emulsion (22%); black gunpowder (13%); negative/inconclusive (11%) and organic - pentaerythritol tetranitrate (PETN) (1%). These results can contribute to investigations related to diversion/loss of explosives for criminal purposes, indicating, for example, through relationships between prevalence in the use of a certain type of explosive with a certain location, its possible origin (mining industry, explosive industries, fireworks factories, among others). The profile observed in the results can guide the selection of explosives to be studied in future research, as the possibilities are vast. Furthermore, despite the expressive number of occurrences in Brazil in the period of interest of this study, only a small fraction of samples was sent to the forensic chemistry laboratory to identify the explosive involved, which suggests that expanding chemical analysis should be encouraged in this field. In combination with an increase in professional training and collaboration trials between the laboratories, these activities can improve the chemical explosive´s profile in Brazil, enabling the search for correlations between occurrences and contributing to the growth and development of this area.

Keywords: Post-explosion Residues; Improvised Explosive Devices (IED); ATM explosions in Brazil; Chemical Profile; Crime Scene Reports; Sampling.

2.1. Introduction

Explosives are legally used in Brazil in various activities, including military, police, mining, oil prospecting, demolitions and explosions, construction of highways or railways, fireworks, industrial use (aeronautical and automotive), welding, among others. On the other hand, the illegal use of explosives in Brazil is also a reality, having been deployed in acts of terrorism, extortion (belt or bomb vest), vandalism, predatory fishing, burglaries, robberies (banks, transport of valuables, etc.) [2].

Commerce related to explosives in Brazil is extremely restricted and controlled by the Brazilian Army [13]. However, the security breaches in the mining industry, factories and fireworks distributors, as well as trade in the illegal market, facilitates the occurrence of diversions. Records of occurrences of seizures of explosives indicate an increase in these diversions from the 2000s onwards [123].

According to surveys of attacks on banks in Brazil produced by the National Confederation of Private Security Workers (CONTRASP, personal communication, 2014-2020), breaching Automated Teller Machines (ATMs)/cash safes is the most common illegal use of explosives in Brazil, and has been deployed since the first pieces of equipment were installed in the country, as the first recorded cases of this type of crime in Brazil date back to 2010 [124,125]. Such use, though, is not limited to Brazil. In several countries all over the world, various types of explosives have been used for this purpose, such as dynamite, explosive emulsions, plastic explosives, etc. This type of crime is proportionally greater in countries with a well-established mining industry [124]. In Brazil though the aforementioned situation escalated in such troublesome fashion that a new law was approved specifically to deal with this type of crime (13.654/2018), with an increase in the legal penalty it carries [126].

In Brazil, these crimes are almost exclusively perpetrated utilizing Improvised Explosive Devices (IED), such as the ones shown in Figure 2.1, prepared from readily available sources obtained in fireworks stores, building supply stores or in locksmith shops. In other instances (Figure 2.2), highly specialized materials, commonly used in activities related to mining or civil construction, are recovered during police raids or crime scenes.

Figure 2.1. Fireworks (left) seized together with "metalon" (right), trade name given to rectangular profile steel tubes used in civil construction and widely used for preparation of improvised devices in ATM/cash safes explosions [127].

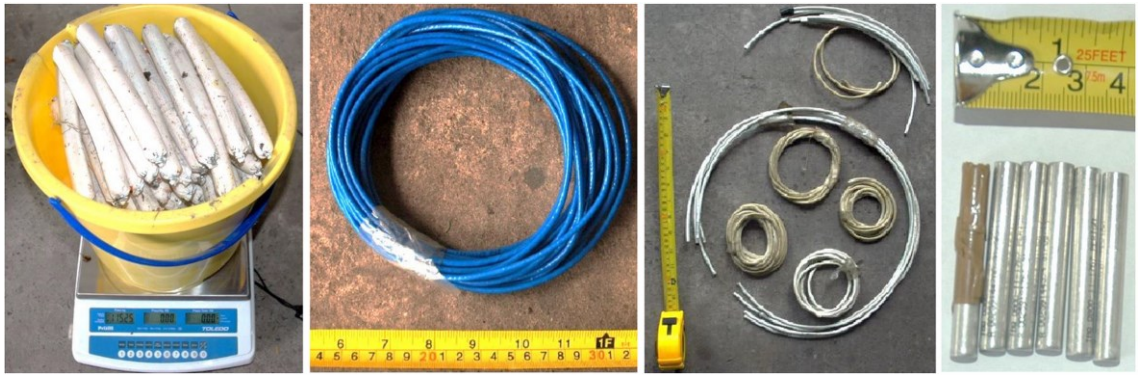

Figure 2.2. Explosive emulsions, detonating cord, fuse and primers (from left to right), part of materials suspected of being used for ATM/cash safes explosion [128].

It is worth noting that Brazil has some intrinsic characteristics that favor ATMs/cash safes theft through the use of explosives: (i) it is one of the countries with the largest number of ATMs in the world (175,947) [129,130]; (ii) it has a robust mining industry both in terms of current volume as well as future mining of ore reserves [131]; (iii) it is the second largest producer of fireworks in the world, behind China [132]; and (iv) has a large number of municipalities (5,568) [133], most of which have a precarious public security system [134], with very little policing, thus being preferential targets for various types of violent crimes, including ATMs/cash safes robberies [135].

Within the scope of the Federal Police´s responsibilities, attacks on ATMs/cash safes currently represent the majority of cases involving the use of explosives in criminal actions. Post-explosion residue detection allows investigators to distinguish between criminal and accidental explosion and to establish relationships between suspects and crime scenes in each specific case [3]. Furthermore, in a broader sense, a survey of the

different cases over time allows forensic experts to distinguish trends and to obtain information regarding the types of explosives most used in criminal actions.

Previous studies have been carried out in this area of forensic chemistry such as surveys for high explosives in public places [136,137], environmental survey relating to improvised and emulsion gel explosives [138] and background level of explosives and related compounds in the environment [139]. Other studies have focused on the identification of explosives used to breach ATM´s but were limited to specific cases [62,64,140]. To the best of our knowledge, there is no comprehensive study to date published proposing a profile on explosives used in ATMs/cash safes attacks based on chemical analysis.

Considering the preponderance of explosive´s use in ATMs/cash safes robberies and the fact that these robberies are documented as part of a report that records the number of occurrences at the national level, this work aims: (i) estimate the percentage of cases that submit collected materials to the laboratory for chemical analysis; (ii) to present the first profile of the types of explosives most commonly used in criminal attacks on ATMs/cash safes in Brazil, within the scope of the Federal Police; (iii) discuss the relevance of this information to assist intelligence services in the investigation of diversion of explosive materials from the mining industry, fireworks factories or internet purchases of ingredients. Moreover, this new information should help law enforcement agencies in making better public policy measures to prevent criminals from having access to explosive material.

2.2. Materials and methods

This is a retrospective study that congregates data obtained from the Federal Police's (PF) Criminalistics System (SISCRIM) database. Technical reports issued by federal criminal experts from January 1st, 2014, to December 31st, 2020, related to explosion cases that occurred throughout the national territory within the scope of the Federal Police, were used as source for this study.

The first step was to obtain all forensic chemistry reports related to the identification of post-explosion residues. To this purpose, searches were carried out for all reports classified as "explosive material examination report" and "post-explosion examination report". Moreover, searches using the words “post-explosion residue”,

“ATM”, “cash safe”, and “electronic box”, were performed, with all reports being examined in detail. For this study, the main focus was criminal expert reports pertaining to chemical analysis of post-explosion residues involving ATMs/cash safes attacks, since they represent the majority of cases involving the use of explosives in criminal actions and is the only category for which occurrences are officially recorded, making data on a national level readily available.

The focus of the data extraction was to obtain information regarding: (a) the type of explosive identified; (b) the year in which the attack occurred; (c) the type of support material analyzed; (d) the date the report was issued; and (e) the place where the attack occurred. For crime scene reports, the words “explosion”, “ATM”, “cash safe” and “ATMs” were used, with each result being evaluated to verify that it was a crime scene report involving attacks on ATMs/ cash safe using explosives.

2.3. Results and discussion

Data extraction revealed 127 reports classified as "Explosive Material Examination Report" and "Post-explosion Examination Report" issued between January 1st, 2014, to December 31st, 2020, referring to the analysis of post-explosion residues. Figure 2.3A shows that 73% (93 cases) are directly related to ATMs/cash safes post-explosion and in another 14% the materials are suspected of being related to robberies of ATMs/cash safes (banknotes and vehicles), totaling 87% of all cases. The remainder of the cases (13%) are distributed among IED neutralization (Bomb Squad), damage to public property and others.

Regarding the types of explosives identified in the materials originating from the ATM/cash safes which were submitted to chemical analyses, Figure 2.3B shows that explosive mixtures based on chlorates and/or perchlorates appear more frequently, representing more than half of the occurrences (53%). The use of explosive emulsion ranks second with about a quarter of the cases (22%). Black gunpowder accounts for 13% of all cases and finally organic explosives (PETN) were detected in 1% of the samples. It is interesting to note that about 11% of the cases produced a negative or inconclusive result, which is probably due to analytical challenges present in this type of analysis, such as the scarcity of material, the different possible matrices and the fact that these types of explosions are an uncontrolled and heterogeneous phenomenon, leading to the unpredictability of the post-explosion scenario to be found.

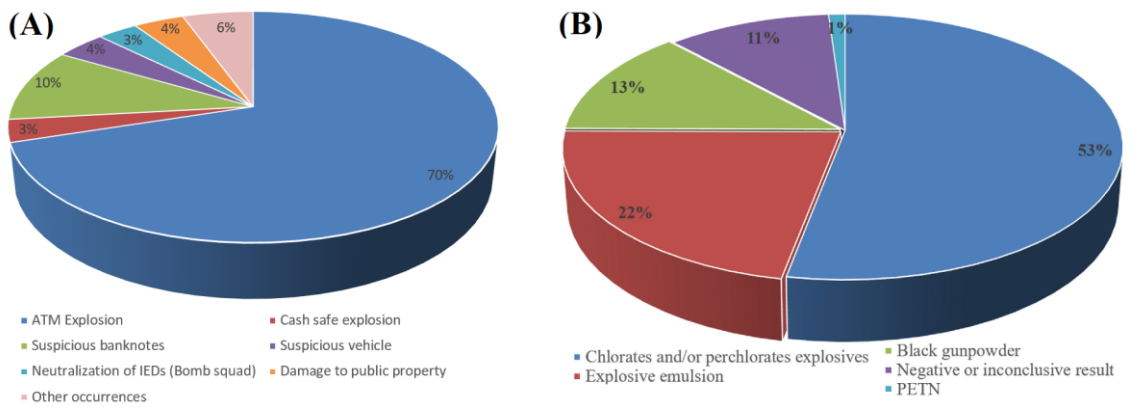

Figure 2.3. (A) Distribution of explosives occurrences according to reports studied in Brazil between 2014 and 2020. (B) Distribution of explosives identified in ATM/cash safes cases studied in Brazil between 2014 and 2020.

To determine an accurate number of explosion attacks against ATMs/cash safes in Brazil, a compiled report was obtained from the National Confederation of Private Security Workers (CONTRASP). The data was compared with the number of crime scene and laboratory reports related to ATMs/cash safes explosions data mined through active search in the Criminalística database. The results presented in Table 2.1 show that in seven years (2014-2020) a total of 5734 explosions were reported against ATMs/cash safes, almost a thousand per year. Regarding cases under the jurisdiction of the Federal Police, the study revealed that in only 13% of ATMs/cash safes post explosion crime scenes processed chemical residues were sampled and submitted to the laboratory for analysis.

It should be highlighted that, apart from the central Federal Police´s Laboratory, which is the only ISO 17025 certified laboratory in the country for explosive´s analysis, there are few states forensic laboratories that carry out chemical analyses of explosion residues. Therefore, not only does the Federal Police´s laboratory perform chemical analysis in all federal cases of interest, but it also supports state forensic labs upon request. This indicates that only a small part of the crimes related to ATMs/cash safes theft with the use of explosives in Brazil are subjected to chemical analysis for explosive identification, representing approximately 1.5% of the total number of cases.

Table 2.1. Number of explosions perpetrated against ATMs/cash safes (per CONTRASP) and reports issued of crime scene and forensic chemistry exams within the scope of the Federal Police.

Year	Explosions against ATMs/cash safes	Crime Scene Reports	Forensic Chemistry Reports	Forensic Chemistry Reports/ Crime Scene Reports	Forensic Chemistry Reports/Explosion against ATMs/cash safes
2014	1306	139	19	13.7%	1.5%
2015	1251	137	18	13.1%	1.4%
2016	1050	107	23	21.5%	2.2%
2017	952	117	20	17.1%	2.1%
2018	756	58	10	17.2%	1.3%
2019	269	38	1	2.6%	0.4%
2020	150	25	2	8.0%	1.3%

Figure 2.4 emphasizes the unpredictable nature of ATM explosion scenarios, where the device successfully detonated and breached ATM 3, but failed to detonate in ATM 2, further complicating Crime Scene analysis on site. Also, as there are many variables involved, such as the quality, type, and degree of containment of the explosive, it is often very difficult to carry out an effective residue collection without specific training for post-explosion scenes processing.

Figure 2.4. ATM post-explosion site, identified as ATM 3 (right), and detail of failed explosive device inserted in ATM 2 dispenser (center) [41].

Another relevant factor that can contribute to inconclusive results is the usual absence of control or blank samples sent to the laboratory alongside the questioned materials. The presence of environmental ions, especially in cases involving inorganic based explosives (explosive mixtures based on chlorates and/or perchlorates; explosive emulsion and black gunpowder), which, as shown, represent the vast majority of the cases studied (88%), might make result interpretation a complex dilemma, especially in cases of low concentrations of analytes, since residues of inorganic explosives, in general,

consist of ions that can be naturally present in the environment [3] and in routinely used materials [35]. In general, environmental control samples should be collected from apparently uncontaminated areas adjacent to the explosion scene, such as building products and chemical fire extinguishers [3], in addition to sampling and pre-processing materials (swabs, cotton balls/rolls/discs and syringe) [35]. These control samples allow for a comparison with the questioned samples and makes it easier to interpret analytical results. Furthermore, in a considerable part of the ATMs/cash safe explosions cases, the destruction may also affect the structure of the building. Thus, the entire environment, including parts of the ATMs/cash safe, are quite contaminated with the "dust" from the physical structure of the building (masonry walls, plaster ceiling, etc.), containing a variety of inorganic species whose presence can complicate result interpretation. Therefore, both the ATMs/cash safes fragments and the swabs used to collect the residues sent to the laboratory may contain these contaminants, being the control samples of fundamental importance for comparisons and to avoid misinterpretation of the results.

Table 2.2 illustrates three examples of the most common explosives´ mixtures used in Brazil and the major target ions in post-explosion residues chemical [12,23,32] .It should be noted that in the analysis of post-explosion residues, it is of the utmost importance to identify not only the primary products, but also the byproducts and the original explosive mixture, since it is rarely completely consumed.

Table 2.2. Common explosive mixtures used in Brazil and major target ions in post-explosion residues.

Explosives	Composition	Major target ions in post-explosion residues
Black Powder	KNO_3, C, S	SO_4^{2-}, NO_2^-, NO_3^-, $S_2O_3^{2-}$, SCN^-, OCN^-, K^+
Flash powder	$KClO_4$, Al	Cl^-, ClO_4^-, ClO_3^-, K^+
Explosive emulsion	NH_4NO_3, generic fuel oil	NH_4^+, Na^+, NO_3^-

During the reports review, it became clear that in the majority of cases, chemical analyses were performed using ion chromatography with electrical conductivity detector (IC/CD) and liquid chromatography coupled to tandem mass spectrometry (LC/MS/MS). In a few cases, when there was enough material, other analyses were carried out, such as gas chromatography coupled to mass spectrometry (GC/MS), Fourier transformation infrared spectroscopy (FTIR) and Raman spectroscopy. Figure 2.5 displays an example of the typical results obtained by means of IC/CD analysis of post-explosion residues of the most commonly identified explosives in Brazil as illustrated in Table 2.

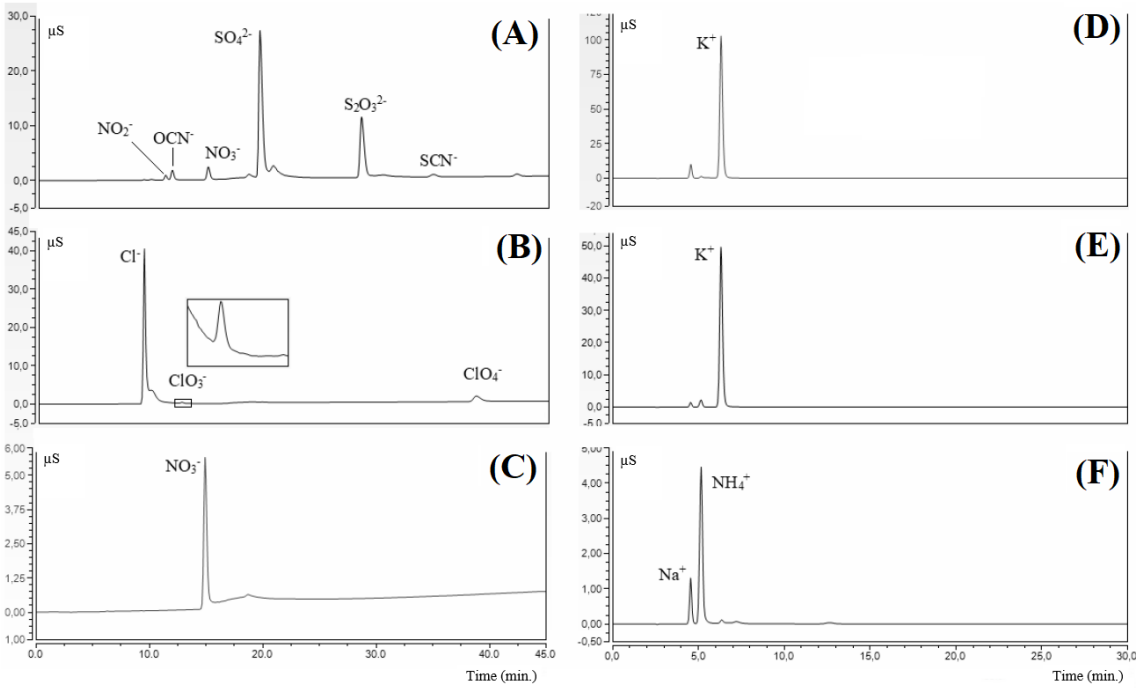

Figure 2.5. (A) Anion exchange chromatograms representative of post-explosion residues of black powder, (B) explosive mixture based on potassium perchlorate, (C) explosive emulsion and (D) cation exchange chromatograms representative of black powder post-explosion.

Figure 2.6 displays examples of typical results obtained on a real case of post-explosion of explosive emulsion, when there is bulk material that allows the analysis to be performed by FTIR, Raman and GC/MS (Figures 6A, 6B and 6C, respectively). For FTIR, the most important and characteristic bands are related to NH_4NO_3 in 3233 cm^{-1}, 3061 cm^{-1}, 1754 cm^{-1}, 1408 cm^{-1}, 1299 cm^{-1}, 1041 cm^{-1}, 826 cm^{-1} and 3061 cm^{-1} [55]. The Raman spectrum is simpler than the FTIR, consisting predominantly of two characteristic signals for NH_4NO_3 in 1044 cm^{-1} and 712 cm^{-1} [64] and GC/MS (with the identification of mixtures of hydrocarbons - mostly n-alkanes - characteristic of fuel oil commonly used in explosive emulsions).

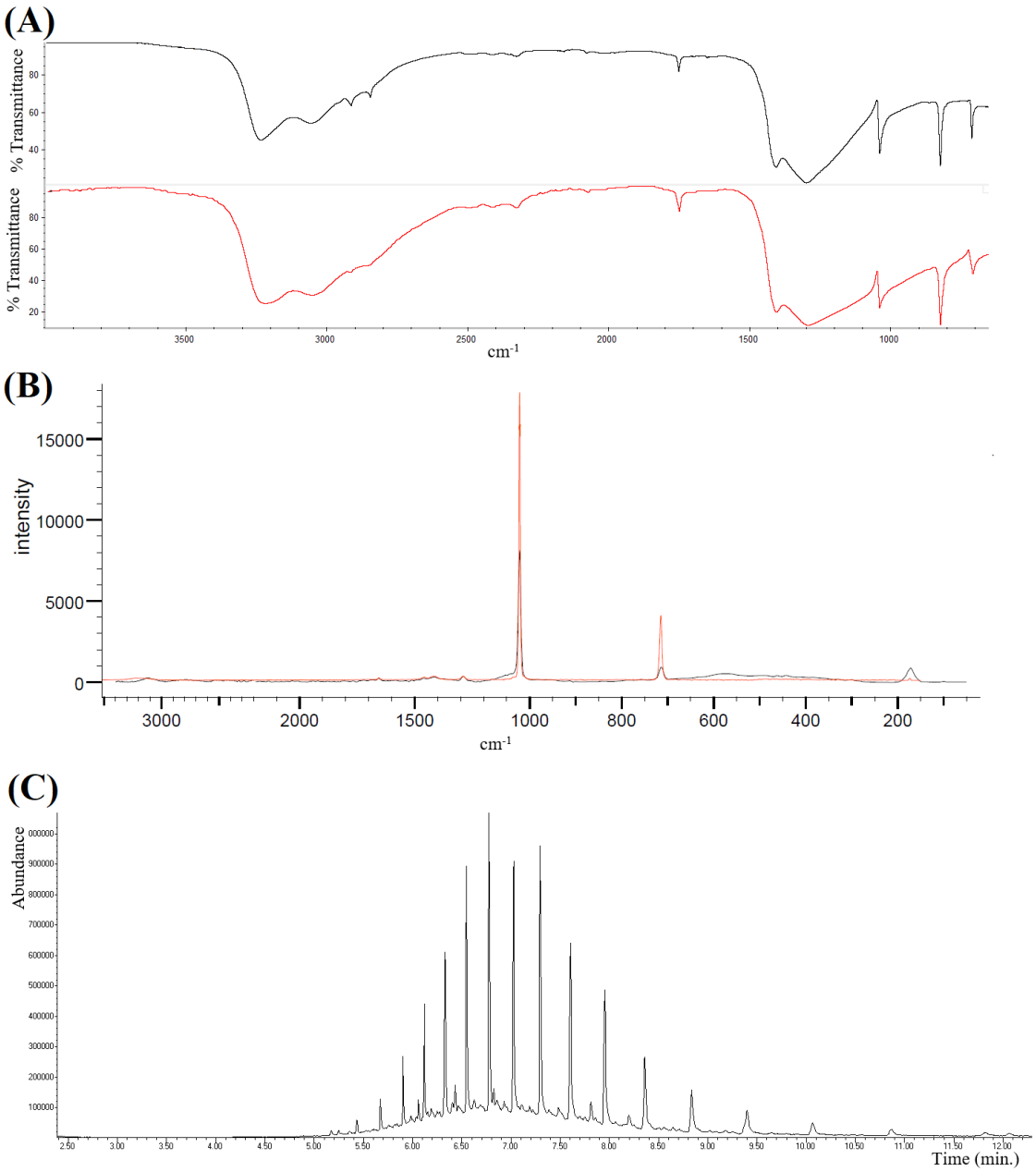

Figure 2.6. Typical results for (A) FTIR and (B) Raman obtained from a real case of post-explosion of explosive emulsion (black lines), with the identification of NH_4NO_3 (standard spectra – red lines). (C) Results of the GC/MS analysis presenting the typical profile for mixture of hydrocarbons - mostly n-alkanes - characteristic of fuel oil commonly used in explosive emulsions.

As previously described, unfortunately the results obtained are not always "clean" chromatograms, without the presence of unrelated ions, as shown in Figure 2.5. Figure 2.7 shows the results by means IC/CD of a real case, without a control sample, and despite the presence of the ions Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+ e K^+, result interpretation becomes quite difficult. Usually, the interpretation is based on the analysis of the whole profile of the ions of interest, and not the isolated analysis of each ion. Therefore, in cases where

no ion of interest stands out in relation to the others, interpretation can become quite difficult and often unfeasible in the absence of the control sample.

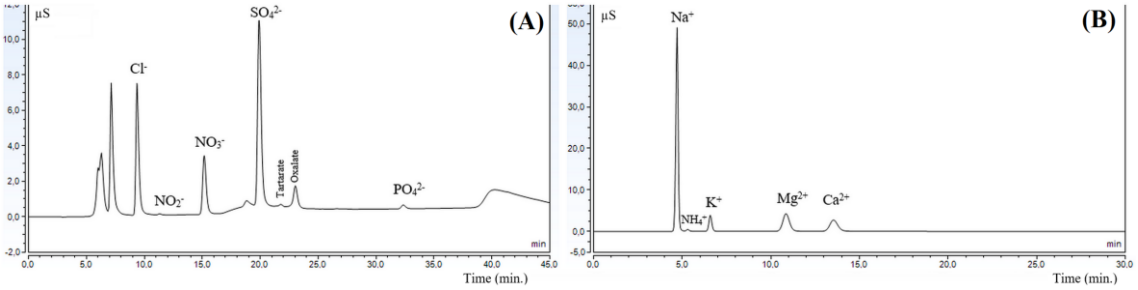

Figure 2.7. (A) Anion exchange chromatogram and (B) cation exchange chromatogram of a real case of post-explosion residue analysis in which no ion of interest stands out in relation to the others, making interpretation difficult, especially in the absence of a control sample.

Another finding of this study is that a considerable part of the ATM/cash safes cases studied come from the state of Minas Gerais, representing 43% (38 cases) of all post-explosion residue analysis in the period of this study, as shown in Figure 2.8A and 2.8B. This result is, nonetheless, unsurprising and is consistent with the CONTRASP data for this type of occurrences in the country, as Minas Gerais lead this list for two consecutive years (2016 and 2017) and is among the top three in the other years of the study period (2014, 2015, 2018 to 2020). This result agrees with fact that Brazil has a very regionalized industrial fireworks hub, where 96% of the factories are concentrated in the State of Minas Gerais, especially in the city of Santo Antônio do Monte, one of the largest fireworks production centers in the world [132] (highlighted in green in Figure 2.8B). Black powders and mixtures based on chlorates and/or perchlorates are widely used for fireworks manufacture and, perhaps not a coincidence, 27 (71%) of the cases analyzed from the State of Minas Gerais used explosive mixtures based on chlorates and/or perchlorates, while only in 16% and 11% of the cases black powder and emulsion were used as the explosive, respectively (Figure S2.1).

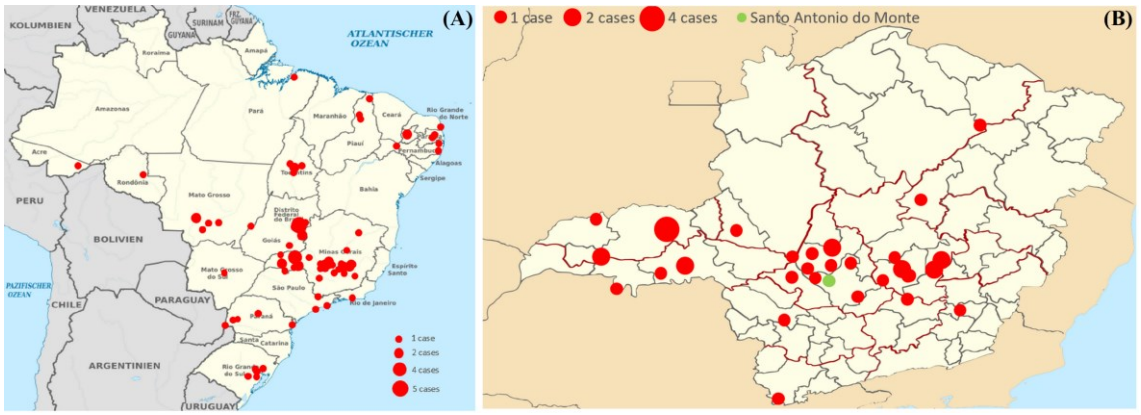

Figure 2.8. (A) Distribution of ATMs/cash safes explosion cases in Brazil submitted to chemical analysis between 2014 and 2020. (B) Distribution of ATMs/cash safes explosion cases in Minas Gerais submitted to chemical analysis between 2014 and 2020. Highlighted in green city of Santo Antônio do Monte.

Additionally, the distribution of ATMs/cash safes explosion cases and (per CONTRASP) in Brazil submitted to chemical analysis between 2014 and 2020 and the distribution of forensic chemistry reports for ATMs/cash safes explosions occurrences according to reports studied in Brazil in the same period by state are presented in Figures S2.2 to S2.5 (Appendix A), respectively.

2.4. Conclusions.

This study represents the first survey carried out in Brazil to create a profile of the types of explosives used in ATMs/cash safes robberies in the country as a whole and by region. The results showed that only a small part of the crimes related to ATMs/cash safes theft with the use of explosives is subjected to chemical analysis for explosive identification. Furthermore, a non-negligible part of the cases was reported as inconclusive and/or negative (11%), which reveals room for improvements in the post-explosion crime scene processing, sample collection and packaging procedures, so that samples from most cases are sent to the laboratory for chemical analysis, accompanied by control samples.

The last three years of the study period (2017 to 2020) reveal a downward trend in the number of crime scene reports involving explosions in ATMs/cash safes, making it even more relevant that a greater number of cases should be submitted to analysis to identify and subsequently monitor the types of explosives being used in these criminal actions.

The information generated by the chemical analysis of explosives used in attacks on ATMs/cash safes, in conjunction to the local characteristics of each state, such as the presence of establishments that produce, use or sell explosive materials (especially explosives and fireworks manufacturing industries, stores and mining or civil construction activities), may be highly relevant in supporting investigations related to possible deviations/loss of these materials. Using this information, forensic intelligence would, in theory, be able to restrict the number of investigative possibilities, as the different types of establishments generally work with different types of explosives. Preliminary analysis of the available data suggests that there might be a direct relation between the use of explosive mixtures based on chlorates and/or perchlorates in attacks on ATMs/cash safes and the abundant presence of fireworks manufacturers in the State of Minas Gerais. However, only with a larger number of cases being submitted to the laboratory could this hypothesis be confirmed.

We hope these results will encourage the Post-Explosion Forensic Units to collect material for chemical analysis and to participate in training and collaborative trials in this field of study. Not only better training and knowledge would help improve case solution, it would certainly also be relevant to improve the profile map of the explosive types used over time and its geographic distribution in Brazil. Training initiatives have been carried out periodically through courses offered by the INC-PF to PF and state criminal experts, but actions to disseminate results and institutional cooperation can catalyze new collaborations that contribute to the growth and development of research in this field.

CHAPTER III - Assessment of banknotes as a matrix for detecting post-explosion residues of fuel-oxidizer explosive mixtures using ion chromatography.

ASSESSMENT OF BANKNOTES AS A MATRIX FOR DETECTING POST-EXPLOSION RESIDUES OF FUEL-OXIDIZER EXPLOSIVE MIXTURES USING ION CHROMATOGRAPHY

Abstract

Banknotes are commonly subjected to chemical analysis in forensic laboratories in the search for post-explosion residues. This matrix presents unique challenges due to the potential presence of target analytes resulting from everyday use, as well as the lack of control samples for comparison. In addition to their relevance in attacks against Automated Teller Machines (ATMs), banknotes are of significant interest when confiscated from suspicious individuals, vehicles, and locations, as they can provide valuable evidence in establishing a connection to this type of crime scene. In such cases, the absence of bulk particles, alternative materials, and control samples is common. This study employed ion chromatography to analyze uncirculated, circulated, and seized banknotes, aiming to determine their ionic profiles. This investigation provides insights into the background levels of target ions in banknotes and aids in the analysis of post-explosion residues. A simple, fast, and precise extraction method was proposed, yielding RSD values below 10% for most analytes in uncirculated banknotes. The study revealed the presence of various ions of interest, some in significant concentrations, even in uncirculated banknotes. PCA analysis demonstrated a clear separation of uncirculated notes based on their banknote value. However, this clustering behavior was not observed in circulated banknotes due to natural variations in analyte concentrations. Interestingly, when uncirculated, circulated, and seized R$ 100 banknotes were analyzed together, the seized samples from an ATM robbery showed a distinct separation from the other groups, indicating the potential for developing classification models.

Keywords: Post-explosion residues, Banknotes, ATM explosions, Chemometrics, Ion Chromatography, Principal Component Analysis (PCA).

3.1. Introduction

The analysis of explosives and post-explosion residues is a critically important area in forensic chemistry, providing crucial insights into various incidents involving the use of explosives. This type of analysis plays a key role in addressing fundamental questions related to the crime, including: i) Was there an explosion? ii) What was the cause of the explosion? iii) Who was responsible for the explosion? iv) Are there any indications of a clandestine explosives production facility? v) Can any patterns or trends be identified? [3,4].

According to a previous study conducted by our research group, in Brazil, most cases involving the use of explosives are targeted against Automated Teller Machines (ATMs). This issue is also prevalent in several other countries worldwide [4]. The study further revealed that these crimes predominantly involve the use of Improvised Explosive Devices (IEDs) based on black powder, mixtures containing chlorate and/or perchlorate salts, and explosive emulsions [4].

Figure 3.1 depicts the unpredictable nature of scenarios resulting from this type of crime, which can vary from the failure of the explosive device with minimal damage to the complete destruction of bank branches, causing significant structural damage. This unpredictability arises from various factors, including the type, quality, and containment of the explosive used, the expertise of the perpetrator, and the structural characteristics of the ATM location [15].

Figure 3.1. Unsuccessful ATM explosion attempt (left) [141], effective ATM explosion with relative level of destruction (center) [142] and ATM explosion with high level of destruction of a bank branch with damage including its building structure (right)[143].

All these diverse variables introduce varying levels of complexity in both the investigation of explosion scenes and the subsequent laboratory analysis of post-explosion residues. When bulk material is available, a wider range of analytical techniques can be employed, resulting in more robust findings and mitigating potential

issues related to matrix interference. Examples of analytical techniques commonly used in these cases include Raman microscopy [4,62,64,144], FTIR [4,54,145], GC/MS [4], and DART/MS [146].

Figure 3.2 presents an illustrative example of typical results obtained from the analysis of post-explosion residue in a real case involving an explosive mixture containing potassium chlorate and sulfur, when there is bulk material for analysis using FTIR and GC/MS techniques [147]. In the FTIR analysis, the most significant and distinctive bands are observed at wavenumbers 955 cm^{-1}, 933 cm^{-1}, and 613 cm^{-1}, which are characteristic of $KClO_3$ [52]. In the GC/MS analysis, the mass-to-charge ratio (m/z) signals at 256, 224, 192, 160, 128, 96, and 64, corresponding to the main peak in the chromatogram, are indicative of elemental sulfur [148].

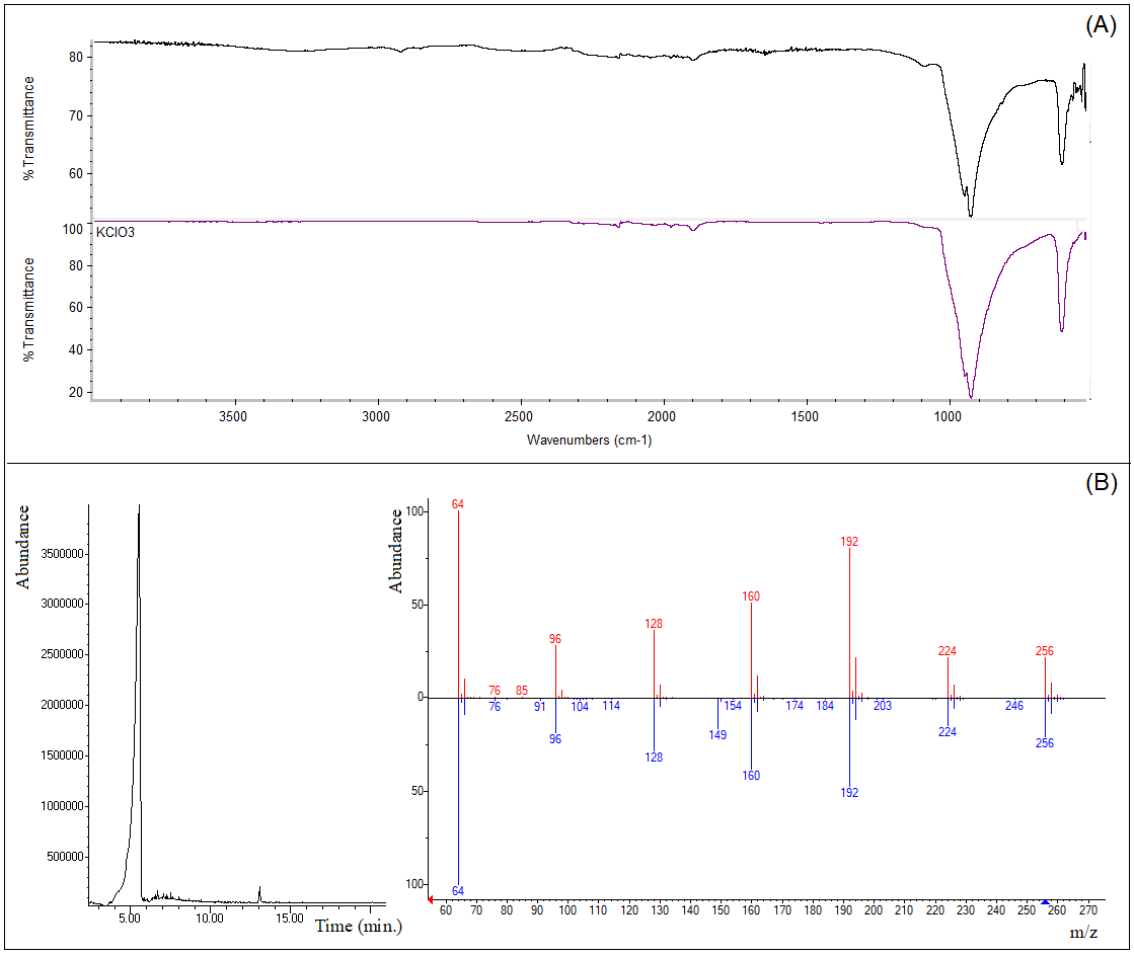

Figure 3.2. Typical results of a post-explosion analysis of an explosive mixture based on $KClO_3$/sulfur from a real case obtained through (A) FTIR (black line) with the identification of $KClO_3$ (standard spectra – purple line) and (B) GC/MS with the GC peak (left in black line) and the corresponding mass spectrum (right in red) with the identification of sulfur (standard spectrum – blue) [147].

Nevertheless, in some cases of explosions, only invisible residues may be left at the crime scene, necessitating solvent extractions for analysis and using a more limited set of techniques. Among these techniques, ionic chromatography with conductivity detection (IC/CD) is the most employed worldwide for the identification of inorganic components present in explosives [23,32,33].

In the analysis of post-explosion residues using IC/CD, the objective is to identify the ions present in the original composition of the explosive mixture, as well as ions of substances formed during the explosive reaction. The interpretation of the ionic profile obtained from the analysis of cations and anions is evaluated to reach a conclusion regarding the identification of the explosive. Table 3.1 provides information on the original components and the main analytes of common fuel-oxidizer explosive mixtures frequently employed in ATM robberies in Brazil, including black powder, $KClO_3$-based mixtures, and explosive emulsion [3,12,23,32].

Table 3.1. Common explosive mixtures used in Brazil and major target ions in post-explosion residues.

Explosives	Composition	Major target ions in post-explosion residues
Black Powder	KNO_3, C, S	SO_4^{2-}, NO_2^-, NO_3^-, $S_2O_3^{2-}$, SCN^-, OCN^-, K^+
$KClO_3$/sulfur-mixture	$KClO_3$, sulfur	Cl^-, ClO_4^-, ClO_3^-, K^+, SO_4^{2-}
Explosive emulsion	NH_4NO_3, fuel oil	NH_4^+, Na^+, NO_3^-

As depicted in Table 3.1, except for explosive emulsion, the presence of potassium cation (K^+) is detected, which is prevalent in the majority of our cases. Potassium salts are commonly used in pyrotechnic products due to their low hygroscopicity. However, salts of other cations, such as lithium (Li^+), sodium (Na^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), can also be utilized for this purpose and should be considered as possible analytes of interest, although less frequently encountered [12].

Figure 3.3 illustrates typical results of IC/CD analyses conducted on residues of each of the explosives listed in Table 3.1, highlighting the identification of the main ions of interest: chloride (Cl^-), chlorate (ClO_3^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-), cyanate (OCN^-), potassium (K^+), ammonium (NH_4^+) and sodium (Na^+), depending on the composition of the explosive.

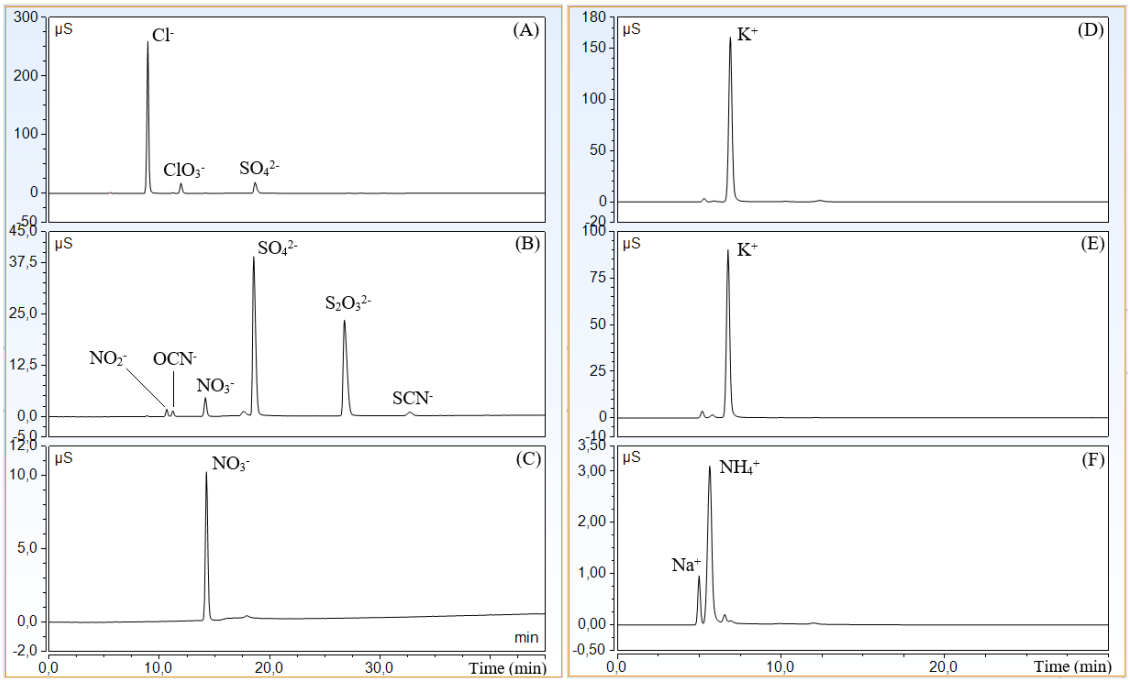

Figure 3.3. Typical anion (left) and cation (right) exchange ion chromatograms of post-explosion residues of an explosive mixture based on potassium chlorate and sulfur (A, D), black powder (B, E) and explosive emulsion (C, F).

As indicated in Table 3.1 and Figure 3.3, most analytes are common ions that can originate from sources other than explosives, including their natural occurrence in the environment [3,12,23,32], materials commonly used in evidence collection and laboratory sample processing [35], and even the materials that support post-explosion residues themselves. Therefore, in cases where the analytes are present in very low concentrations in the analyzed materials, the inherent presence of ions of interest and other interfering substances in the samples becomes a significant concern.

For this reason, when analyzing post-explosion residues, especially those involving fuel-oxidizer explosive mixtures, it is crucial to have knowledge about the various materials involved, such as matrices, sampling and laboratory materials. This understanding facilitates the interpretation of the obtained results. While some studies have investigated background levels of these target analytes in various locations/matrices [136–139], and sampling materials commonly used in routine laboratory practices [35,94], no specific study has been conducted to determine the background levels of these analytes in a crucial matrix for this type of analysis: banknotes. This is particularly relevant in regions where ATM explosions are frequent.

An ATM explosion often leaves various types of trace evidence, allowing for the collection of multiple materials at the post-explosion scene. These materials may include fragments of plastic, metal, and paper from Improvised Explosive Devices (IEDs) or objects/structures affected by the explosion. Additionally, it is possible to collect soil, clothing, banknotes, swabs, and cotton balls or disks impregnated with residues. The collection of multiple types of materials generally increases the chances of obtaining results that enable a simpler and more conclusive interpretation, as it allows for the selection of more suitable materials that are less prone to interference issues.

Nevertheless, there are instances when the banknotes seized for forensic analysis do not come directly from the explosion scene but are obtained from suspicious individuals, vehicles, properties, or found abandoned on the street. These banknotes can be submitted to the forensic laboratory with the aim of establishing a connection to criminal activities involving ATM robberies using explosives. Unlike in post-explosion scenes, in these cases, there is often not more than one type of material, but rather only the banknotes. In these situations, the lack of control samples (blanks), coupled with the inherent presence of target analytes even in banknotes unrelated to ATM robberies, poses a significant challenge in interpreting the results of the analysis. Figure 3.4 illustrates some real cases involving the collection of banknotes for post-explosion residue analysis.

Figure 3.4. Examples of banknotes seized in different situations and sent to the laboratory for post-explosion residue analysis: ATM post-explosion scene (left)[149], suspect vehicle (center) [150], suspect banknotes found on the street (right) [151].

Some studies have focused on identifying explosives in banknotes through direct analysis of bulk particles [62,64,152]. However, the analysis becomes considerably more challenging when bulk particles are absent, requiring prior extractions. In such cases, the background level of target analytes present in the banknote matrix becomes highly relevant. Based on our experience, this is the most common scenario, particularly when the banknotes are not directly obtained from post-explosion locations but from suspicious individuals, vehicles, or locations. As previously mentioned, the limited presence of

residues and the impracticality of collecting control samples greatly hinder the interpretation of results through direct observation of ion chromatograms.

Chemometric models can be useful for data analysis of complex matrices containing interferences or variations from different sources [153]. The application of these models is quite popular in spectroscopy and have been applied to help explosive analysis in near infrared [154], laser-induced thermal emission [155] and laser-induced breakdown spectroscopy data [156]. However, the application of chemometrics for the analysis of ion IC/CD data is scarce, probably because the chromatograms usually present very good resolution and a lower number of peaks in comparison with other chromatographic techniques, which leads to univariate analysis. To the best of our knowledge, no study has been reported applying multivariate analysis to explore the IC/CD data of banknotes involved in post-explosion cases.

In this context, this chapter presents an exploratory study that examines the viability of using IC/CD analysis to identify banknotes containing post-explosion residues. Furthermore, a simple, fast, and precise water extraction method was proposed to enable the analysis of the target analytes usually present in post-explosion cases. The study clarify the background level of target ions that can be detected through water extraction in uncirculated, circulated, and seized banknotes containing post-explosion residues. The exploratory and pattern recognition analysis of the data was performed using principal component analysis (PCA).

3.2. Materials and methods

3.2.1. Reagents and materials

A total of 166 real banknotes were included in the analysis. This comprised ten uncirculated banknotes and fifteen circulated banknotes for each denomination, including R$ 2, R$ 5, R$ 10, R$ 20, R$ 50, and R$ 100. Additionally, sixteen seized banknotes of R$ 100 were included in the study. The uncirculated banknotes were obtained from the Banco do Brasil branch of the Central Bank of Brazil, while the circulated banknotes were collected randomly from various tolls and commercial establishments in Brazil. The suspected banknotes were obtained through a seizure conducted by the Federal Police.

Standard ion solutions were prepared following the procedures of the Forensic Chemistry Laboratory of the National Institute of Criminalistics of the Federal Police,

which is certified according to ISO 17025, including the analysis of post-explosion residues within its scope. Anion standard solutions were prepared from a 500 mg/L stock solution prepared from sodium salts ((chloride (Vetec Ltd.), chlorite, perchlorate, nitrite (Sigma-Aldrich Ltd.), sulfate (Cinetica Ltd.), thiosulfate (Carlo Erba Ltd.), nitrate (QEEL Ltd.) and chlorate (Baker Ltd.)) and potassium salts ((thiocyanate (Vetec), cyanate (Sigma-Aldrich Ltd.)). Cation standard solutions were prepared from a commercial stock solution ((Dionex Six Cation-II Standard (lithium - 50 mg/L, sodium - 200 mg/L, ammonium - 250 mg/L, potassium 500 mg/L, magnesium - 250 mg/L and calcium - 500 mg/L)). All standards solutions and extracted samples were prepared using ultrapure water (18, 2 MΩ cm at 25 ºC) obtained from a Millipore Direct-Q5 purification system.

3.2.2. Instrumentation

Ion chromatography was performed with a Thermo Scientific Dionex ICS-5000 Ion Chromatography System with self-regenerating electrolytic suppression and AS-AP Autosampler. The anion separations were performed in a Dionex IonPacTM AS19 column (2 x 250 mm) using a EGC eluent generator configurated with a potassium hydroxide (KOH) eluent cartridge, operating in multi-step gradient mode, starting from 10 mM (0 min) to 45 mM (40 min), whereas the suppressor current was set to 28 mA. For cation separations, a Dionex IonPacTM CS12A column (2x250 mm) was operated under an isocratic condition, 20 mM (30 min) methane sulfonic acid (MSA) generated in-situ from reagent water with EGC eluent generator using an MSA cartridge, and the suppressor current was set to 15 mA. The temperatures of the column and detector cell were held at 30 ºC and 25 ºC, respectively. A loop size of 10 mL and constant flow rate of 0.25 mL/min for both methods. After each run, approximately 2 mL of pure milli-Q water (18,2 MΩ cm a 25 ºC) was pumped into the column to avoid cross contamination. Instrument control and data acquisition were performed using Chromeleon® software.

Two calibration curves were prepared for each analyte (except for sodium and cyanate), one for low concentrations and another for higher concentrations (Figures S3.1 to S3.4). Only linear determination coefficients (R^2) over 0.99 were used. The limit of detection (LOD) and limit of quantitation (LOQ) were calculated through linear regression method, using the Eq. 1 [157]:

$$\text{LOD or LOQ} = \frac{\text{F x SD}}{\text{b}} \quad (1)$$

Where F are the factors 3.3 or 10 for LOD or LOQ, respectively; SD is the residual standard deviation of the linear regression; and b is the slope of the regression line, both for low concentrations curves. The resolutions were calculated by the Chromeleon software, according with the equation:

$$R = 2 \text{ x } \frac{t_{ref\ peak} - t_r}{BW_{ref\ peak} + BW_r} \quad (2)$$

Where $t_{ref\ peak}$ is the retention time of the reference peak for the resolution; t_r is the retention time of the current peak; $BW_{ref\ peak}$ and BW_r are the widths of the two peaks.

The target analytes of this study were: chloride (Cl^-), chlorite (ClO_2^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), sulfate (SO_4^{2-}), nitrite (NO_2^-), nitrate (NO_3^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-), cyanate (OCN^-), potassium (K^+), ammonium (NH_4^+), sodium (Na^+), lithium (Li^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}).

3.2.3. Sample preparation

Initially, a study was conducted to establish a sample preparation methodology that would enable the use of a small volume of water and good reproducible results. Uncirculated banknotes were employed to evaluate various factors, including the type of plastic tube, the way the samples were placed in these tubes (folded or rolled), the water volume, and the sonication time (5, 15, and 30 minutes). The findings indicated that the optimal extraction condition was obtained using 2.500 mL of water in a 4.30 mL plastic tube with a rolled banknote. Interestingly, all tested time periods yielded comparable results, suggesting that the extraction of target analytes is rapid. The methodology used in sample preparation is described in detail below and depicted in Figure 3.5.

Each banknote was carefully rolled up and inserted into a 4.30 mL plastic tube. Subsequently, 2.500 mL of ultrapure water was added to the tube, which was then sealed with its respective lid. The tube was subjected to sonication for five minutes, followed by vortexing for one minute, and subjected to centrifugation at 4000 rpm for five minutes. The resulting solution was filtered through a 0.45 µm filter directly into an IC/CD vial. Additionally, a dilution step was performed by transferring a portion of the solution into another IC/CD vial at a dilution ratio of 1:20. Both vials, containing the original and diluted solutions, underwent IC/CD analyses in duplicate.

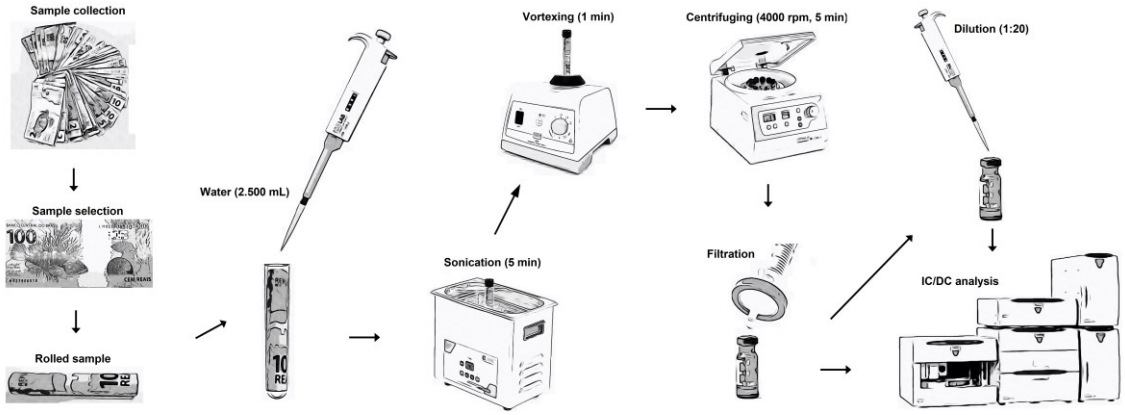

Figure 3.5. Schematic diagram of the sample preparation for the IC/CD analysis.

3.2.4. Statistical analysis

All chromatograms were processed in the Chromeleon software to obtain the peak areas for all analytes, data were autoscaled before analysis. Principal Component Analysis (PCA) were performed using PLS-Toolbox version 8.8.1 (2022) for MATLAB R2022a. The data matrix was composed by the peak areas of the sixteen target analytes previously described and the PCA was performed using Singular Value Decomposition (SVD) and 95% confidence level for Q residuals and Hotelling T^2 limits for outlier detection.

3.3. Results e discussion

Table 3.2 presents the figures of merit obtained for the method used to quantify the ten anions and six cations in the samples. All analytes demonstrated very good resolution, and the detection and quantification limits were deemed suitable for determining explosive residues in banknotes and other common forensic samples.

Table 3.2. Figures of merit from anion and cation of interest standard samples.

Analyte	t_R (min)	Range (mg/L)		Resolution	LOD (mg/L)	LOQ (mg/L)
		Curve 1	Curve 2			
Cl^-	9.037	0.20-1.00	0.80-300.00	4.95	0.009	0.031
ClO_2^-	7.574	0.20-1.00	0.80-300.00	2.78	0.022	0.073
ClO_3^-	12.160	0.20-1.00	0.80-300.00	1.97	0.010	0.033
ClO_4^-	36.680	0.20-1.00	0.80-300.00	3.14	0.019	0.062
SO_4^{2-}	19.070	0.20-1.00	0.80-200.00	3.83	0.036	0.117
NO_2^-	10.847	0.20-1.00	0.80-150.00	1.34	0.009	0.031
NO_3^-	14.374	0.20-1.00	0.80-300.00	2.27	0.037	0.120
$S_2O_3^{2-}$	27.464	0.20-1.00	0.80-150.00	2.07	0.053	0.175
SCN^-	32.977	0.20-1.00	0.80-100.00	3.51	0.004	0.013
OCN^-	11.394	0.20-1.00	------	1.79	0.011	0.036
K^+	6.400	0.063-2.500	2.50-250.00	7.93	0.044	0.144
NH_4^+	5.193	0.031-1.250	1.25-125.00	4.37	0.015	0.050
Na^+	4.587	------	0.80-150.00	2.43	0.279	0.921
Ca^{2+}	12.970	0.063-2.500	2.50-250.00	3.13	0.023	0.076
Mg^{2+}	10.427	0.031-1.250	1.25-250.00	3.25	0.022	0.074
Li^+	3.900	0.006-0.250	0.25-25.00	3.09	0.005	0.015

The results in Table 3.3 show that the presence of several ions of interest was observed in all banknotes, including the uncirculated ones. These detected ions include chloride (Cl^-), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), calcium (Ca^{2+}), ammonium (NH_4^+), magnesium (Mg^{2+}), and nitrate (NO_3^-). However, most of the uncirculated banknotes presented considerably lower concentrations than the circulated banknotes and, as expected, the former showed a more homogeneous concentration (lower RSD) profile of the ions studied. This result highlights the relevance of knowing the ionic profile of materials commonly submitted to analysis, especially in the absence of a control/blank, in order to avoid false positive or inconclusive results. Furthermore, it emphasizes the importance of prioritizing the search for the minority ions, such as perchlorate (ClO_4^-), chlorate (ClO_3^-), chlorite (ClO_2^-), nitrite (NO_2^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-) and cyanate (OCN^-). Depending on the composition of the explosive (Table 3.1 and Figure 3.3), these minority ions may represent valuable information to determine the presence of an explosive residue. However, in the samples used in this study, these minority target ions were not identified, further increasing the degree of difficulty in interpretation of the results.

Table 3.3. Mean concentrations (mg L^{-1}) and RSD%, shown in parentheses, of identified target ions (mg L^{-1}) present in each set of uncirculated (u), circulated (c) and seized (s) banknotes extracts.

Bank Notes/Ions	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	NO_3^-
R$ 2 (u)	71.6 (3)	124.5 (3)	33.9 (5)	21.5 (3)	24.1 (4)	57.5 (6)	2.6 (8)	2.8 (34)
R$ 2 (c)	1631.7 (49)	205.2 (52)	1060.8 (51)	571.3 (55)	31.4 (42)	243.0 (110)	37.8 (73)	17.6 (56)
R$ 5 (u)	199.8 (4)	150.4 (5)	82.8 (4)	28.5 (4)	7.7 (4)	89.2 (4)	2.0 (166)	5.2 (178)
R$ 5 (c)	2083.1 (54)	234.6 (37)	1159.0 (50)	627.5 (51)	21.8 (45)	193.7 (66)	35.8 (86)	23.0 (55)
R$ 10 (u)	252.7 (4)	297.3 (5)	82.2 (5)	34.5 (3)	6.7 (4)	137.9 (4)	19.0 (148)	1.8 (96)
R$ 10 (c)	2500.1 (39)	309.9 (47)	1438.4 (36)	794.8 (38)	30.9 (35)	249.6 (63)	48.7 (77)	26.5 (42)
R$ 20 (u)	198.3 (3)	171.5 (2)	85.9 (4)	40.3 (4)	7.7 (3)	134.0 (5)	1.1 (151)	2.9 (273)
R$ 20 (c)	2675.5 (24)	239.5 (40)	1559.8 (24)	863.4 (29)	32.6 (25)	274.9 (52)	70.6 (71)	28.6 (46)
R$ 50 (u)	224.5 (6)	168.1 (7)	74.3 (7)	39.7 (3)	8.1 (5)	115.9 (6)	9.4 (13)	3.2 (70)
R$ 50 (c)	2162.5 (38)	247.3 (28)	1395.8 (40)	779.1 (36)	31.6 (36)	414.5 (59)	59.6 (93)	16.1 (79)
R$ 100 (u)	293.8 (4)	303.9 (4)	81.1 (4)	50.1 (4)	10.3 (17)	159.9 (21)	37.2 (136)	1.2 (240)
R$ 100 (c)	1363.4 (59)	418.9 (28)	686.8 (62)	414.5 (65)	20.3 (46)	297.8 (79)	138.5 (51)	1.8 (192)
R$ 100 (s)	2269.1 (17)	238.4 (25)	1018.0 (16)	522.0 (17)	20.0 (17)	142.5 (28)	29.4 (110)	0.7 (397)

The results presented in Table 3.3 also draw special attention to the typical expected results for $KClO_3$/sulfur-based mixtures, as the most prevalent anions detected in all banknotes (Cl^- and SO_4^{2-}) align with the major anions found in the post-explosion residues of these mixtures. Consequently, they exhibit a closely matching anionic IC/CD profile. Additionally, in terms of cation analysis, the presence of potassium ions is also a complicating factor, as potassium is a very common counter-ion in explosive mixtures, as mentioned earlier.

It is important to clarify that, unlike the typical chromatogram examples depicted in Figure 3.3, where the concentrations of the analytes enabled the identification of significant minor ions, there are instances where only the major ions are detected, further complicating the interpretation of results. This situation can arise due to various factors,

including a more thorough explosive reaction, a minimal amount of residue, the utilization of a technique with a high detection limit, or an improper collection/sampling or extraction process.

In order to illustrate the aforementioned challenge in result interpretation, Figure 3.6 demonstrates the striking similarity in IC/CD anionic profiles obtained from (1) a forensic case involving the analysis of post-explosion residue on a cotton ball collected at an ATM explosion scene (Figure 3.6A), (2) one of the circulated banknotes examined in this study (Figure 3.6B), and (3) residues from a controlled burning of a $KClO_3$/sulfur mixture, where the minor ions (such as chlorate and/or perchlorate) were not detectable due to their insufficient concentrations (Figure 3.6C). Regarding the results for cations, the analysis of the controlled burning residue reveals the presence of K^+ as the sole cation in the profile (Figure 3.6F), which generally facilitates the interpretation of the results. However, in real cases, the cationic profile is often not as clean as in controlled burning, with the detection of various other naturally occurring ions (Figure 3.6D). When this occurs, the resulting cationic profile for the banknotes (Figure 3.6E) and a real case can be quite similar as well.

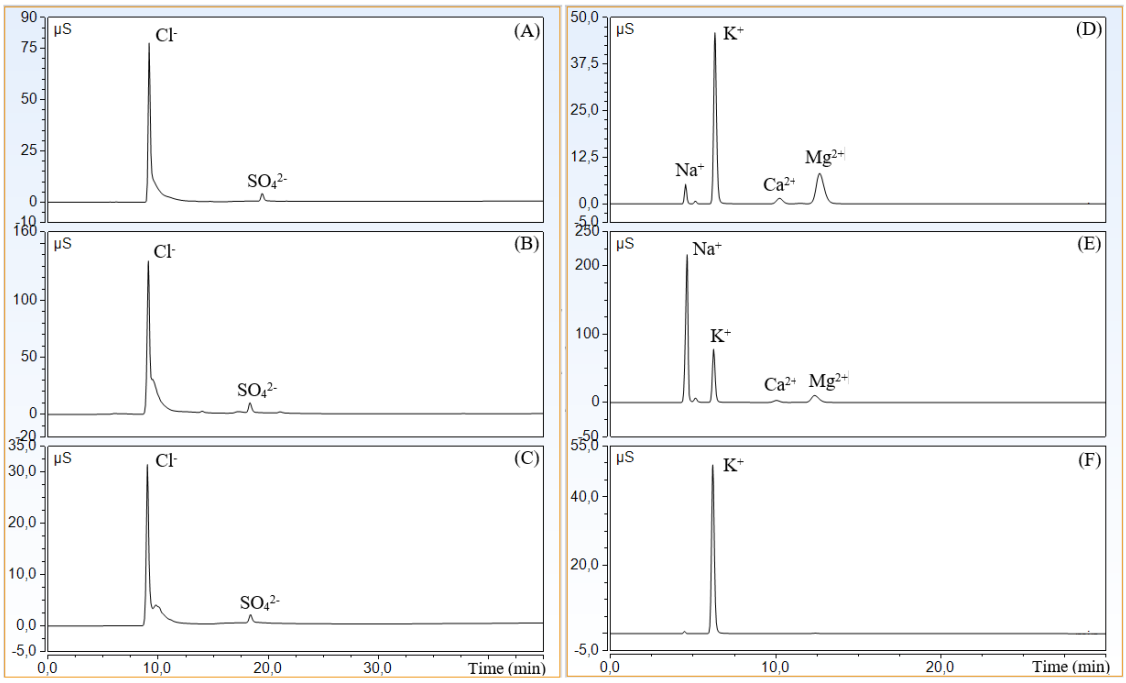

Figure 3.6. Anion (left) and cation (right) exchange ion chromatograms of post-explosion residue from a real post-explosion residue collected with a cotton ball (A, D), one of the circulated R$ 20 bank notes used in this study (B, E) and a controlled burning of a $KClO_3$/sulfur mixture (C, F).

Due to this difficulty of interpretation, that especially occurs in cases involving banknotes, unsupervised exploratory analyses based on PCA were carried out to verify the existence of patterns in this forensic problem. The results were obtained using the concentrations of six ions of interest (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- e SO_4^{2-}) for three sets of data, as follows: i) uncirculated banknotes, ii) circulated banknotes and iii) uncirculated, circulated and seized R$ 100 banknotes. These analytes were selected because they were common ions observed in all three groups of data (uncirculated, circulated and seized banknotes).

The first two principal components explained 91% of the variance present in the ionic profile formed by the six ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- e SO_4^{2-}) detected in the uncirculated banknotes. The score plot presented in Figure 3.7 show that the uncirculated banknotes form well defined clusters according to each of the denominations studied (banknote value). This interesting pattern might be related to the ink and other materials used for the manufacture of each note value. Based on the loadings plot, it can be seen that: i) all ions are important for both principal components (PC), except for Cl^- in relation to PC2; ii) magnesium has the opposite sign to the other ions, appearing to explain a significant part of the different behavior of the R$ 2 notes; iii) K^+ e Ca^{2+} ions present a high correlation.

Although the presence of distinct clusters in non-circulating banknotes (Figure 3.7) may not appear to be of forensic interest, it is still an interesting finding that also highlights the accuracy and precision of the proposed method. Additionally, it reveals that banknotes have two categories of interferents: intrinsic ones related to their manufacturing process and extrinsic ones related to their circulation. The latter can be better observed in the following results presented for circulating banknotes.

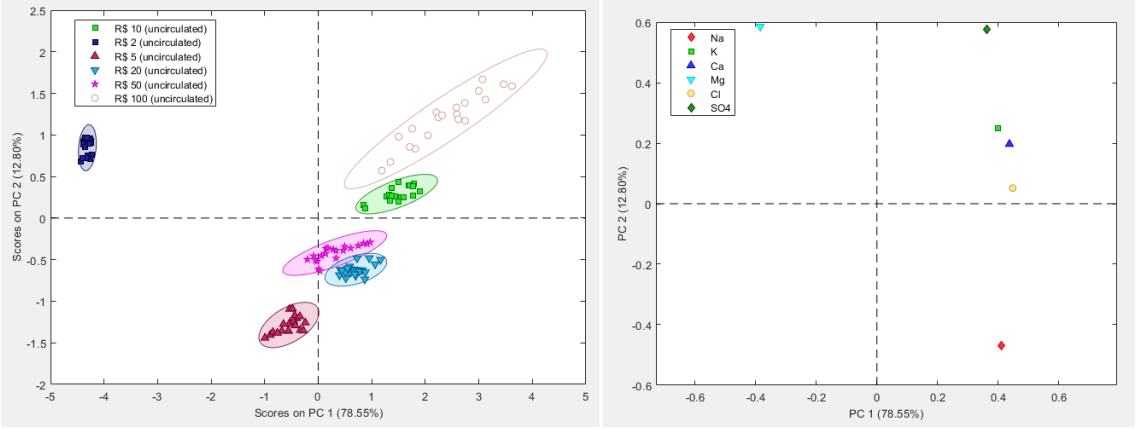

Figure 3.7. Scores plot (left) and loadings plot (right) for the first two principal components for uncirculated banknotes.

The two-dimensional PCA model for the circulating banknotes using the same ions explained only 78% of the variance, which may suggest the presence of a more complex variance structure in the data. As shown in Figure 3.8, the clear presence of clusters is no longer observed in the score plot. Furthermore, the loadings distribution is also significantly different from the one observed in the uncirculated banknotes. This result shows that, due to their circulation, the concentration of the analytes in each note value is changed and ionic profile becomes indistinguishable, obfuscating the intrinsic differences observed in uncirculated banknotes. Even with the use of the third and fourth PCs no clear pattern of class separation is observed.

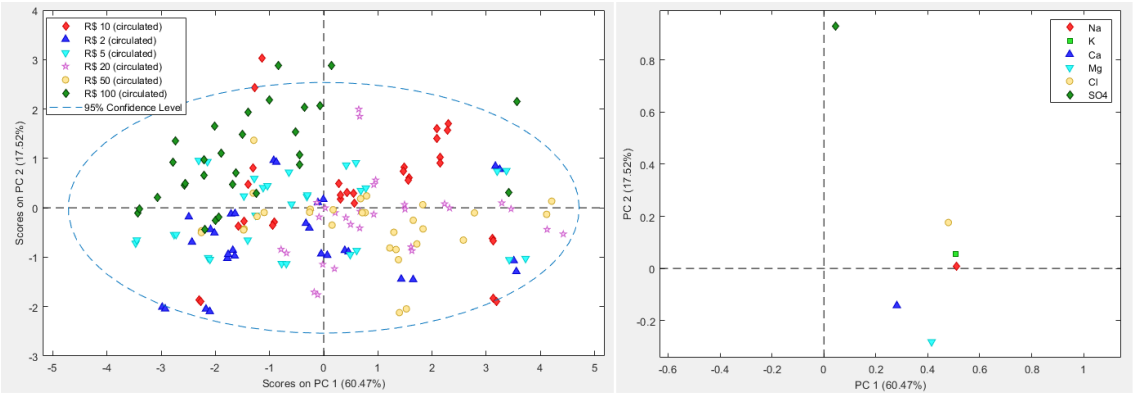

Figure 3.8. Scores plot (left) and loadings plot (right) for the first two principal components for circulated banknotes.

In the third dataset the first two PCs explained 90% of the variance and the score plot presented in Figure 3.9A shows that uncirculated/circulated and seized R$ 100 banknotes tend to form distinct groups, in which PC2 seems to be the most important

component for the separation between the groups of seized and circulated banknotes. The uncirculated samples presented the most negative values in PC1, but were very close to the circulated samples. This proximity or overlap between uncirculated and circulated notes is, in a way, expected, since among the circulated banknotes there may be the presence of banknotes with just a little circulation, therefore, making them close to the uncirculated ones. Similarly, among the seized banknotes, there may be the occurrence of banknotes that suffered negligible contact with post-explosion residues, thus approaching to the non-suspicious circulated banknotes. After removing the 4 outliers (highlighted by red circles in Figure 3.9A), two referring to seized banknotes and two referring to circulated banknotes, the scores plot presented in Figure 3.9C is obtained, where a considerable separation between seized banknotes and the others two groups is observed, considering the 95% confidence ellipses.

Based on the loadings and scores plots (Figure 3.9B-C), apparently there is a correlation between the seized banknotes and higher concentrations of the ions Cl, K^+ and Na^+ that seems to be important for the distinction of the seized banknotes. Thus, considering that potassium chloride (KCl) is the main product in the explosive reaction of explosives based on chlorate and/or potassium perchlorate and that this type of explosive is widely used in criminal actions in Brazil [4], this result indicates that the seized banknotes may have come into contact with residues of this type of material. Regarding the importance observed for the Na^+ ion, it may be related to the fact that these types of explosives are often not composed of pure potassium salts, but often with the presence of sodium salts.

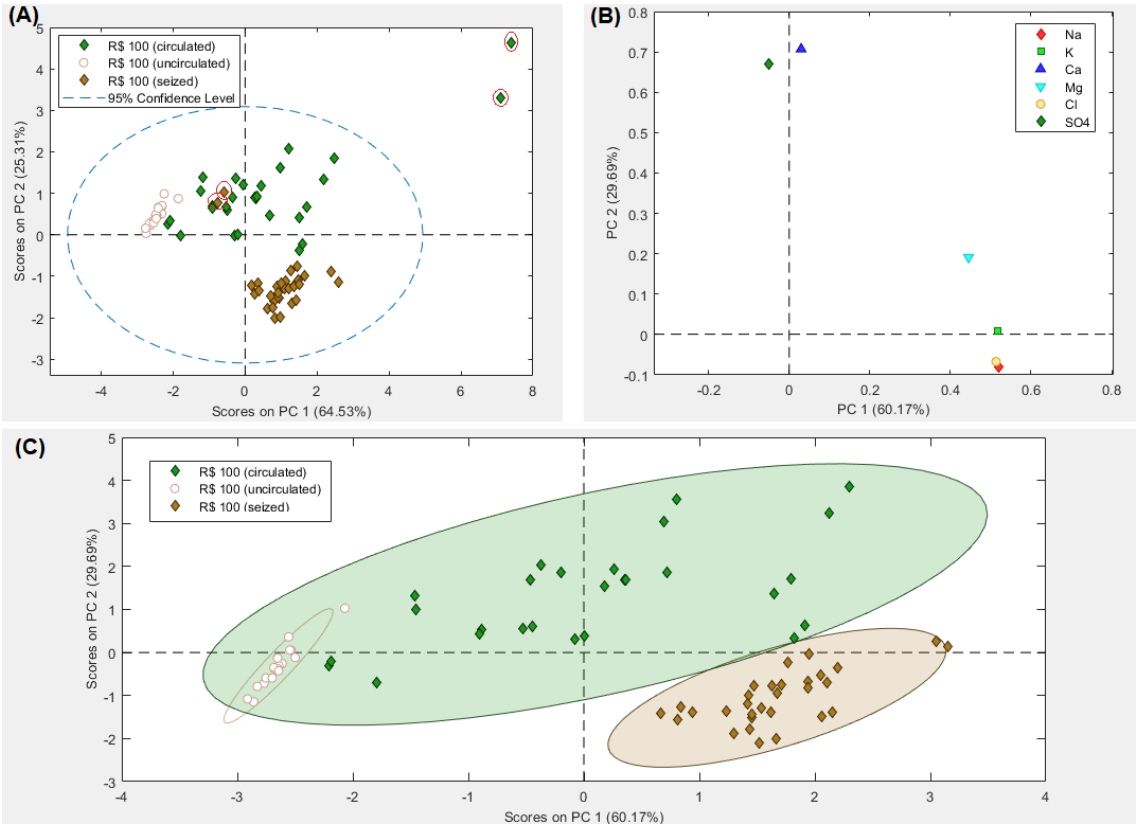

Figure 3.9. Score plot before removing the outliers (highlighted by red circles) (A), loadings and score plots (B and C, respectively) after removing the outliers for the first two principal components for uncirculated, circulated and seized R$ 100 banknotes. (ellipses) 95% confidence regions of each class.

Additionally, the Q residuals versus Hotelling's T^2 plots for the PCA models used in this work are presented in Figures S3.5 to S3.8 (Appendix B).

3.4. Conclusions

The assessment of background levels for the main analytes usually detected in post-explosion residues was demonstrated, wherein their presence in both non-circulated and circulated banknotes was observed, with higher concentrations and greater variability in the latter. This finding highlights the importance of prioritizing alternative materials with lower susceptibility to interferences, whenever feasible, for such purposes.

On the other hand, the study also revealed the absence of highly relevant target ions, such as chlorite (ClO_2^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-), cyanate (OCN^-). Therefore, the absence of these ions in the analyzed banknotes is an important finding, as their potential presence in real cases within this context can be indicative of contact with post-explosion residues.

The chemometric analysis performed by PCA showed promising results for the identification of explosives on banknotes in the absence of bulk particles. In spite of the utilization of a limited dataset in this study, consistent results were attained in this case study, indicating that discrimination between unsuspected and suspected banknotes can be achieved through a straightforward water extraction process followed by IC/CD and PCA. Furthermore, a formal and robust classification model can be developed by investigating a larger sample of unsuspected circulating banknotes and validating this model with real-world cases and/or conducting controlled explosions using banknotes as matrices. This second study is currently underway in our laboratory and will be presented subsequently.

Although this study specifically focuses on Brazilian banknotes, it introduces, for the first time, the analysis of banknotes for the identification of post-explosion residue. This not only highlights the relevance within the context of Brazil but also draws attention to other countries facing similar challenges. It serves as an encouragement for them to conduct similar studies on their own banknotes.

CHAPTER IV - Evaluation of interferents in sampling materials used for analysis of post-explosion residues (explosive emulsion/ANFO) by gas chromatography coupled to mass spectrometry (GC/MS)

EVALUATION OF INTERFERENTS IN SAMPLING MATERIALS USED FOR ANALYSIS OF POST-EXPLOSION RESIDUES (EXPLOSIVE EMULSION/ANFO) BY GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY (GC/MS)

Abstract

Chemical analysis aimed at identifying post-explosion residues can contribute considerably to investigations of crimes or accidents involving the use of explosives, thus being an important area of forensic chemistry. Most cases involve the search for traces of explosive mixture components. Therefore, understanding potential interfering factors throughout the entire process, from crime scene collection to sample processing in the laboratory, becomes crucial to prevent inconclusive results or false positives resulting from contamination due to the use of improper materials or procedures. ANFO (ammonium nitrate-fuel oil) and explosive emulsion are widely used worldwide as the primary charge in improvised explosive devices for criminal activities. In this chapter, various materials commonly used in forensics laboratories for sample pre-processing and/or storage, as well as in crime scene processing for evidence collection and transport, were tested to identify potential sources of interference. Plastic films, bottle caps, disposable gloves, syringes, swabs, disposable cups, plastic tubes, and plastic pipette were investigated in this study. The findings indicated that certain materials (syringe plungers, gloves and plastic films) can cause interference in gas chromatography/mass spectrometry (GC/MS) analyses, particularly when searching for components of post-explosion residues of explosive emulsions and ANFO. Therefore, ideally, the materials used in the analysis should be evaluated for potential interferences before sample collection and processing.

Keywords: Post-explosion Residues, ANFO, Explosive emulsion, Sampling, Interferents, Gas chromatography/mass spectrometry (GC/MS).

4.1. Introduction

Explosion and bombing scene investigations, combined with chemical analysis to identify explosives and post-explosion residues in collected materials, can significantly contribute to elucidating various aspects of a crime. These include: i) confirming the occurrence of an explosion; ii) determining its cause; iii) identifying the individual responsible for the explosion; iv) detecting clandestine explosives production laboratories; and v) identifying trends, such as the prevalence of a specific explosive or possible connection between cases [3,4].

Ammonium nitrate (NH_4NO_3) is extensively employed in the explosives industry. ANFO (ammonium nitrate fuel oil), the most widely used commercial explosive, is essentially a combination of NH_4NO_3 and fuel oil. Another notable explosive, explosive emulsion, is typically composed of an aqueous solution of NH_4NO_3 and fuel oil, along with an emulsifying agent [158,159].

Worldwide, ANFO is one of the favored explosives used as the main charge in improvised explosive devices (IEDs) by terrorist groups due to its low cost and high stability [55]. In Brazil, the most common crimes involving the use of explosives are ATM robberies, an issue also prevalent in numerous other countries worldwide [3,4]. Figure 4.1 displays post-explosion scenes of ATMs with varying levels of destruction, highlighting the unpredictable nature of ATM explosion scenarios.

Figure 4.1. ATM post-explosion scenes depicting varying degrees of destruction [160–162].

Among the explosives utilized in these incidents, those based on NH_4NO_3 and fuel oil (explosive emulsion/ANFO) are also widespread. This is primarily due to their large-scale production for legitimate purposes, particularly in the mining industry,

unfortunately leading to diversions for illegal applications [3,4]. Figure 4.2 presents examples of seized IEDs that were prepared using explosive emulsion as the primary charge.

Figure 4.2. Examples of seized IEDs prepared with explosive emulsion for ATM attacks in Brazil [36,163,164].

As mentioned earlier, this category of explosives primarily consists of ammonium nitrate (NH_4NO_3) and fuel oil. However, it is also common for other nitrates, particularly sodium nitrate ($NaNO_3$), to be present alongside NH_4NO_3 [165,166]. Therefore, the comprehensive chemical identification of this explosive, along with its post-explosion residues, preferably requires the use of multiple analytical techniques, considering it is a mixture of both organic and inorganic substances.

For this purpose, in the case of bulk material, various chemical analysis techniques can be employed to identify the involved explosive. These techniques include infrared spectroscopy (IR)[4,54–56,167], RAMAN spectroscopy [59–62,64,65,144,167], X-ray diffraction (XRD)[73,168], ion chromatography (IC) [32,85,90–92] and gas chromatography coupled to mass spectrometer (GC/MS)[4,55,169], among others [24].

Figure 4.3 depicts examples of typical results obtained for explosive emulsion when there is sufficient material for FTIR and RAMAN analyses [170]. In FTIR analysis, the most characteristic bands correspond to NH_4NO_3 in 3232 cm^{-1}, 3066 cm^{-1}, 1753 cm^{-1}, 1405 cm^{-1}, 1308 cm^{-1}, 1041 cm^{-1}, 826 cm^{-1} and 714 cm^{-1}, as well as hydrocarbons at 2917 cm^{-1} and 2848 cm^{-1}. The Raman spectrum predominantly exhibits two characteristic bands for NH_4NO_3 in 1044 cm^{-1} and 712 cm^{-1}.

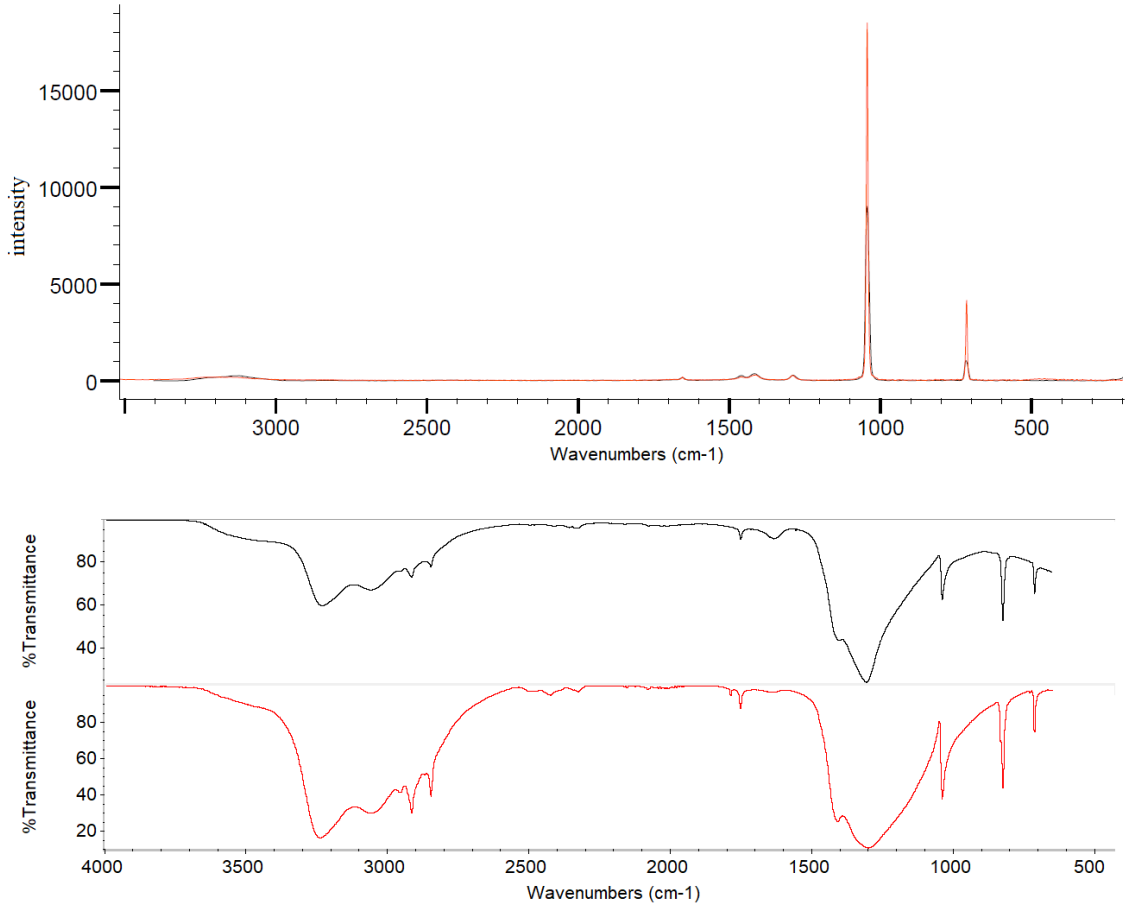

Figure 4.3. Typical results for Raman (top) and FTIR (bottom) obtained from a bulk sample of explosive emulsion (black lines), compared to the standard ANFO spectrum (red lines)[170].

In cases where bulk particles are absent, which is common in most scenarios, the analytical challenges become more significant. One of these challenges is the limitation regarding the possible analytical techniques to be used, as solvent extractions are invariably necessary in these cases. Commonly employed techniques for this purpose include ion chromatography with conductivity detector (IC/CD) for analysis of inorganic analytes and gas chromatography coupled with mass spectrometry (GC/MS) for organic analytes. Figures 4.4 and 4.5 present typical results for IC/CD and GC/MS analyses with the identification of nitrate (NO_3^-), sodium (Na^+) and ammonium (NH_4^+) ions, along with to a mixture of n-alkanes (C_{23} to C_{34}), which corresponds to the organic phase of this type of explosive [171].

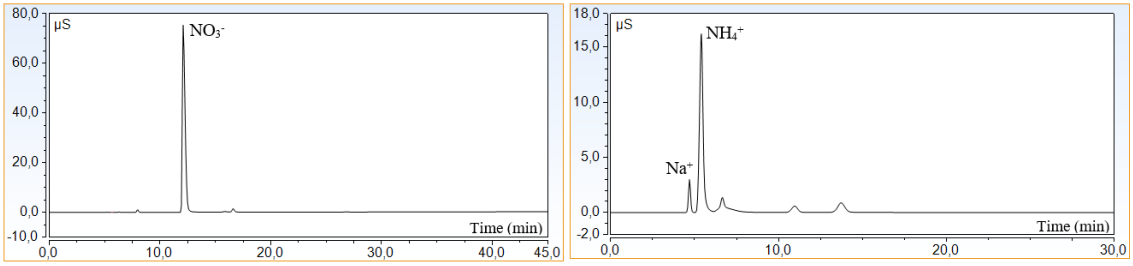

Figure 4.4. Anion (left) and cation (right) exchange chromatogram of aqueous extract of post-explosion residues from explosive emulsion, with identification of nitrate, sodium and ammonium ions [171].

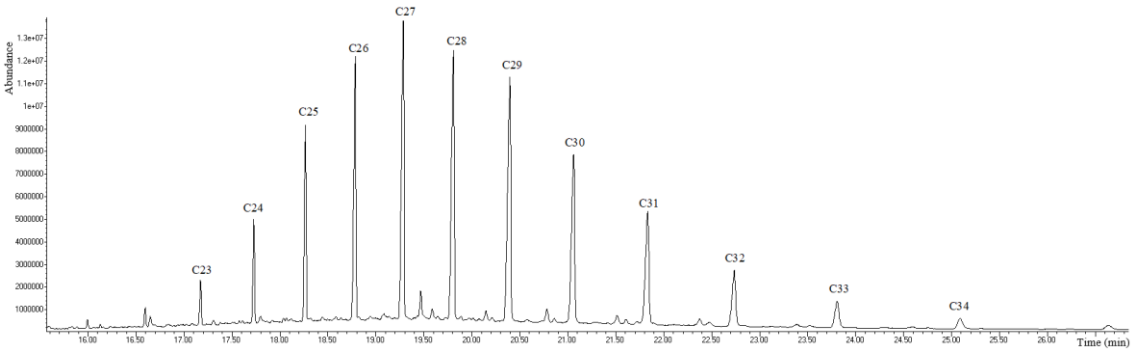

Figure 4.5. Chromatogram of n-hexane extract of emulsion explosive, with identification of a mixture of n-alkanes (C_{23} to C_{34}) [171].

Another relevant challenge when bulk particles are absent is the increased concern about the presence of interferents. The scarcer the post-explosion residues, the more important it becomes to address the potential presence of interferences in both the matrices and the materials used for evidence collection at the crime scene and sample processing in the laboratory. Therefore, it is crucial to understand the potential contamination that these materials can introduce into the analysis, ideally before their utilization.

In a previous study, the presence of interferences was assessed in sampling materials, predominantly disposable, such as cotton, swabs, and syringe filters. The primary objective was to minimize the possibility of cross-contamination. The focus of this study was on the identification of inorganic residues in post-explosion samples using ion chromatography. Aqueous extracts were examined specifically for the presence of interfering cations and anions associated with post-explosion residues [35]. Although the previous study provided significant findings concerning oxidizer salts, it did not address the interferents present in certain disposable materials commonly utilized in forensic laboratories when it comes to common fuel components. To address this gap, a supplementary study was conducted in this chapter focusing on the examination of fuel

components and a wide range of materials commonly employed during sample collection, processing, and storage. Specifically, materials such as plastic wraps, syringe filters, plastic caps, disposable cups, swabs, syringes, gloves, plastic tubes, and plastic pipette were investigated to identify any potential interferents that could contaminate samples intended for GC/MS analysis.

4.2. Materials and methods

4.2.1. Reagents and materials

Twenty-two materials commonly utilized in chemistry laboratories were assessed, including 2 syringe filters (SF), 2 plastic films (PF), 4 vial caps (VC), 5 disposable gloves (DG), 2 cotton swabs (CS), 2 syringe plungers (SP), 2 disposable cups (DC), 2 plastic tubes (PT), and 1 plastic pipette (PP-1). Specifications and corresponding brands can be found in Table 4.1.

Table 4.1. Relation of materials used in the tests and their respective coding.

Type	Brand/Specification	Code
Syringe filters	Millipore® (0,45 µm hydrofobic)	SF-1
	Analítica® (0,45 µm hydrofobic)	SF-2
Plastic films	Parafilm® (parafilm)	PF-1
	Tecfilm® (PVC)	PF-2
Vial caps	Meta química® (plastic sttoper)	VC-1
	Meta química® (screw cap)	VC-2
	Agilent® (headspace septa)	VC-3
	Unknown (screw cap with rubber ring)	VC-4
Disposable cups	Totalplast® (50 mL)	DC-1
	Querocopo® (200 mL)	DC-2
Disposable gloves	Lemgruber® (natural latex)	DG-1
	Medix® (natural latex)	DG-2
	Danny® (nitrile – natural latex free)	DG-3
	Nugard® (nitrile – natural latex free)	DG-4
	Kimberly-Clark® (nitrile – natural latex free)	DG-5
Cotton swabs	Absorve® (plastic rod)	CS-1
	Agilent® (wooden rod)	CS-2
Syringe plungers	SR® (3 mL)	SP-1
	SR® (5 mL)	SP-2
Plastic tubes	Eppendorf® microtube	PT-1
	Falcon® tube (15 mL)	PT-2
Plastic pipette	Olen® disposable pipette	PP-1

Extractions were performed using Baker Analyzed® HPLC grade hexane (97% n-Hexane) following the procedures established by the Forensic Chemistry Laboratory of the National Institute of Criminalistics of the Federal Police, which is noteworthy for holding ISO 17025 certification with post-explosion residue analysis in its scope. The samples of explosive emulsion utilized in this study were sourced from the laboratory's

available stock. Reference standards for n-alkanes (C_7–C_{40}) were procured from Sigma-Aldrich®. Grade 5 helium, supplied by White Martins Gases, served as the carrier gas during the analysis.

4.2.2. Sample preparation

4.2.2.1. Disposable cups, vial caps, plastic tubes, and plastic pipette

To extract potential interferents, 1 mL of n-hexane was added to each new and clean disposable cup or vial cap or plastic tube or plastic pipette and agitated for 1 minute. The extracts were then centrifuged at 4000 rpm for 5 minutes and transferred to GC-MS vials.

4.2.2.2. Disposable gloves, plastic films and swabs

A small fragment of each plastic, gloves/films, and swabs was extracted with 3 mL of n-hexane in a test tube using vortex agitation for 1 minute. The extracts were then centrifuged at 4000 rpm for 5 minutes and transferred to GC-MS vials. Additionally, to assess the potential for contamination, swabs moistened with water were manipulated with each type of glove, and the resulting swab fragments were subsequently extracted with n-hexane.

4.2.2.3. Syringes

3 mL of n-hexane was added directly to each of the syringes, which were closed with a luer lock cap, along with the plunger. After vortexing for 1 minute, the extracts were centrifuged for 5 minutes at 4000 rpm and transferred to the GC-MS vials.

4.2.2.4. Syringe filters

2 mL of n-hexane was added directly into a syringe, without agitation. The solution was then filtered through a 0.45 µm syringe filter and transferred directly into the GC-MS vials.

4.2.3. Instrumentation

The GC-MS analysis was performed on an Agilent 6890N gas chromatograph coupled with an Agilent 5973 mass selective detector and Agilent 7683B autosampler.

The chromatographic conditions were as follows: injection volume of 0.2 µL, splitless mode, and a column of RXi-1MS methyl siloxane with dimensions of 25 m × 200 µm (i.d.) × 0.33 µm film thickness. The oven temperature program consisted of an initial temperature of 150 °C, followed by an increase of 40 °C per minute until reaching 315 °C, which was maintained for 14.87 minutes. The injection port temperature was set at 280 °C, and the carrier gas used was helium at a flow rate of 0.9 mL/min.

Data analysis was conducted using Agilent GC/MSD ChemStation version 17 software for Enhanced Data Analysis. The mass spectra of the analytes were compared with spectra in the NIST 17 MS Database (Agilent Technologies) using the MS Search Program v.2.3 (Agilent Technologies).

4.3. Results e discussion

Among the tested materials, syringe filters (SF), vial caps (VC), cotton swabs (CS), disposable cups (DC), PF-2 plastic film, DG-3 to DG-5 disposable gloves, plastic tubes (PT), and plastic pipette (PP-1) did not exhibit relevant interferences, with only a few plasticizing additives being identified in some of them, such as tributyl-aconitate and acetyl tributyl citrate (PF-2), diisobutyl phthalate (VC-4), and hexadecanamide, oleamide and octadecanamide (PP-1) (Figures S4.1 to S4.3). On the other hand, syringe plungers (SP), DG-1 and DG-2 gloves, and Parafilm plastic film (PF-1) demonstrated some degree of interference.

Regarding the syringe plungers (SP), Figure 4.6 reveals a signal that extends over a wide range of the chromatogram, potentially masking the presence of target analytes at low concentrations, which is common in post-explosion residue analysis. Additionally, the extracted ion chromatogram (EIC) for ions with m/z values of 43, 57, 71, and 85 showed low levels of C_{20} to C_{25} n-alkanes, which can complicate the interpretation of the results (Figure S4.4).

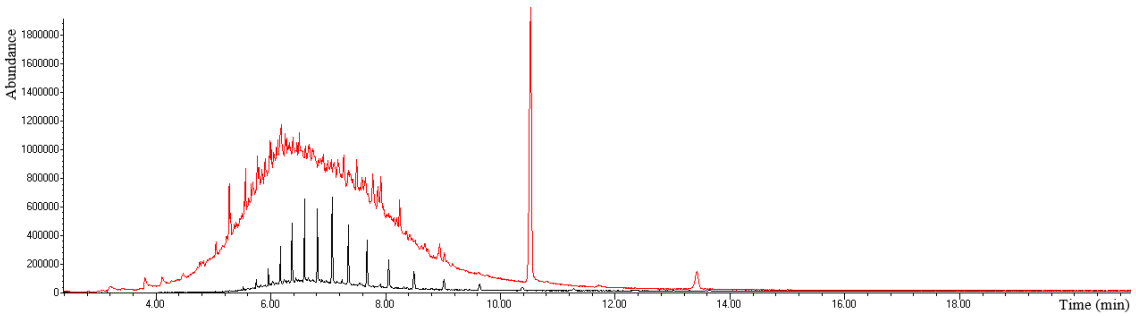

Figure 4.6. Overlapping chromatograms of the SP-1 syringe plunger (in red) and the explosive emulsion (in black) extracts.

The interference observed for the DG-1 glove (Figure 4.7) is similar to that previously discussed for syringe plungers, with the presence of a signal in a long range of the chromatogram in the region of interest, but with a much lower intensity. In theory, this interference could generate false negatives. However, simulations of handling moistened swabs with the DG-1 glove, followed by extraction of the swab fragments with n-hexane, did not show transfer of these interferents. This indicates a low potential for contamination in real cases.

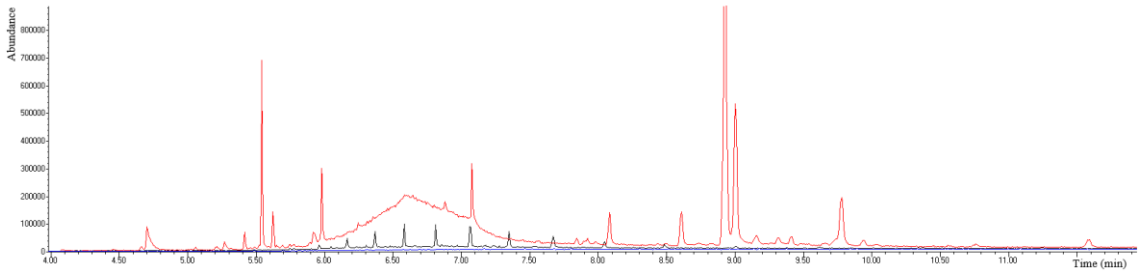

Figure 4.7. Overlapping chromatograms of the DG-1 disposable glove (in red), handling simulations with DG-1 glove (in blue), and the explosive emulsion (in black) extracts.

In addition, tests were conducted to assess the potential cumulative effect of the two aforementioned procedures (handling with gloves and extraction with a syringe). However, it was observed that the interference caused by the syringe plunger is significantly more pronounced than that caused by the gloves, leading to essentially the same results as depicted in Figure 4.6 (Figure S4.5).

Among all the materials examined, the PARAFILM® plastic film (PF-1) and the DG-2 disposable gloves presented the most significant concern due to the presence of interferents that could potentially result in false positive results in visual analysis of the data. The extracts obtained from these materials consisted of a mixture of hydrocarbons closely resembling those found in explosive emulsions (C_{23}-C_{34}). This similarity is

visually evident when comparing the chromatograms of the emulsion extract with those of the aforementioned plastic film and disposable glove, as illustrated in Figure 4.8. Furthermore, when swabs moistened with water were handled using the DG-2 glove and the resulting swab fragments were subsequently extracted with n-hexane, substantial transfer of interferents was observed. This discovery indicates a high likelihood of contamination in real-world scenarios, as swabs, as well as other materials, can be damp when collected/analyzed.

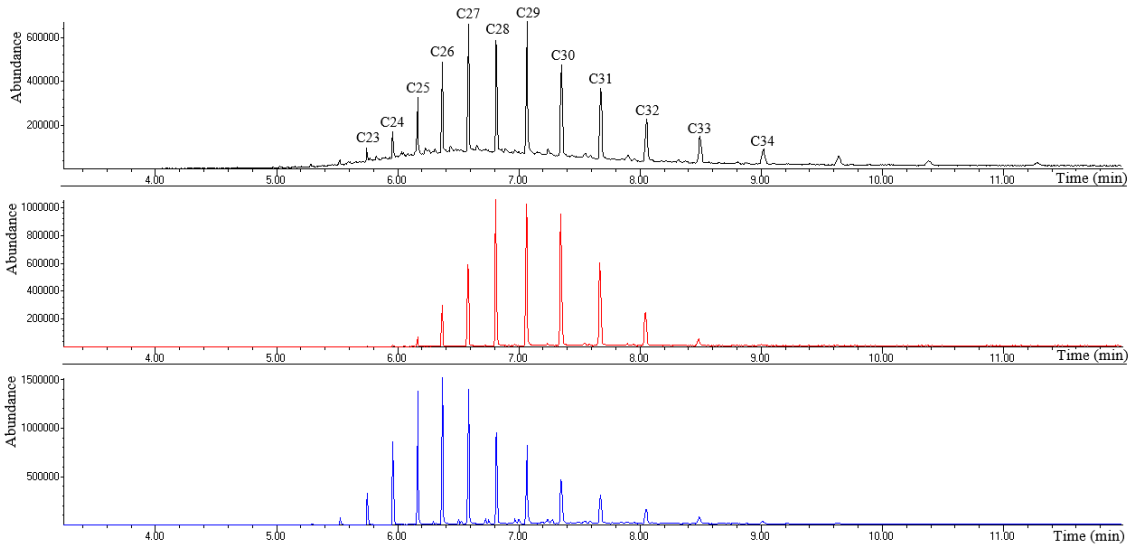

Figure 4.8. Chromatogram Comparison of Extracts: Explosive Emulsion (in black), handling simulations with DG-2 glove (in red), and PF-1 parafilm (in blue).

Given that laboratory extraction procedures often involve using syringes to filter analyte extracts for subsequent analysis, and some even involve shaking the syringes (with luer lock caps) during extraction (as shown in Figure 4.9A), it is crucial to consider the potential for interferent contamination when using such materials. It is highly recommended to use glass materials for extractions or syringes without rubber plungers for filtration.

When it comes to using disposable gloves for sample handling in the laboratory or collecting materials at the explosion scene, which is always recommended, it is advisable to select gloves that are known for their absence of these interfering substances (such as, for example, the DG-3 to DG-5 nitrile gloves evaluated in this study, which showed no significant interferences - Figures S4.6 and S4.7). When such assurance is not available, appropriate precautions must be taken when handling the materials to be collected or analyzed to avoid direct contact. For this purpose, disposable or clean

tweezers should ideally be used to handle these materials. Figure 4.9B illustrates the removal of part of a cotton wool from a swab for later solvent extraction and Figure 4.9C illustrates the removal of a part of a cotton ball in order to extract the most impregnated fraction for later solvent extraction. Often, these materials are damp, increasing the potential for the transfer of undesirable interferents.

Parafilm-type plastic films are commonly used to enhance the sealing of vials that hold solutions, especially extracts composed of solvents and/or volatile analytes. These vials are typically sealed with lids, and in some cases, the plastic film is also employed to seal test tubes during extraction procedures or for temporary storage on the laboratory bench (as depicted in Figure 4.9D). Thus, using plastic films for these purposes poses a significant risk of contamination, making it advisable to avoid their use for this purpose.

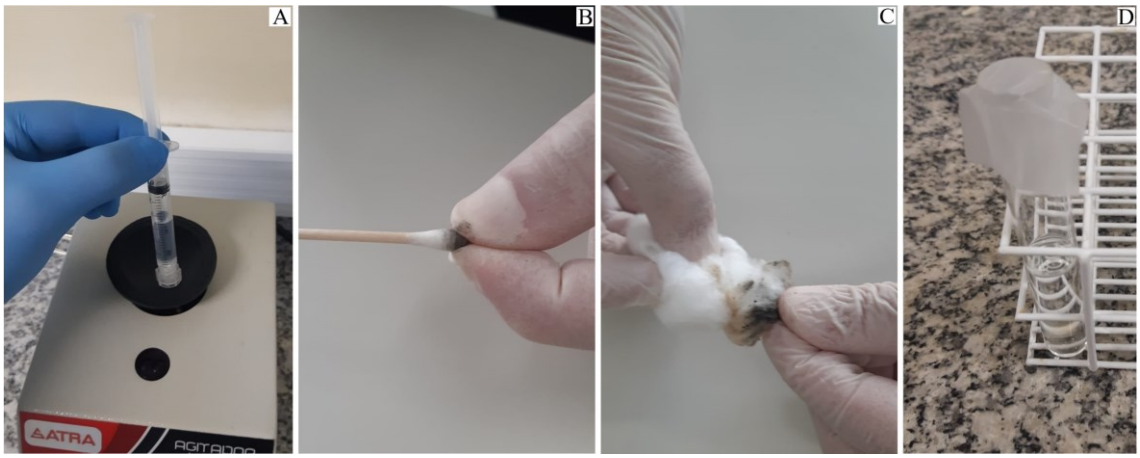

Figure 4.9. Examples of sample processing procedures in the laboratory that can lead to interferent transfer in extracts. Solvent extraction directly into a syringe with vortexing (A), handling of swabs and cotton balls with latex gloves (B and C), and test tube sealed with parafilm (D).

4.4. Conclusions

Despite the fact that the selection and examination of tested materials were not exhaustive, the results presented in this chapter complement the previous studies in the literature and provide a critical analysis that emphasizes the importance of being aware and conducting thorough testing on new materials used for sample collection, transportation, and processing in the search for post-explosion residues.

The results revealed that certain materials investigated have the potential for contamination, leading to undesirable effects on the analysis results, particularly in the identification of analytes in post-explosion residues of explosive emulsion/ANFO. It was observed that certain materials are more susceptible to contamination than others,

emphasizing the critical role of adhering to proper procedures and implementing rigorous laboratory practices.

Performing blank tests is essential to prevent false positives in any chemical analysis, particularly when dealing with samples at trace or ultra-trace levels, such as post-explosion residues. However, even with these measures in place, the quality results can be compromised if the analyst fails to account for interferents present in these materials. Given the limited availability of such samples, often consisting of only a swab or small wrapper fragment, it is often impractical to repeat the analysis once these interferences are identified in the results. Therefore, the ensure beforehand that the materials used are free from interfering contaminants is crucial to minimize the risk of contamination and, consequently, to reduce the occurrence of inconclusive results or false negatives/positives.

Although this study focused on explosive emulsion/ANFO, the findings can be extrapolated to other explosives that contain combustible ingredients. The range of possibilities is extensive [172,173]. Moreover, the results presented in this chapter have broader applicability to other types of analyses that involve the identification of hydrocarbon mixtures at low concentrations, such as the investigation of accelerants in fire debris analysis.

CHAPTER V - Stability study of extracts of post-explosion/burning residues of fuel-oxidizer explosive mixtures

STABILITY STUDY OF EXTRACTS FROM POST-EXPLOSION/BURNING RESIDUES OF FUEL-OXIDIZER EXPLOSIVE MIXTURES

Abstract

Post-explosion residue analysis is vital in forensic chemistry, providing valuable insights into incidents involving explosives. This field poses numerous challenges, including: i) unpredictable scenarios hindering standardized collection procedures; ii) diverse analytes with varying physicochemical properties; iii) low sample concentrations; iv) limited material availability; and v) potential interferents from various sources. Another significant challenge in this field, closely linked to the limited availability of material, is the preservation of samples for long-term storage to enable reanalysis. Presently, many laboratories conducting post-explosion analyses worldwide do not retain samples. This is due to the extraction process for sample preparation, which often necessitates the complete consumption of the scarce material. Even in cases where a portion of the material remains, such as a swab, it is difficult to ensure its representativeness and select a specific portion for preservation. One possible solution to overcome this challenge is to consider preserving the extracts used in the analyses for potential reanalysis. However, the stability characteristics of these extracts are currently unknown, which poses a significant obstacle in utilizing them for this purpose. The results presented in this chapter provide valuable insights into the feasibility of long-term storage for samples containing target analytes in extracts derived from post-explosion/burning residues of frequently encountered fuel-oxidizer explosive mixtures, such as flash powder, explosive emulsion, and black powder. These results shed light on the potential viability of preserving such extracts for future reanalysis, offering promising prospects for enhancing forensic investigations in this field. Based on the current findings, it has been demonstrated that the aqueous extracts can be effectively preserved as long-term storage samples for a minimum of 24 months, encompassing all the studied explosives. Additionally, the organic extract, specifically in the case of emulsion explosive, can be maintained for at least 12 months. It is important to note that to ensure the preservation of the cyanate ion and maintain its ionic profile over time, it is necessary to store the samples at low temperatures of 4.5 ºC or below, due to its susceptibility to degradation.

Keywords: Post-explosion Residues, Long-term storage, Stability of extracts, Explosives, Ion Chromatography, Gas chromatography-mass spectrometry.

5.1. Introduction

Explosives have extensive civilian applications, but unfortunately, their misuse in criminal activities has been steadily rising in recent years [2,174,175]. In such crimes, perpetrators typically employ readily available materials, ranging from illegally obtained industrial explosives to improvised explosive devices (IEDs) and homemade explosives (HMEs). Consequently, the appearance and content of these explosives, including the specific types of materials used, exhibit considerable variation [176,177].

Forensic chemistry plays a significant role in the investigation of crimes involving explosives, among other areas of forensic science. The determination of the chemical composition of explosive components is of paramount importance, as it significantly impacts multiple facets of criminal prosecution. It helps differentiate between intentional crimes and accidental incidents, establish connections between crime scenes, objects, and suspects, and provides valuable insights into the prevalent types of explosives used in criminal actions within a specific region over time [3,4].

The analysis of post-explosion residues presents significant challenges due to the limited sample quantities and low concentrations of target compounds. Additionally, there are multiple potential sources of interferences, including sampling, collection, and processing materials [35], environmental factors [3], matrices [178,179], countermeasures [3,47], and others. Furthermore, the wide range of analytes of interest adds to the complexity of the analysis.

Another challenge in this type of analysis is the preservation of long-term storage samples for potential reanalysis, which is a standard recommendation in good forensic laboratory practices [180–182]. In Brazil, it is also a legal requirement as outlined in the Brazilian Criminal Procedure Code [183], which states that "experts must retain an adequate amount of material for the possibility of further examination" during laboratory examinations.

This challenge arises due to the limited availability of material typically encountered in samples collected for post-explosion residue analysis. As a result, often, the entire sample needs to be consumed, or there are no assurances of sample homogeneity that would allow for the preservation of a portion for reanalysis purposes. In some instances, retaining the extracts obtained after analysis could serve as a potential solution to mitigate this issue and compensate for the absence of long-term storage samples. However, a new concern emerges: can these extracts be stored for an extended period without significant degradation, thus enabling future reanalysis?

Stability studies play a crucial role in determining the optimal time interval and storage conditions for preserving a sample for future reanalysis. These studies are also valuable in minimizing the loss of important analytes by determining the appropriate time frame between sample collection and analysis, since, in practice, there can be delays of several days to months due to transportation delays, logistical considerations, and laboratory workload. Therefore, understanding the stability of samples during this period is essential for accurate and reliable analysis [180–182].

Specifically, when analyzing organic explosives, numerous stability studies have been conducted on explosives in various matrices [182,184–189]. However, there is a significant scarcity of studies on explosives that are based on mixtures containing inorganic oxidants, which are prevalent in Brazil and widespread globally. Furthermore, the limited studies that do exist primarily focus on the actual explosive components rather than their burning or explosion residues, and even in those cases, they are typically conducted for short durations [182]. Additionally, degradation studies on certain ions of interest have been carried out, but in different contexts and samples unrelated to post-explosion residues [190–194].

A study conducted in Brazil, using data from Federal Police reports that identify the composition of explosives in samples collected at scenes of ATM/safe explosions, which encompass the majority of criminal actions involving explosives in the country, revealed that the most commonly utilized types of explosives are mixtures based on chlorates and/or perchlorates, explosive emulsion, and black powder [4].

Ionic chromatography is a prominent technique employed in forensic chemistry to analyze post-explosion residues of mixtures containing inorganic oxidants [32,33,35,90–94]. The objective of analyzing post-explosion residues through this technique is to identify not only the ions that were originally present in each explosive's composition but also those associated with the primary products and by-products generated during the explosive reaction. The interpretation is based on analyzing the complete profile of the target ions rather than individually analyzing each ion in isolation [4].

In the case of explosive emulsions, it is generally feasible to identify the organic phase of the explosive mixture even when the material is limited. This can be achieved through extraction with non-polar organic solvents followed by GC-MS analysis. While the target analytes within this phase are not expected to degrade rapidly due to their resilient chemical composition, experimental confirmation is still crucial to provide a solid basis for practical decisions concerning the long-term preservation of these samples.

Several studies have been published concerning the degradation of hydrocarbons [195–198], including diesel as a component of ANFO used in open cast coal mining operations [169]. However, to the best of our knowledge, no studies have been conducted to investigate the degradation of extracts obtained from the analysis of post-explosion residues under typical storage conditions for long durations.

This chapter aims to assess the stability of the target ions within aqueous extracts derived from samples of post-explosion/burning residues originating from frequently employed fuel-oxidizer explosive mixtures, including flash powder, explosive emulsion, and black powder. The evaluations encompass different temperature conditions over a 24-month period, with monthly analyses conducted. Additionally, an investigation was conducted to evaluate the stability of the extract in n-hexane (in addition to the aqueous extract) obtained from an actual sample of an ATM explosion involving explosive emulsion, over a 12-month period.

5.2. Materials and methods

5.2.1. Reagents and materials

Three fuel-oxidizer explosive mixtures (flash powder, explosive emulsion and black powder), as well as their corresponding burning/explosion residues, were utilized for this study. The explosives were obtained from seizures made by the Brazilian Federal Police.

To confirm the chemical composition of the mentioned explosives, Ion Chromatography (IC), Infrared Spectroscopy (FTIR), and Gas Chromatography coupled with Mass Spectrometry (GC/MS) analyses were conducted on all explosives. Moreover, X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analyses were performed on flash powder and black powder, while RAMAN Spectroscopy was employed for the explosive emulsion. The obtained results are presented as supplementary material in Figures S5.1 to S5.7 (Appendix D).

In addition to the aforementioned materials, real samples of post-explosion residues collected from a crime scene involving an ATM explosion with the use of explosive emulsion were also included in this study.

The standard ion solutions for IC analysis were prepared following the procedures established by the Forensic Chemistry Laboratory of the National Institute of

Criminalistics of the Federal Police. This laboratory holds ISO 17025 certification with post-explosion residue analysis in its scope. Anion standard solutions were prepared using a 500 mg/L stock solution obtained from sodium salts, including chloride, phosphate, tartrate (Vetec Ltd.), fluoride, chlorite, perchlorate, nitrite, citrate (Sigma-Aldrich Ltd.), sulfate (Cinetica Ltd.), thiosulfate (Carlo Erba Ltd.), nitrate (QEEL Ltd.), and chlorate (Baker Ltd.). After dilution, the concentration of the standard solution used was 10 mg/L for each of the mentioned anions. Cation standard solutions were prepared using a commercial stock solution called Dionex Six Cation-II Standard, which included lithium (50 mg/L), sodium (200 mg/L), ammonium (250 mg/L), potassium (500 mg/L), magnesium (250 mg/L), and calcium (500 mg/L). After dilution, the concentration of each cation in the standard solution used was as follows: lithium (2 mg/L), sodium (8 mg/L), ammonium (10 mg/L), potassium (20 mg/L), magnesium (10 mg/L), and calcium (20 mg/L). All standard solutions and extracted samples were prepared using ultrapure water obtained from a Millipore Direct-Q5 purification system, which had a resistivity of 18.2 MΩ cm at 25°C. As observed, the standard solutions include various other ions, in addition to those investigated in this study, as it is the standard working solution used in the routine of our laboratory.

For GC-MS analyses, extractions were carried out using n-hexane (97%) obtained from Baker Analyzed® HPLC. For comparisons with the obtained results, a reference standard of n-alkanes (C7-C40), 1000 mg/L, was purchased from Sigma-Aldrich®. From this, a 20 mg/L solution was prepared for use at each step of the study. Grade 5 Helium was supplied by White Martins Gases Industriais LTDA.

5.2.2. Sample preparation

5.2.2.1 Flash powder and black powder

Each explosive mixture underwent extraction using ultrapure water. The resulting extracts were then subjected to IC analysis. Following this, both explosives were burned, and their residues were extracted using ultrapure water. The extracted residues were subsequently diluted to fall within the intensity ranges typically encountered in this type of analysis. The extraction procedures involved vortexing, ultrasound, and filtering, following an analogous extraction procedure to the one described in Chapter III (section 3.2.3), which was employed for the banknote samples.

5.2.2.2. Explosive emulsion

For explosive emulsions, a portion of the original mixture underwent extraction using ultrapure water, and the resulting extract was subsequently diluted to fall within the typical intensity ranges encountered in this type of analysis. This extraction procedure was conducted without burning, as explosive emulsion is categorized as a tertiary explosive and does not undergo combustion. Furthermore, the target ions analyzed using IC are identical to those found in the original composition, as the explosive emulsion primarily produces gases and water upon detonation, unlike the other two explosives studied that also generate solid by-products. A real case sample underwent the same procedures and analyses, including extraction with n-hexane for GC/MS analysis. The extraction followed an analogous procedure to the one employed for the banknote samples as described in Chapter III (section 3.2.3).

5.2.2.3 Sample identification and storage conditions

Aliquots of 1.5 mL from each obtained solution were divided into vials, labeled, and stored under three distinct temperature conditions (-20.0 °C, 4.5 °C, and 18.0 °C). The exception to this was the extracts obtained from the real case, which were solely evaluated at the lower temperature (-20.0 °C) due to limited sample availability. Table 5.1 provides the coding system used to identify each explosive extract at the different temperatures examined.

Table 5.1. Relation of explosives studied, storage temperature, and respective coding.

Explosives	Temperature		
	-20.0 ºC	**4.5 ºC**	**18.0 ºC**
Flash powder	FP -20.0	FP 4.5	FP 18.0
Black Powder	BP -20.0	BP 4.5	BP 18.0
Explosive emulsion	EE -20.0	EE 4.5	EE 18.0
Explosive Emulsion - water (Real Case)	RC -20.0	----	----
Explosive Emulsion - n-hexane (Real Case)	OF -20.0	----	----

Aqueous extracts were analyzed monthly using IC in triplicate for a duration of 24 months. The organic extract (n-hexane) was analyzed bimonthly in triplicate using GC-MS for a period of 12 months. During the analysis of the aqueous extracts, standard solutions of cations and anions were consistently analyzed together in the same batches. Similarly, during the analysis of the organic extract, standard solutions of n-alkanes were consistently analyzed together in the same batches.

5.2.3 Instrumentation

5.2.3.1 Ion chromatography analysis

Ion chromatography was conducted using the Thermo Scientific Dionex ICS-5000 Ion Chromatography System equipped with self-regenerating electrolytic suppression and AS-AP Autosampler. Anion separations were performed on a Dionex IonPacTM AS19 column (2 x 250 mm) using an EGC eluent generator configured with a potassium hydroxide (KOH) eluent cartridge. The system operated in a multi-step gradient mode, starting from 10 mM at 0 minutes and reaching 45 mM at 40 minutes. The suppressor current was set to 28 mA. For cation separations, a Dionex IonPacTM CS12A column (2 x 250 mm) was utilized under isocratic conditions with a 20 mM methane sulfonic acid (MSA) eluent generated on-line from reagent water using an MSA cartridge. The suppressor current was set to 15 mA. The columns temperature was maintained at 30° C, and the detector cell temperature was set at 25°C. Both methods employed a 10 µL loop size and a constant flow rate of 0.25 mL/min. To prevent cross-contamination, approximately 2 mL of pure Milli-Q water (18.2 MΩ cm at 25°C) was pumped into the column after each run. Instrument control and data acquisition were performed using Chromeleon® software.

5.2.3.2 Gas chromatography coupled to mass spectrometry

GC-MS analysis was performed using an Agilent 6890N gas chromatograph coupled with an Agilent 5973 mass selective detector and Agilent 7683B autosampler. The following chromatographic conditions were employed: an injection volume of 0.2 µL, splitless mode, and an RXi-1MS methyl siloxane column with dimensions of 25 m × 200 µm (i.d.) and a 0.33 µm film thickness. The oven temperature program consisted of an initial temperature of 150 °C, followed by a ramp of 40° C/min to reach 315° C, and a hold at 315 °C for 14.87 minutes. The injection port temperature was set to 280 °C, and the carrier gas used was helium at a flow rate of 0.9 mL/min.

Data analysis was performed using Agilent GC/MSD ChemStation version 17 software for Enhanced Data Analysis. Mass spectra of the analytes were compared with spectra in the NIST 17 MS Database (Agilent Technologies) using the MS Search Program v.2.3 (Agilent Technologies).

5.3 Results e discussion

This chapter aimed to monitor specific target ions associated with the studied explosives, as presented in Table 5.2. The target ions included chloride (Cl^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), sulfate (SO_4^{2-}), nitrite (NO_2^-), nitrate (NO_3^-), thiosulfate ($S_2O_3^{2-}$), thiocyanate (SCN^-), cyanate (OCN^-), potassium (K^+), ammonium (NH_4^+) and sodium (Na^+), depending on the particular explosive being analyzed. Table 2 provides an overview of the three explosive mixtures examined in this study and their corresponding main target ions found in the chemical residues resulting from burning/explosion processes, as determined through ion chromatography (IC).

Table 5.2. Explosives´ mixtures studied and major target ions in their post-explosion residues.

Explosives	Composition	Major target ions in post-explosion residues
Flash powder	$KClO_4$, Al	Cl^-, ClO_4^-, ClO_3^-, K^+
Black Powder	KNO_3, C, S	SO_4^{2-}, NO_2^-, NO_3^-, $S_2O_3^{2-}$, SCN^-, OCN^-, K^+
Explosive emulsion	NH_4NO_3, generic fuel oil	NH_4^+, Na^+, NO_3^-

Figure 5.1 displays the IC/CD analysis results conducted on the explosive mixtures prior to burning or detonation. On the other hand, Figure 5.2 presents the representative outcomes of IC/CD analysis performed on the extracts obtained from the residues of the explosive mixtures after burning or detonation. It is important to note that in the case of the explosive emulsion, no burning was carried out since the target analytes for this sample remain the same before and after explosion. Furthermore, the results for the real case sample of an ATM explosion involving explosive emulsion are presented in Figures 5.2 C and 5.2 F, exclusively under temperature conditions at -20 ºC.

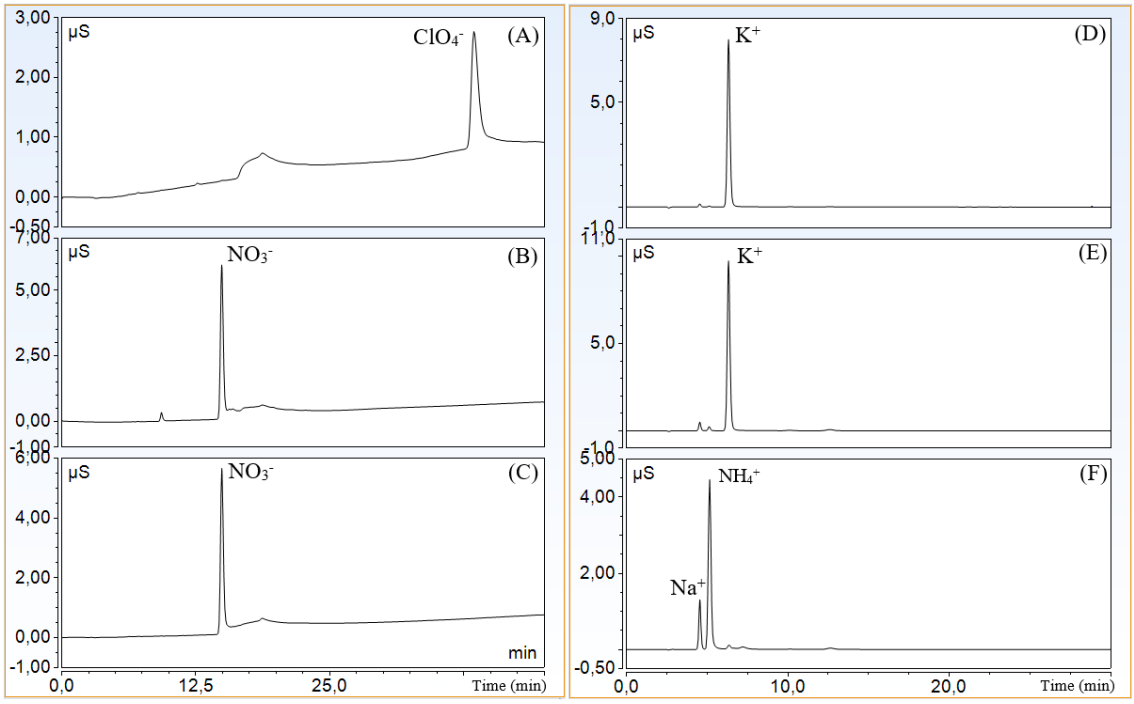

Figure 5.1. Anion (left) and cation (right) exchange chromatograms of pre-explosion flash powder (A, D), black powder (B, E) and explosive emulsion (C, F).

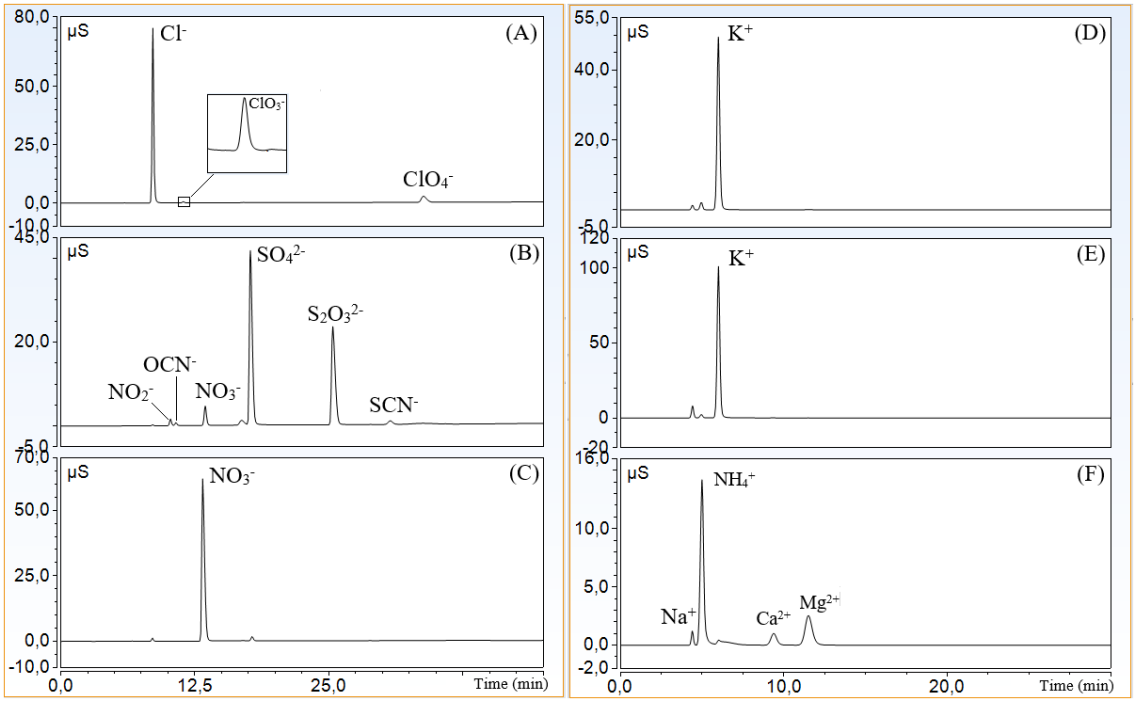

Figure 5.2. Anion (left) and cation (right) exchange chromatograms of post-burning/explosion residues of flash powder (A, D), black powder (B, E) and real case explosive emulsion (C, F).

To assess the stability of the studied explosive residues, the peak areas corresponding to each evaluated analyte were monitored on a monthly basis for IC analyses and bimonthly for GC/MS analyses. The analyte areas were adjusted relative to the areas of the standards solutions to mitigate any potential impact arising from variations in equipment performance and maintenance, since this study spanned a significant period of time, and regular preventive and corrective maintenance may result in fluctuations in the instrument's sensitivity.

An assessment of the stability of the standard solutions was conducted at the end of the study. For IC analysis, each target ion was quantified in the solution prepared at the beginning of the study and compared to its initial concentration (Figures S5.8 and S5.9). The results revealed that, with the exception of chloride, cyanate, and thiosulfate ions, all other standards remained stable throughout the study period. Chloride, cyanate, and thiosulfate ions displayed variations of 23%, -48%, and -39%, respectively, over the course of the study. Consequently, the results obtained for these ions necessitated adjustment using other different stable ions (nitrate for the first two and thiocyanate for the latter). For all other target ions, the same ion from the standard solutions was used for each adjustment.

The stability of the standard solution of n-alkanes (C_7 - C_{40}) was evaluated for GC-MS analysis throughout the study period. At the end of the study, a fresh solution was prepared with the same concentrations (20 mg/L) as the solution prepared at the beginning of the study. Both solutions were analyzed in ten replicates, with the mean areas of each analyte being compared using the Student's t-test. The results showed that the two solutions did not exhibit significant differences, indicating stability over the study period. Thus, the C_{25} n-alkane was selected to adjust the areas of all the n-alkanes of interest in the real sample extracts, as it yielded the lowest t-value in the t-test considering the n-alkanes between C_{22} and C_{34}. This stability can also be observed through the overlap of chromatograms obtained from the analysis of the standard n-alkane solution prepared at the end and at the beginning of the study (Figure S5.10).

To assess stability, regression analysis was performed on the data obtained for each target analyte of each explosive at all tested temperatures. The degradation rates were evaluated by examining the slope values of each curve, with a confidence level of 95%.

Figure 5.3 presents a summary of the results obtained for the target ions in the burning residues of black powder (SO_4^{2-}, NO_2^-, NO_3^-, $S_2O_3^{2-}$, SCN^-, OCN^-, K^+). The results demonstrate good stability, with slopes that are statistically equal to or close to zero for most of the ions studied. The confidence intervals for the slopes (at a 95% confidence level) are provided in Table 5.3.

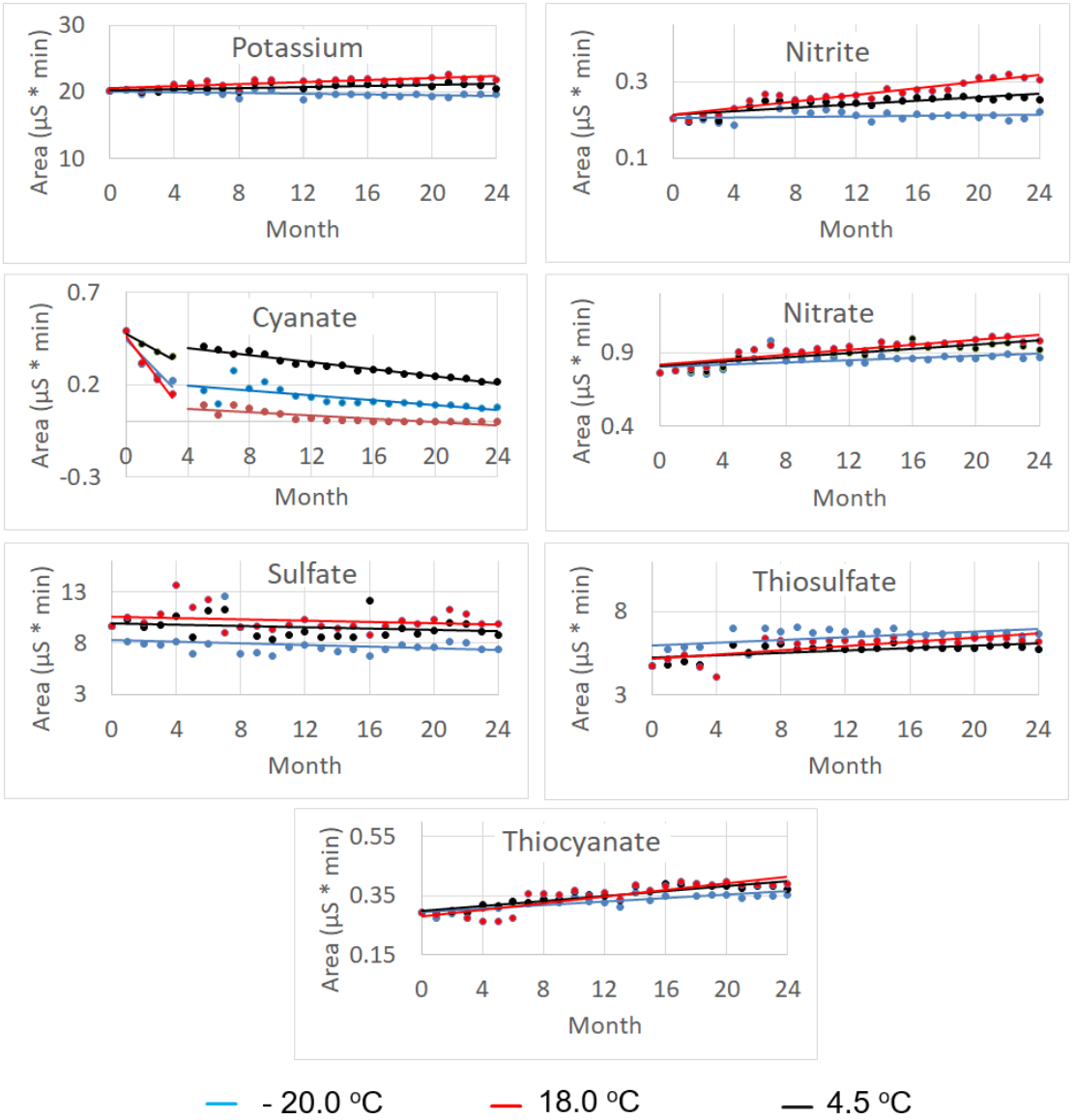

Figure 5.3. Monthly monitoring of target ions (K^+, NO_2^-, OCN^-, NO_3^-, SO_4^{2-}, SCN, $S_2O_3^{2-}$) for black powder afterburning residue extracts for 24 months.

The most significant degradation was observed for cyanate ions, particularly within the first four months. As expected, a higher degradation rate was observed at the highest temperature tested (18.0 °C). However, surprisingly, the samples kept at freezing temperatures (-20.0 °C) exhibited greater degradation compared to those at the

intermediate temperature (4.5 ºC). The variation in relative area for cyanate ions, meaning the percentage of relative area in the last month of the study compared to the first month, was 16% for the lowest temperature (-20.0 °C) and 44% for the intermediate temperature (4.5 °C). As for the highest temperature studied (-18.0 °C), from the 17th month onward, this analyte was no longer detected.

It is known that cyanate ions can undergo decomposition into carbon dioxide and ammonia, with the latter being in equilibrium with ammonium ions [199,200]. This is consistent with the increase in the signal of ammonium ions observed in the cation analysis results during the same period, particularly at 18.0 ºC (Figure S5.11).

Furthermore, an increase in the intensity of thiosulfate ion signals at the two highest temperatures was also observed. It is known that sulfate and thiosulfate can be generated from sulfide, which is one of the byproducts formed during the burning reaction of black powder [25]. However, sulfide ions were not evaluated in this study, as they are not detectable by the conductivity detector. Additionally, previous studies have demonstrated the possibility of sulfate-to-thiosulfate conversion [201]. Therefore, further investigations are needed to gain a more comprehensive understanding of this finding.

Potassium ions also exhibited small variations in their signals throughout the studied period. Previous studies have indicated the presence of retention-release mechanisms that regulate the availability of K^+ ions in charcoal [202] and coals, as well as their combustion products [203]. Considering that charcoal is one of the components of black powder, it is possible that the observed variations in potassium ion signals are associated with this process.

Table 5.3. Confidence interval for the slopes for the target ions for the post-burning residues of black powder (confidence level 95%). Slopes that are statistically less than zero were highlighted in red.

Confidence Interval for the slopes (confidence level 95%)												
Coding	**K^+**			**NO_2^-**			**OCN^- (4 first months)**			**OCN^- (20 last months)**		
	slope	**min.**	**max.**	**slope**	**min.**	**max.**	**slope**	**min.**	**max.**	**slope**	**min.**	**max.**
BP -20.0	-0.03	-0.05	-0.01	0.00	0.00	0.00	-0.09	-0.19	0.02	-0.01	-0.01	0.00
BP 4.5	0.04	0.02	0.06	0.00	0.00	0.00	-0.05	-0.07	-0.02	-0.01	-0.01	-0.01
BP 18.0	0.07	0.05	0.10	0.00	0.00	0.01	-0.11	-0.17	-0.05	-0.01	-0.01	0.00
	NO_3^-			**SO_4^{2-}**			**$S_2O_3^{2-}$**			**SCN^-**		
	slope	**min.**	**max.**	**slope**	**min.**	**max.**	**slope**	**min.**	**max.**	**slope**	**min.**	**max.**
BP -20.0	0.00	0.00	0.01	-0.04	-0.11	0.02	0.00	0.00	0.00	0.00	0.00	0.00
BP 4.5	0.01	0.00	0.01	-0.03	-0.09	0.02	0.04	0.02	0.05	0.00	0.00	0.01
BP 18.0	0.01	0.01	0.01	-0.03	-0.09	0.03	0.07	0.03	0.10	0.01	0.00	0.01

The results obtained for the target ions (Cl^-, ClO_4^-, ClO_3^-, K^+) in burned flash powder residue extracts are presented in Figure 5.4. The data indicate good stability for all the studied ions over the observed period. Table 5.4 provides the confidence intervals for the slopes, with a confidence level of 95%.

Several ions have been found to be adsorbed by alumina in previous studies [204–207], and since alumina is one of the main products formed during flash powder reactions [30], the slight variations observed in the intensity of certain ions may be attributed to this phenomenon.

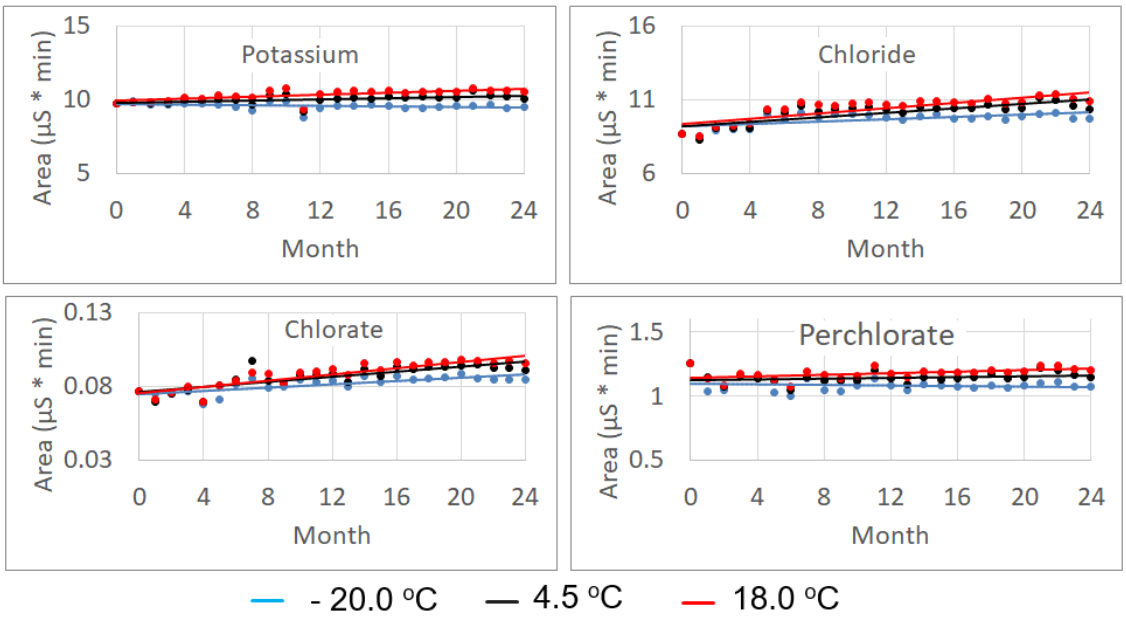

Figure 5.4. Monthly monitoring of target ions (K^+, Cl^-, ClO_3^-, ClO_4^-) for flash powder afterburning residue extract for 24 months.

Table 5.4. Confidence interval for the slopes for the target ions for the post-burning residues of flash powder (confidence level 95%). None of the slopes are statistically less than zero.

Confidence Interval for the slopes (confidence level 95%)												
Coding	**K^+**			**Cl^-**			**ClO_3^-**			**ClO_4^-**		
	slope	**min.**	**max.**	**slope**	**min.**	**max.**	**slope**	**min.**	**max.**	**slope**	**min.**	**max.**
FP -20.0	-0.01	-0.02	0.00	0.04	0.02	0.06	0.00	0.00	0.00	0.00	0.00	0.00
FP 4.5	0.02	0.01	0.03	0.08	0.05	0.10	0.00	0.00	0.00	0.00	0.00	0.00
FP 18.0	0.04	0.02	0.05	0.09	0.06	0.11	0.00	0.00	0.00	0.00	0.00	0.01

Regarding the explosive emulsion, Figure 5.5 presents the results for the target ions (NH_4^+, Na^+, NO_3^-). The data obtained from both the pre-explosion explosive extracts and the post-explosion residue extracts from a real case indicate the stability of all ions during the studied period of 24 months and 23 months, respectively. The confidence intervals for the slopes (confidence level 95%) are provided in Table 5.5, confirming the stability of the ions.

Powdered aluminum metal is frequently incorporated into explosives, including explosive emulsions, to amplify the pressure of gaseous products and augment the heat of explosion. Due to the high reactivity of aluminum, a protective layer of Al_2O_3 is rapidly formed on its surface [208,209]. As mentioned earlier, alumina can adsorb specific ions [204–207], which could explain the slight variations observed in the intensity of nitrate ions under different experimental conditions.

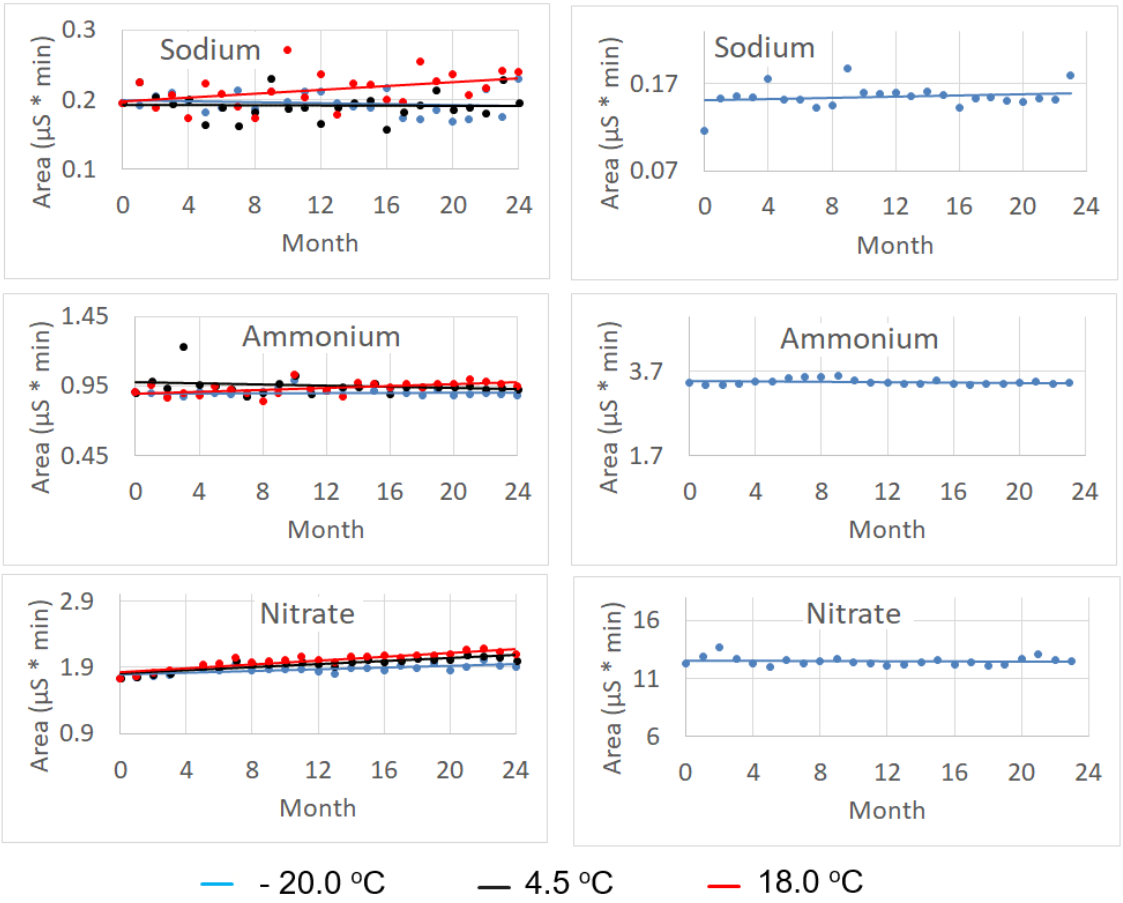

Figure 5.5. Monthly monitoring of target ions (NH_4^+, Na^+, NO_3^-) for pre-explosion explosive emulsion extract for 24 months (left) and its post-explosion residues from a real sample (right) for 23 months.

Table 5.5. Confidence interval for the slopes for the target ions for the emulsion explosive (confidence level 95%). None of the slopes are statistically less than zero.

Confidence Interval for the slopes (confidence level 95%)									
Coding	**Na^+**			**NH_4^+**			**NO_3^-**		
	slope	**min.**	**max.**	**slope**	**min.**	**max.**	**slope**	**min.**	**max.**
EE -20.0	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01
EE 4.5	0.00	0.00	0.00	0.00	-0.01	0.00	0.01	0.01	0.01
EE 18.0	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02
RC -20.0	0.00	0.00	0.00	0.00	-0.01	0.00	-0.01	-0.03	0.02

Considering all the ions studied, it is observed that, in addition to the cyanate ions discussed earlier, only the potassium ions at -20 °C showed a significant negative variation between the first and last month of this study, and even then, it was quite low (< 3%). This result indicates the feasibility of long-term storage for the residues of the three explosives studied.

In addition to the monthly monitoring graphs presented in the previous figures, Figures S5.12 to S5.15 (Appendix D) provide direct comparisons of the chromatograms obtained in the first and last month, illustrating the overall stability of the ion profiles discussed earlier.

Regarding the organic phase of the explosive emulsion, Figure 5.6 displays the representative results of the n-hexane extract analyzed by GC/MS, revealing the presence of a mixture of C_{22} to C_{34} n-alkanes. This identification was confirmed by comparing the retention times and mass spectra with standard n-alkanes, as shown in Figures S5.16 and S5.17 in Appendix D. Figure 5.7 and Table 5.6 provide a summary of the bimonthly monitoring study conducted on these n-alkanes over a period of 12 months. The results indicate that all n-alkanes demonstrate good stability thus far, with statistically insignificant slopes (CI 95%).

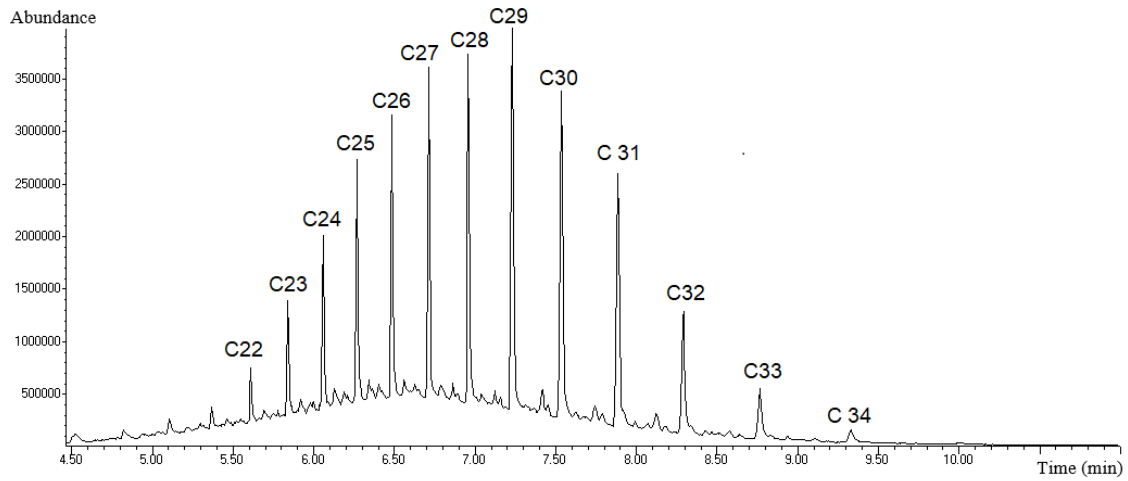

Figure 5.6. Representative chromatogram of the n-hexane extract of explosive emulsion post-explosion residues from the real case.

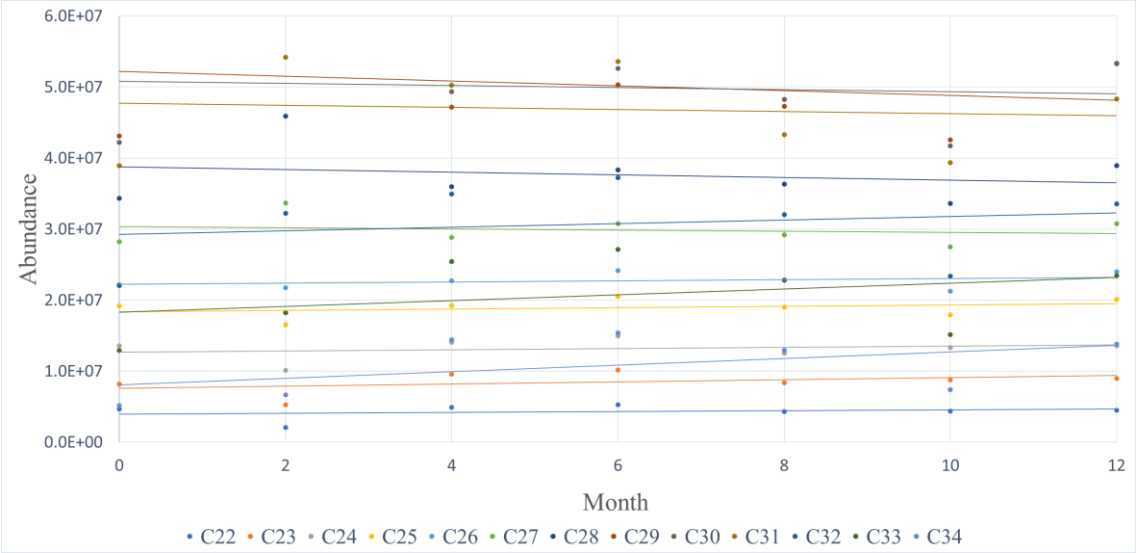

Figure 5.7. Bimonthly monitoring of the studied n-alkanes (C_{22} to C_{34}) in n-hexane extract of explosive emulsion post-explosion residues of a real case, kept at -20º C, for 12 months.

Table 5.6. Confidence interval for the slopes for the n-alkanes (C_{22} to C_{34}) in n-hexane extract of explosive emulsion post-explosion residues of a real case.

n-alkanes	Slope (x 10^6)	Confidence Interval (x 10^6)	
		Min.	Max.
C_{22}	0.06	-0.21	0.33
C_{23}	0.15	-0.23	0.53
C_{24}	0.09	-0.30	0.48
C_{25}	0.10	-0.24	0.44
C_{26}	0.08	-0.19	0.36
C_{27}	-0.08	-0.62	0.47
C_{28}	-0.18	-1.26	0.89
C_{29}	-0.34	-2.57	1.89
C_{30}	-0.15	-2.00	1.70
C_{31}	-0.15	-1.84	1.54
C_{32}	0.25	-1.27	1.77
C_{33}	0.41	-0.95	1.76
C_{34}	0.46	-0.54	1.46

In addition to the bimonthly monitoring graphs presented earlier, Figure S5.18 in Appendix D showcases a direct comparison of the chromatograms obtained in the first and last month (twelfth), providing further evidence of the stability of the target analyte profiles throughout the study period, as discussed previously.

5.4 Conclusions

The results indicate that, under the experimental conditions and within the examined time period (24 months), the aqueous extracts of post-explosion/burn residues for all the evaluated explosives exhibited good stability when stored at the three studied temperatures (-20.0, 4.5, and 18.0 °C). Considering that only significant negative variations would be a concern regarding long-term storage, only the cyanate ion raised concerns. At the highest temperature studied (18.0 °C), it became undetectable from the 17^{th} month onwards, and for the other two temperatures, degradation was considerable (84% for -20.0 °C and 66% for 4.5 °C, in relative area).

Therefore, this result indicates that low temperatures should be preferable for the purpose of long-term storage of black powder residues, mainly due to the degradation of the cyanate ion. Additionally, the reduction in cyanate ion signals over time alone is not sufficient to alter the conclusion regarding the identification of post-explosion residues, since the remaining ions, which stayed stable, are sufficient to reach the same conclusion.

Regarding the organic phase related to the explosive emulsion, the results indicated stability for all analytes, n-alkanes (C_{22} to C_{34}), at the evaluated temperature (-20.0 °C) within the examined time period (12 months), also indicating their suitability for long-term storage.

Thus, overall, this study demonstrated that for all evaluated explosive mixtures (flash powder, explosive emulsion, and black powder), throughout the studied period, long-term storage for reanalysis purposes is viable.

GENERAL CONCLUSIONS

GENERAL CONCLUSIONS

This research emphasizes the importance of analyzing explosives and post-explosion residues within the field of forensic chemistry, as it serves as a critical tool in unraveling crimes involving the use of explosives. By addressing the common challenges encountered during the routine analysis of post-explosion residues at the National Institute of Criminalistics, the presented results hope to contribute to providing solutions and knowledge for handling the most complex cases.

The comprehensive retrospective study of post-explosion cases handled by the Federal Police successfully established the initial profile of the most commonly used explosives in criminal activities across Brazil. The insights gained from this survey played a vital role in shaping the conceptualization and experimental design of this PhD thesis. Furthermore, the findings obtained are expected to provide valuable support for future studies aimed at addressing the specific challenges and casuistic related to explosives and illicit materials in Brazil.

Despite the inherent challenges posed by banknotes as a matrix in post-explosion analysis, the results of this study have demonstrated the promising potential of PCA analysis for discriminating between crime scene samples and banknotes obtained from everyday circulation. These findings pave the way for future research within our research group, focusing on the development of classification models to enhance the capabilities of forensic analysis in this domain.

An assessment of potential interferences in sampling materials used for the analysis of post-explosion residues, specifically focusing on explosive emulsion/ANFO by GC/MS, was conducted. The study revealed that certain materials such as syringe plungers, gloves, and plastic films have the potential to introduce contamination, leading to inconclusive results or false negatives/positives. These findings highlight the importance of careful selection and evaluation of sampling materials to ensure the accuracy and reliability of forensic analyses in post-explosion investigations.

The stability study of target analytes in post-explosion/burn residues has provided evidence their long-term stability in both aqueous and organic extracts from commonly used fuel-oxidizer explosive mixtures in criminal activities. The results indicate that the aqueous extracts can be stored as long-term samples for a minimum of 24 months, while the organic extracts can be stored for at least 12 months. Among all the analytes evaluated,

only the cyanate ions showed significant concerns, as they exhibited considerable degradation at all studied temperatures, especially at the highest (18.0 °C). However, this fact does not invalidate the purpose of this study, since the remaining ions, which stayed stable, are sufficient to reach the same conclusion. These results have important implications for the storage and analysis of post-explosion residues.

Finally, the studies conducted in this work have made significant contributions towards enhancing the analysis of post-explosion residues, particularly in challenging cases encountered in forensic laboratories. The results and methodologies developed through these studies provide valuable insights and solutions to address the difficulties faced in the analysis of post-explosion residues. By improving the analytical techniques, identifying potential interferences, obtaining profiles of commonly used explosives, and assessing the stability of target ions, this research enhances the overall accuracy and effectiveness of forensic investigations involving post-explosion residues. These advancements contribute to the continuous improvement of forensic chemistry and the field of explosives analysis, ultimately aiding in the successful resolution of criminal cases related to explosives.

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APPENDIX A

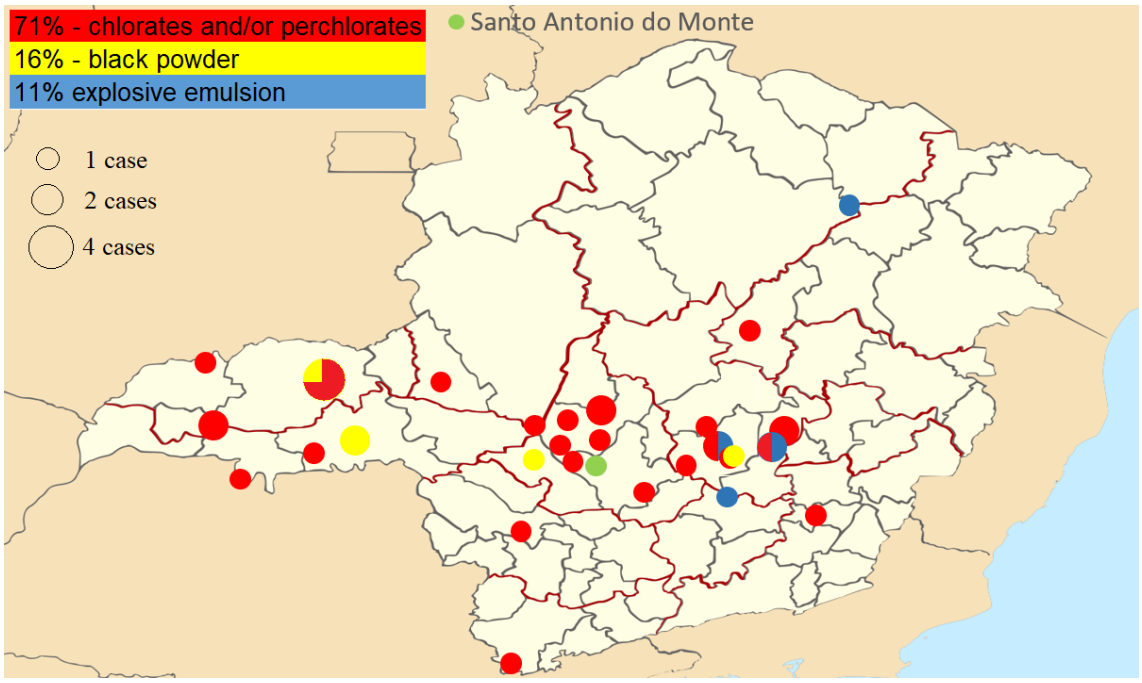

Figure S2.1. Distribution of ATM/cash safe explosion cases in Minas Gerais, by type of explosive, submitted to chemical analysis between 2014 and 2020. The cases involved explosive mixtures based on chlorates and/or perchlorates (red), black powder (yellow), and explosive emulsion (blue). The city of Santo Antônio do Monte is highlighted in green.

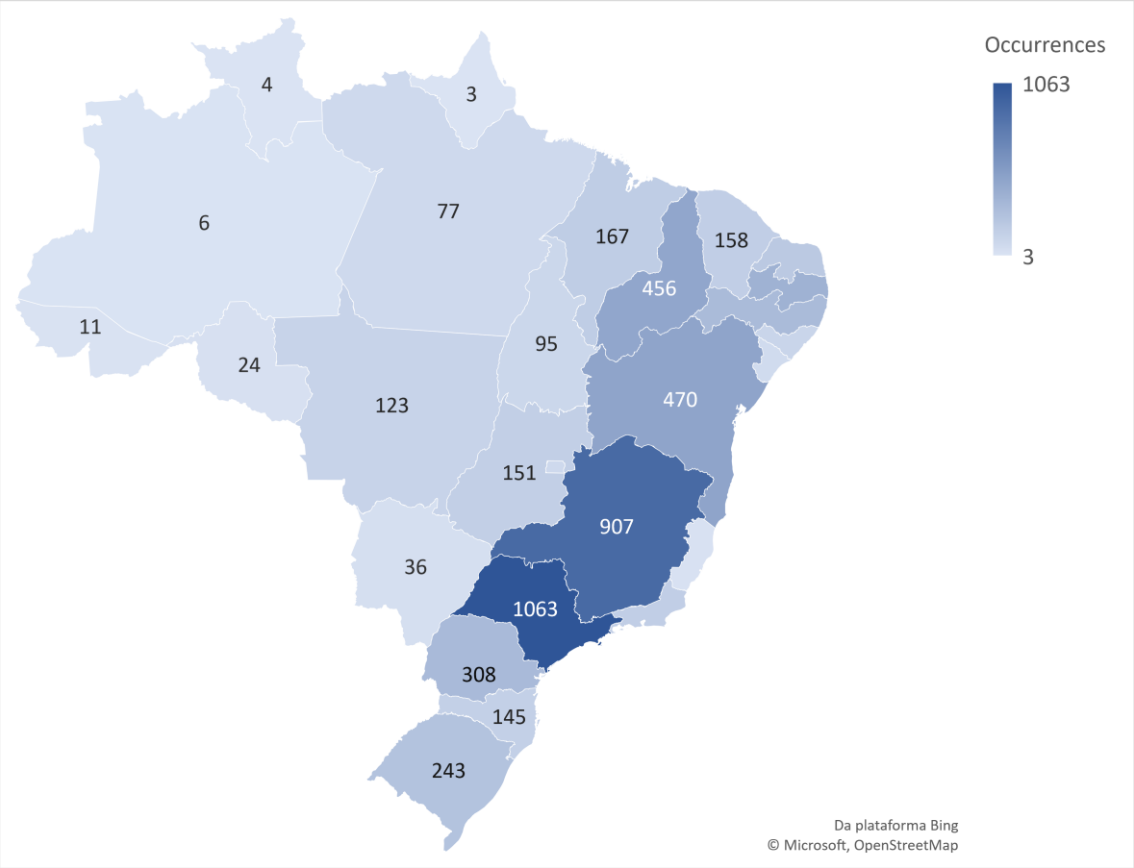

Figure S2.2. Distribution of ATMs/cash safes explosion cases (per CONTRASP) in Brazil between 2014 and 2020.

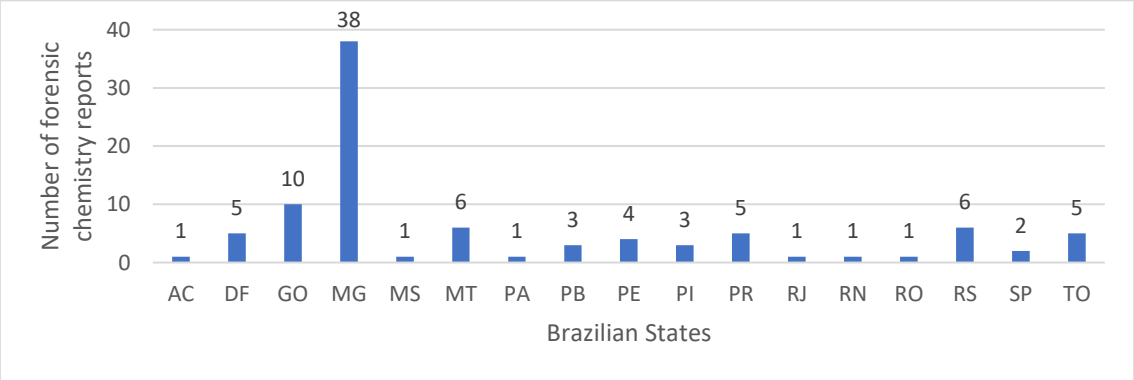

Figure S2.3. Distribution of forensic chemistry reports for ATMs/cash safes explosions occurrences according to reports studied in Brazil between 2014 and 2020 by state.

APPENDIX B

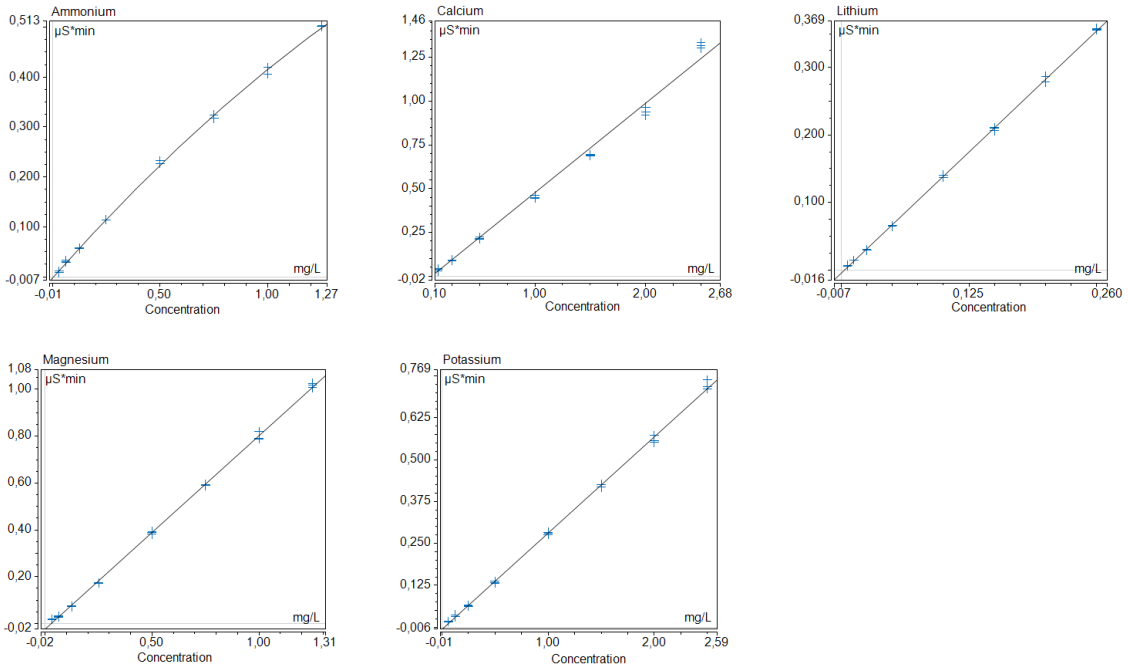

Figure S3.1. Low calibration curve for Cations.

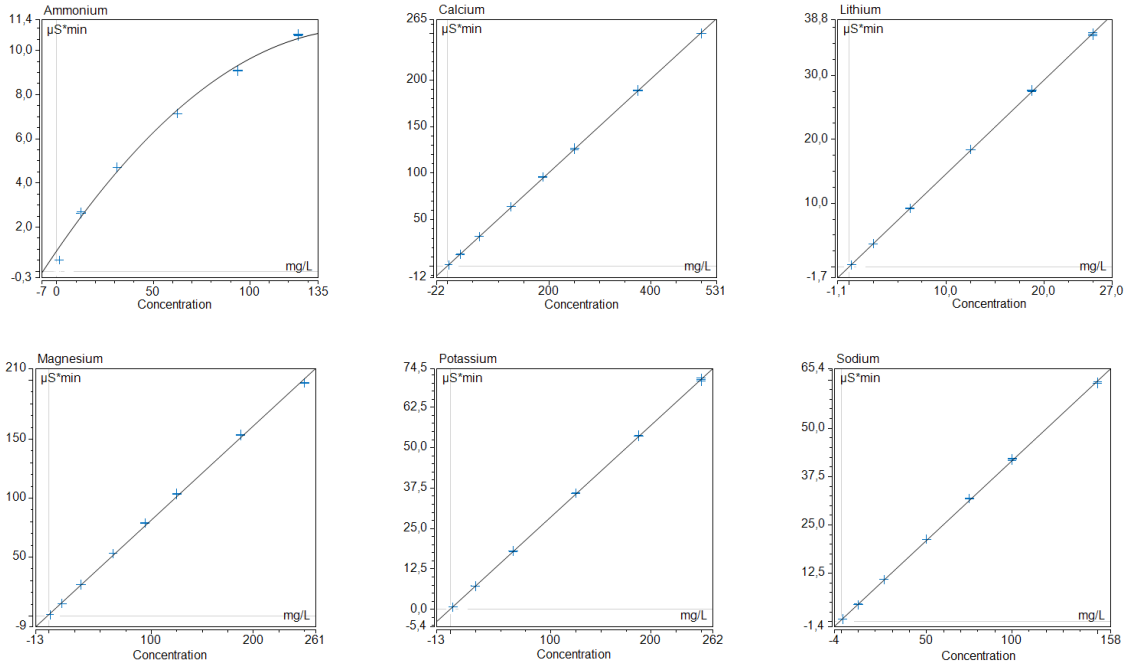

Figure S3.2. Hight calibration curve for Cations.

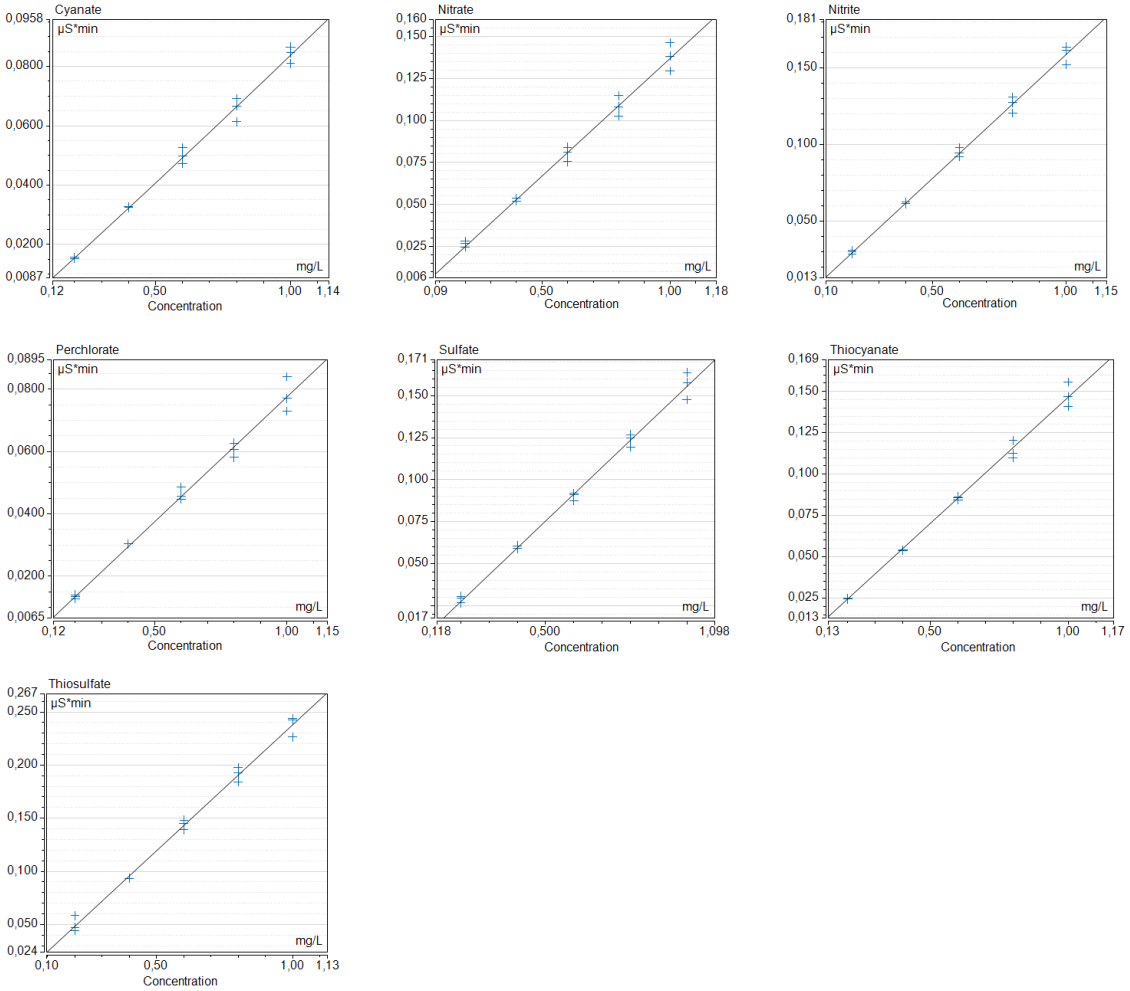

Figure S3.3. Low calibration curve for Anions.

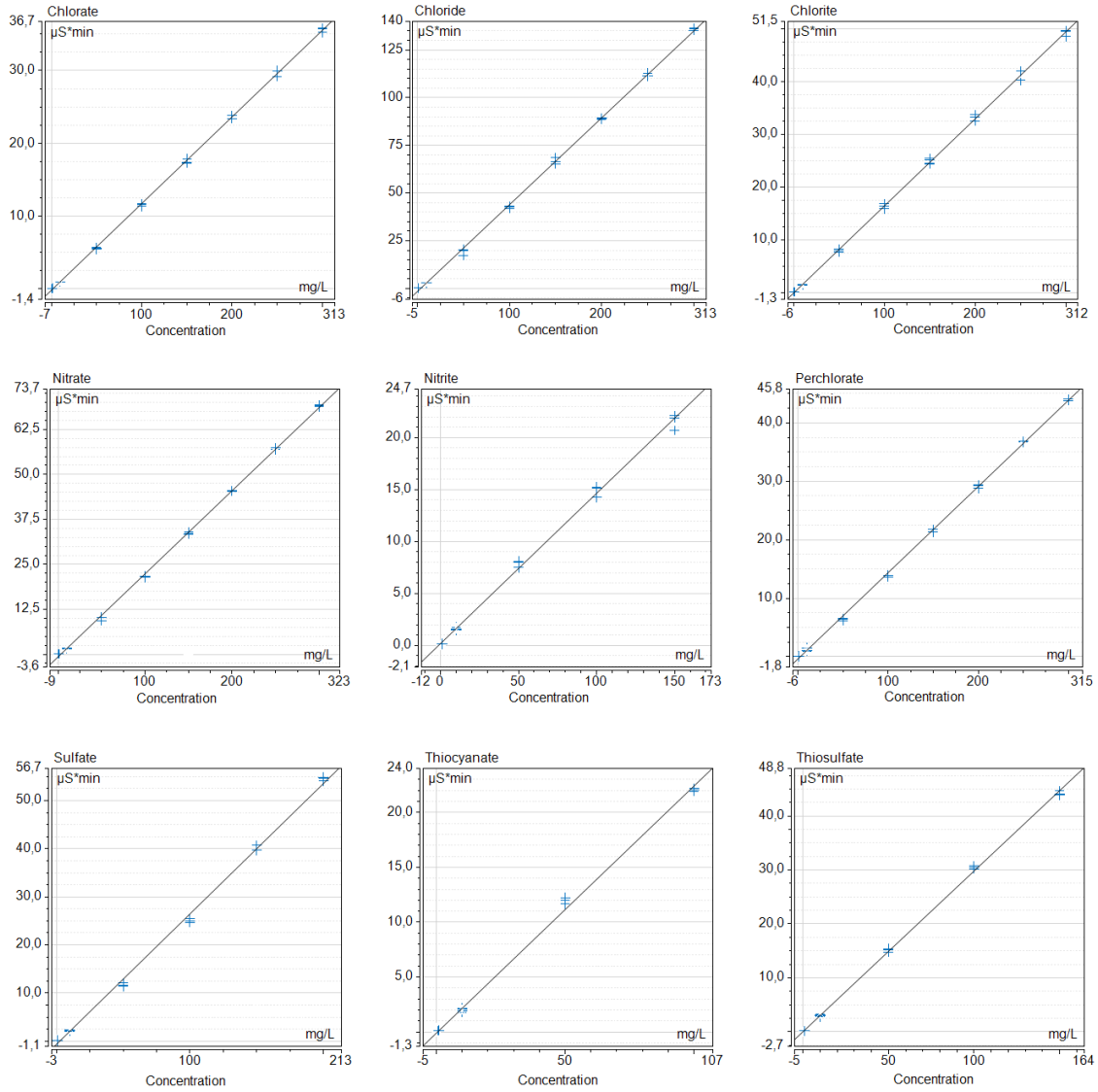

Figure S3.4. Hight calibration curve for Anions.

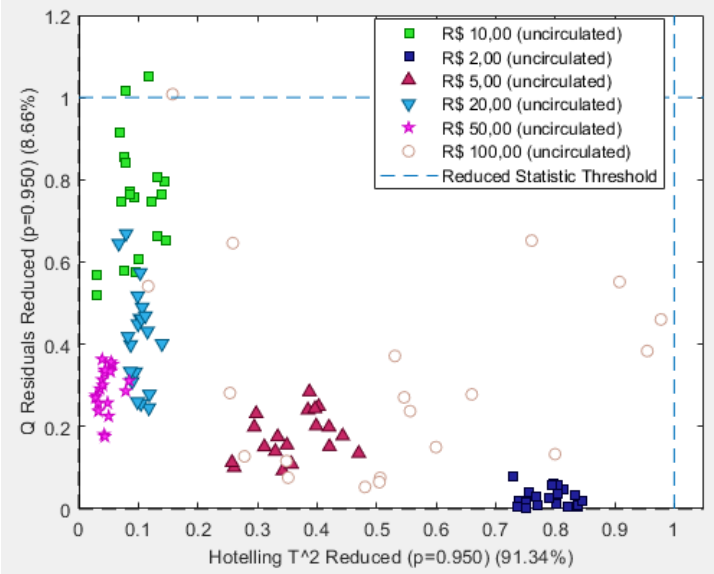

Figure S3.5. Q residuals versus Hotelling's T^2 plot for the PCA model shown in Figure 3.7 – Chapter III.

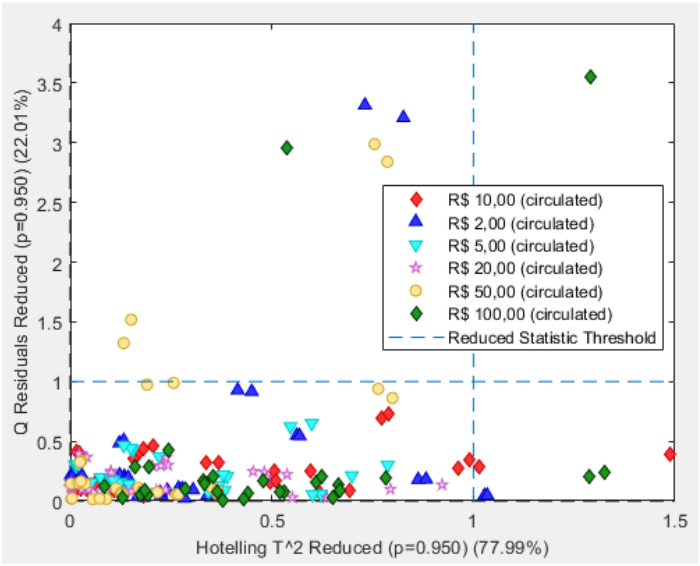

Figure S3.6. Q residuals versus Hotelling's T^2 plot for the PCA model shown in Figure 3.8 – Chapter III.

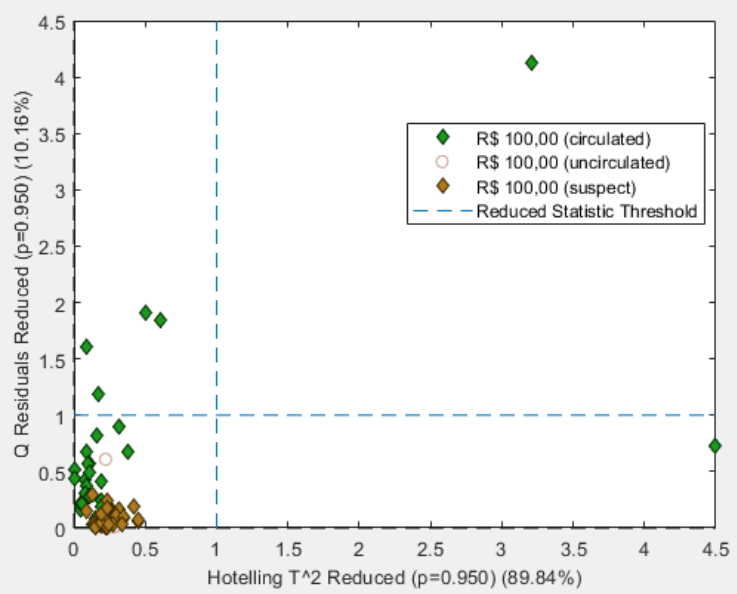

Figure S3.7. Q residuals versus Hotelling's T^2 plot for the PCA model shown in Figure 3.9A – Chapter III.

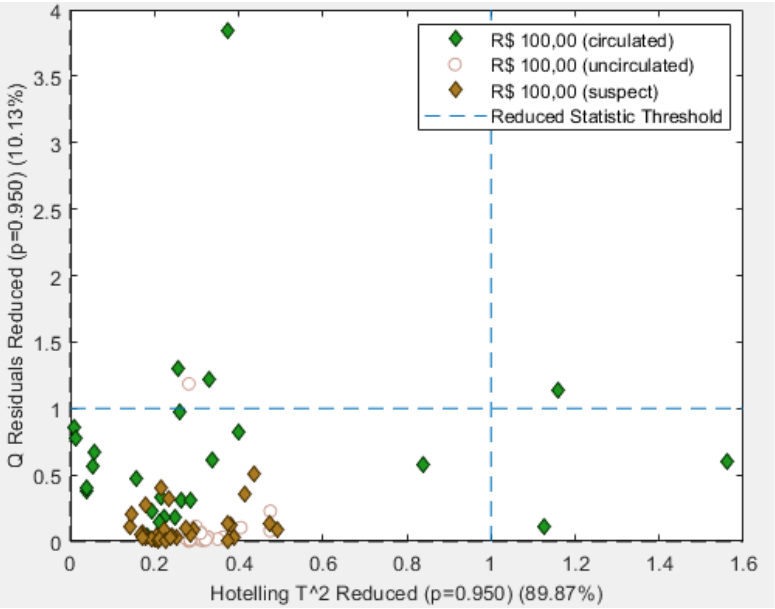

Figure S3.8. Q residuals versus Hotelling's T^2 plot for the PCA model shown in Figure 3.9C – Chapter III.

APPENDIX C

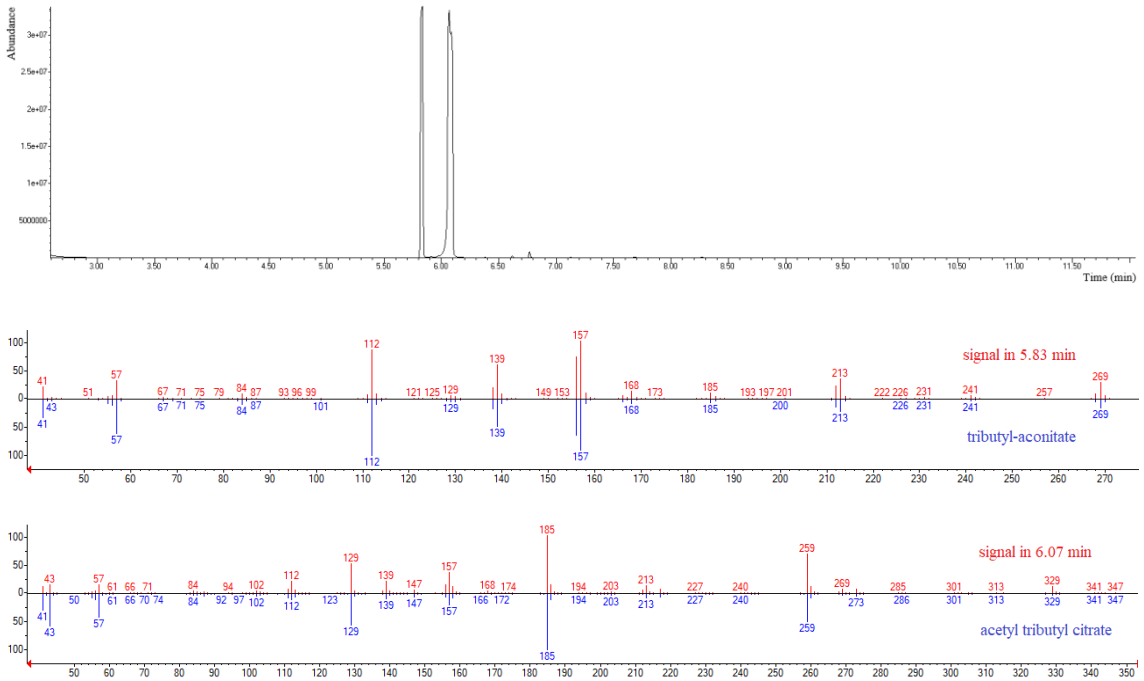

Figure S4.1. Results of the GC/MS analysis of plastic film PF-2. Total ion chromatogram (top) and comparison of the mass spectra corresponding to the two main signals (red lines) with standard spectra (blue lines) of tributyl-aconitate (center) and acetyl tributyl citrate (bottom).

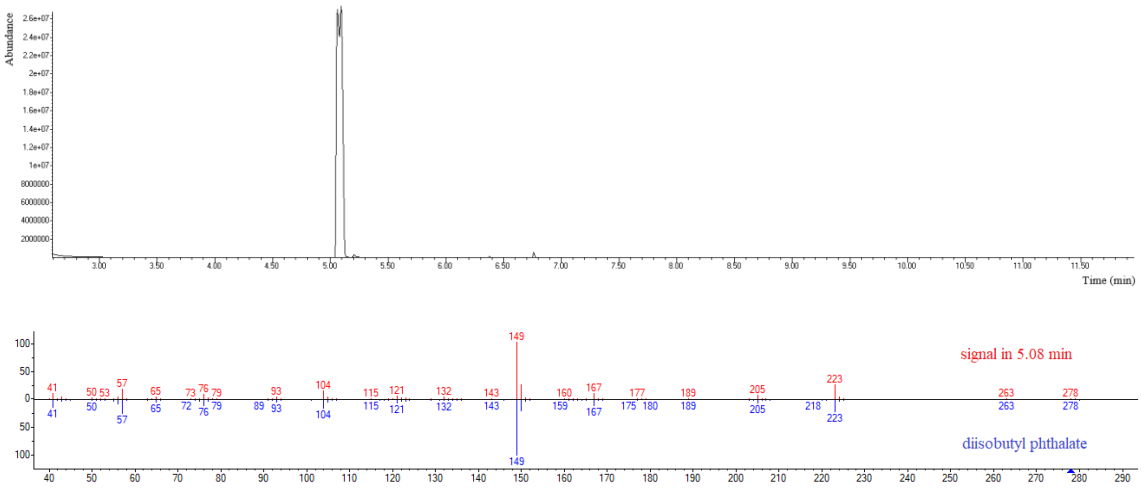

Figure S4.2. Results of the GC/MS analysis of vial cap VC-4. Total ion chromatogram (top) and comparison of the mass spectrum corresponding to the main signal (red lines) with the standard spectrum (blue lines) of diisobutyl phthalate (bottom).

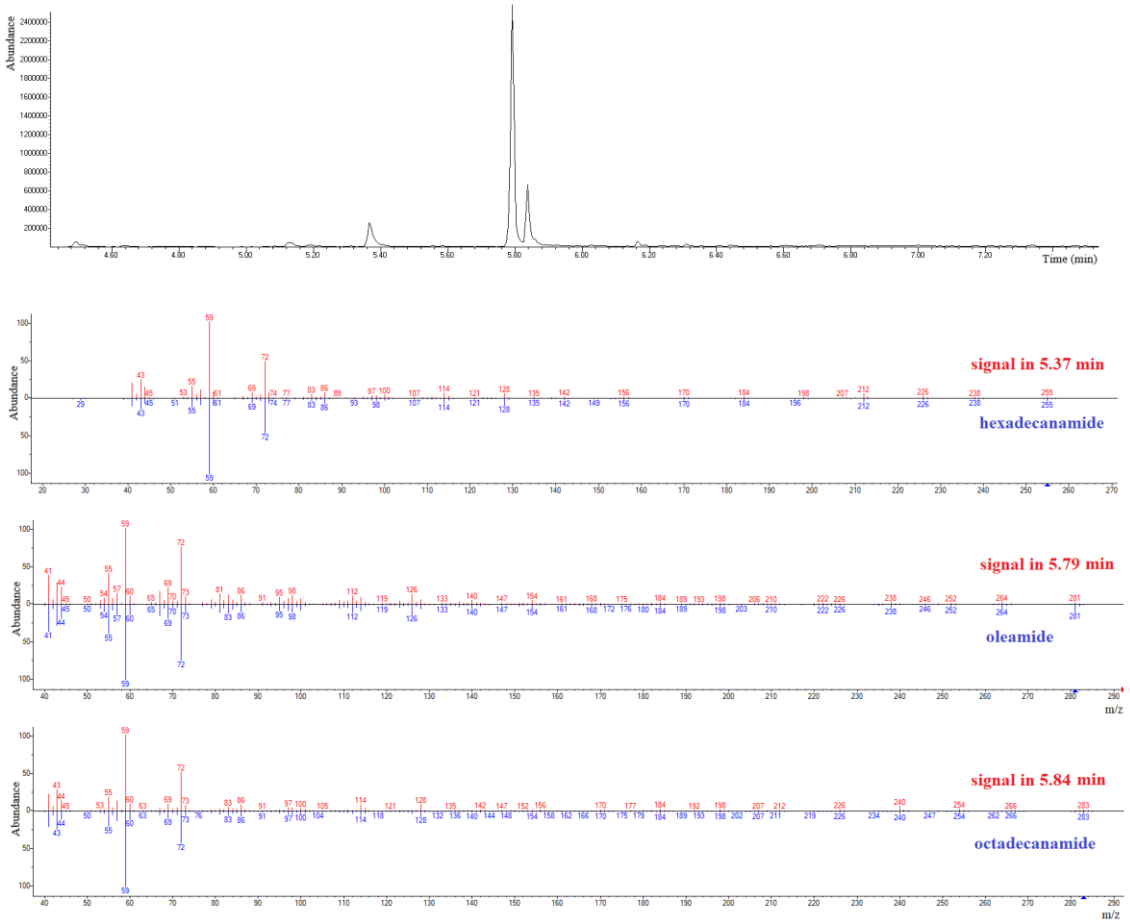

Figure S4.3. Results of the GC/MS analysis of plastic pipette PP-1. Total ion chromatogram (top) and comparison of the mass spectrum corresponding to the main signal (red lines) with the standard spectrum (blue lines) of diisobutyl phthalate (bottom).

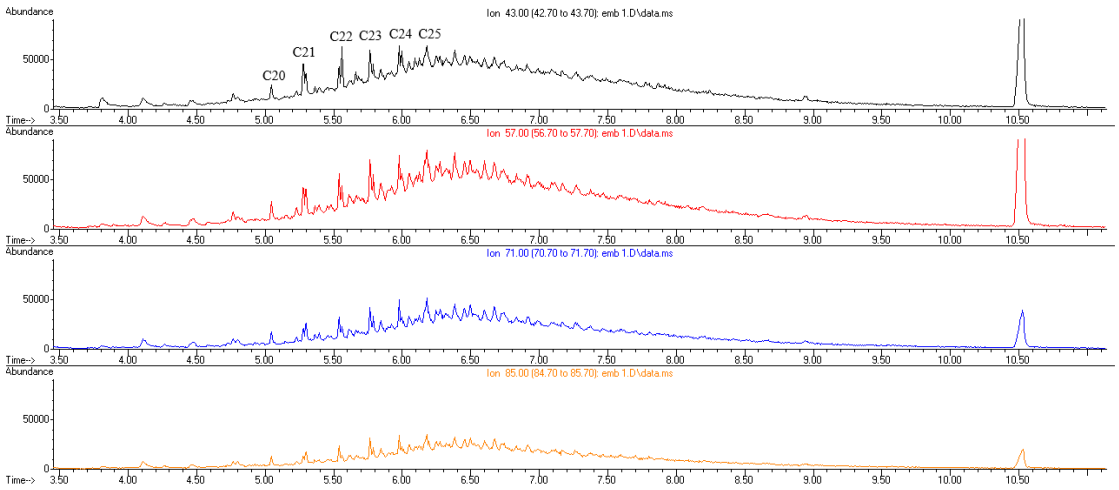

Figure S4.4. Extracted ion chromatograms (EIC) of m/z 43, 57, 71 and 85 of the SP-1 syringe plunger extract.

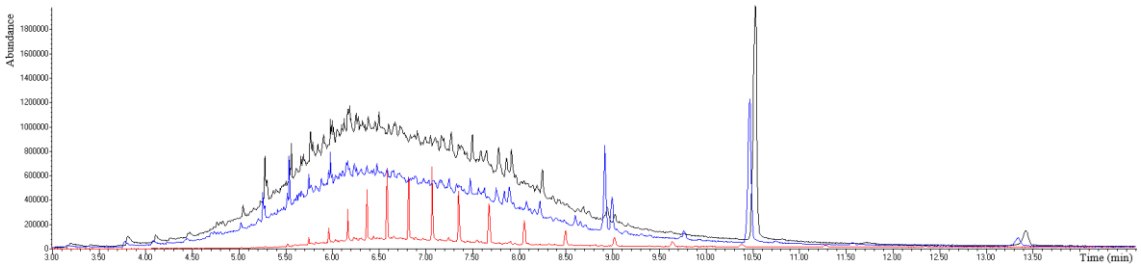

Figure S4.5. Overlapping chromatograms of the extracts of SP-1 syringe plunger (in black), cumulative effect procedures (handling with gloves and extraction with a syringe) (in blue), and explosive emulsion (in red).

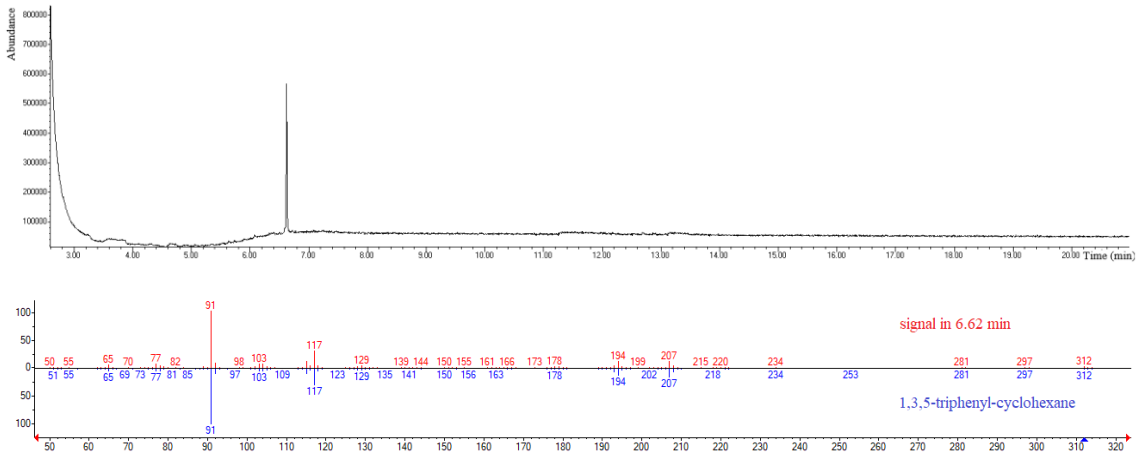

Figure S4.6. Results of the GC/MS analysis of disposable gloves DG-3. Total ion chromatogram (top) and comparison of the mass spectrum corresponding to the main signal (red lines) with the standard spectrum (blue lines) of 1,3,5-triphenyl-cyclohexane (bottom).

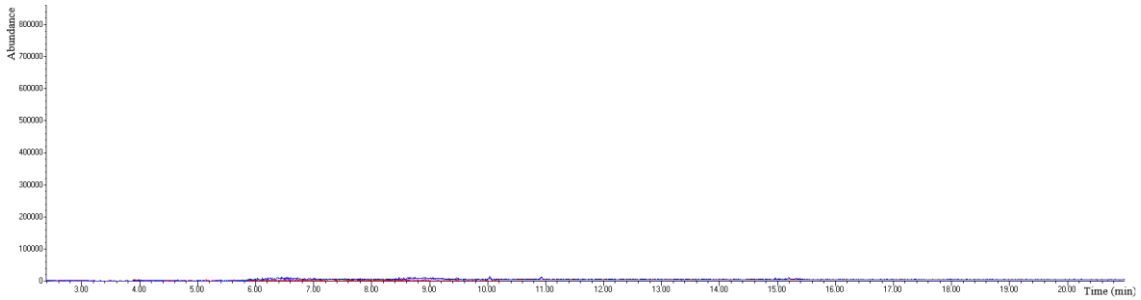

Figure S4.7. Results of the GC/MS analysis of disposable gloves DG-4 (blue lines) and DG-5 (red lines). Total ion chromatograms without the identification of interfering compounds.

APPENDIX D

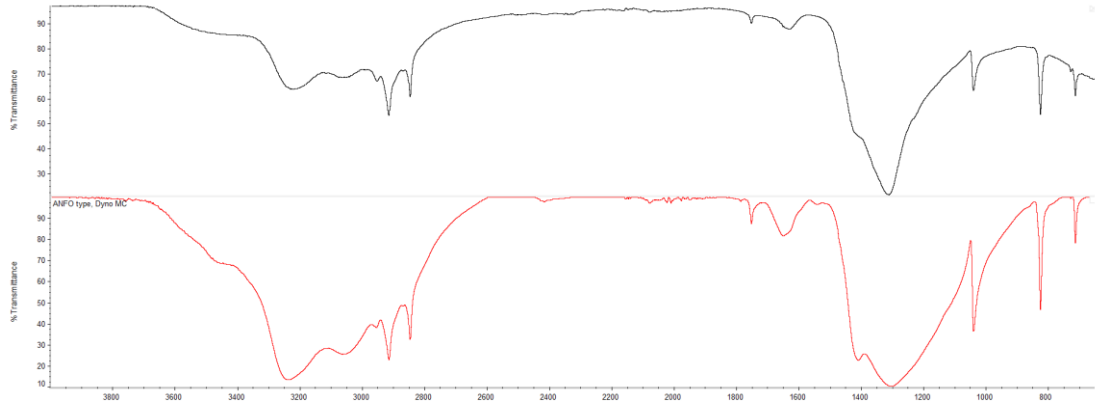

Figure S5.1. FTIR spectra of the explosive emulsion used in the stability study (black lines) compared to ANFO (standard spectra in red lines).

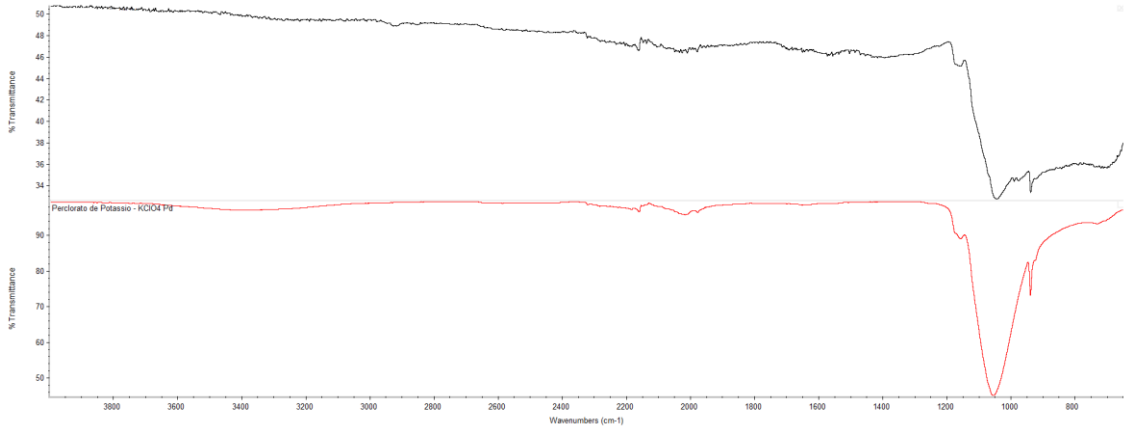

Figure S5.2. FTIR spectra of the flash powder used in the stability study (black lines) compared to potassium perchlorate (standard spectra in red lines).

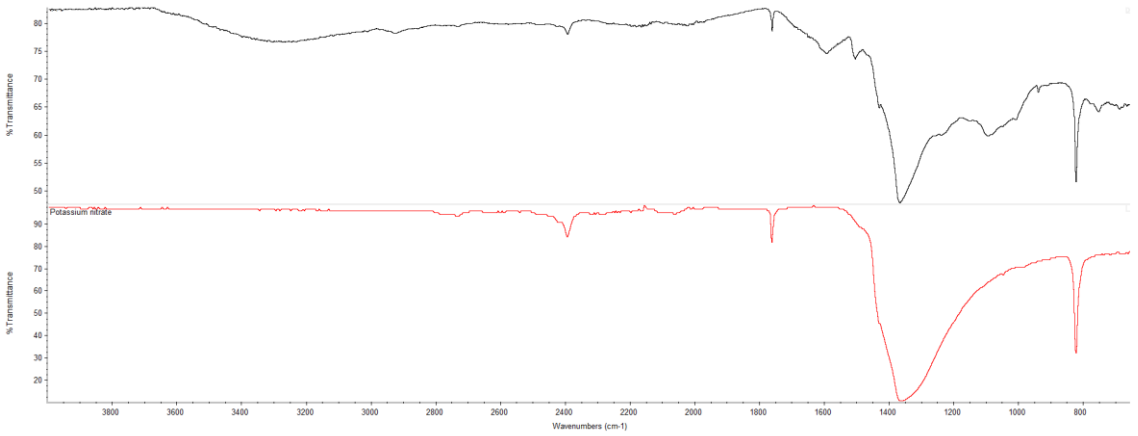

Figure S5.3. FTIR spectra of the black powder used in the stability study (black lines) compared to potassium nitrate (standard spectra in red lines).

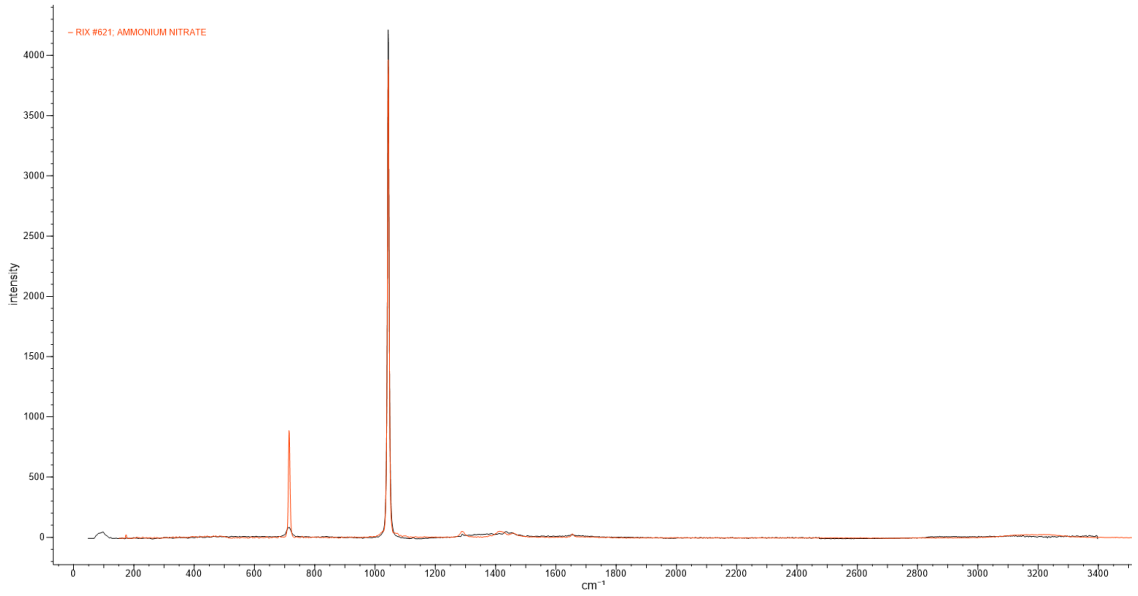

Figure S5.4. Raman spectra of the explosive emulsion used in the stability study (black lines) compared to ammonium nitrate (standard spectra – red lines).

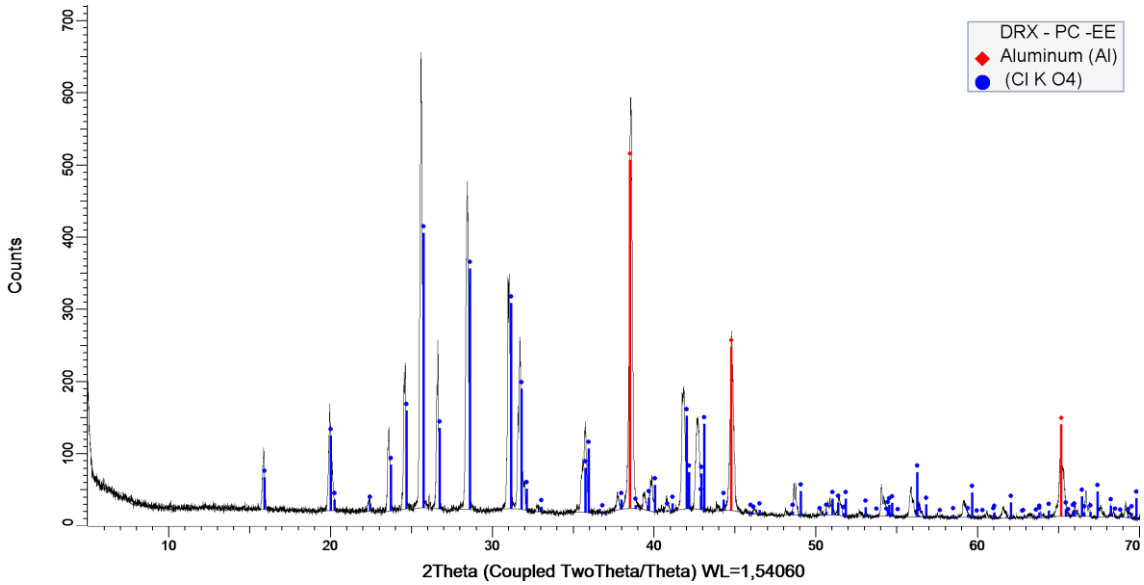

Figure S5.5. X-ray diffractogram of the flash powder used in the stability study (black lines) compared to the X-ray diffractogram of potassium perchlorate (blue lines) and metallic aluminum (red lines).

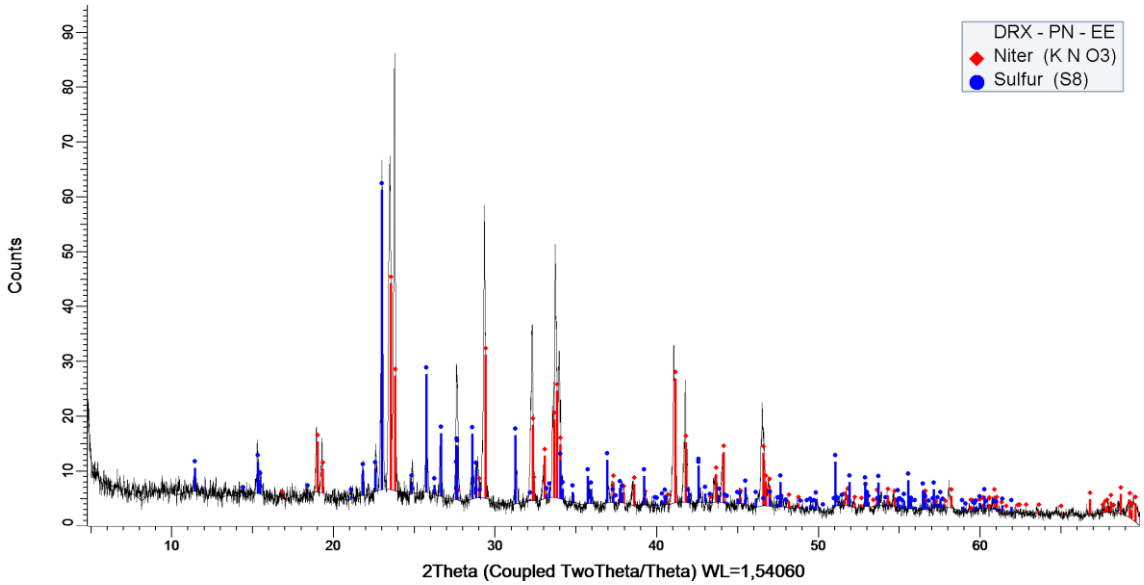

Figure S5.6. X-ray diffractogram of the black powder used in the stability study (black lines) compared to the X-ray diffractogram of potassium nitrate (red lines) and sulfur (blue lines).

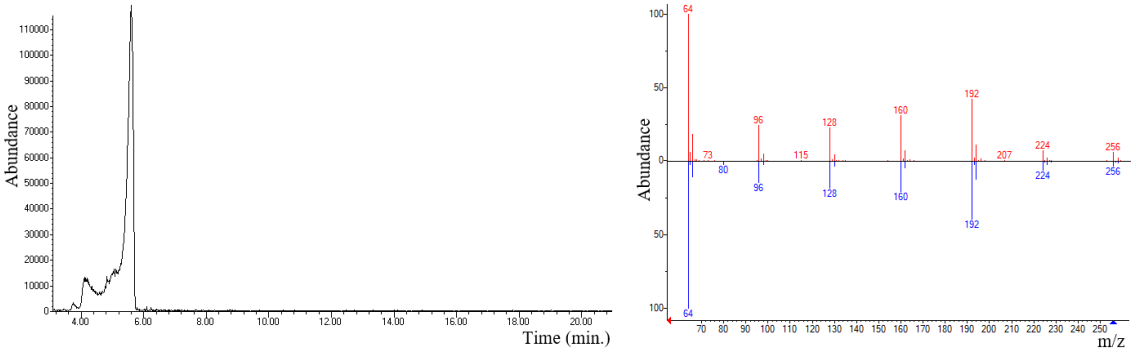

Figure S5.7. Results of the GC/MS analysis (IEC m/z 128) of black powder used in the stability study (left) and comparation of the mass spectra corresponding to the main signal (red lines) to sulfur (standard spectra – blue lines) (right).

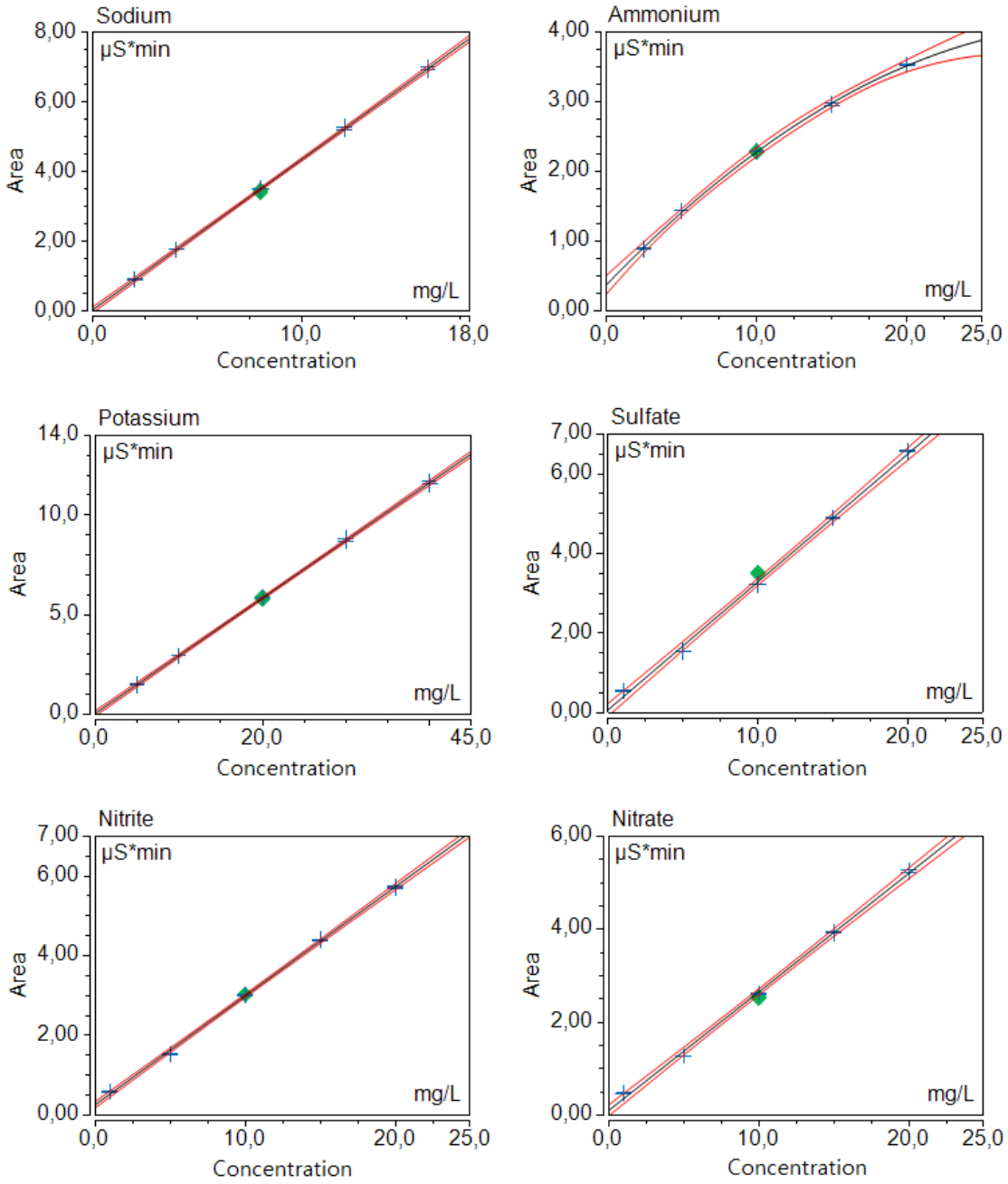

Figure S5.8. Calibration curves with their 99.9% confidence intervals (red lines) and the results, for each analyte of interest, obtained for the standard solutions prepared at the beginning of the study and used to adjust the results of the samples analyzed monthly (each analyte was evaluated using the "check standard" option of the Chromeleon® software set to its initial concentration (green square).

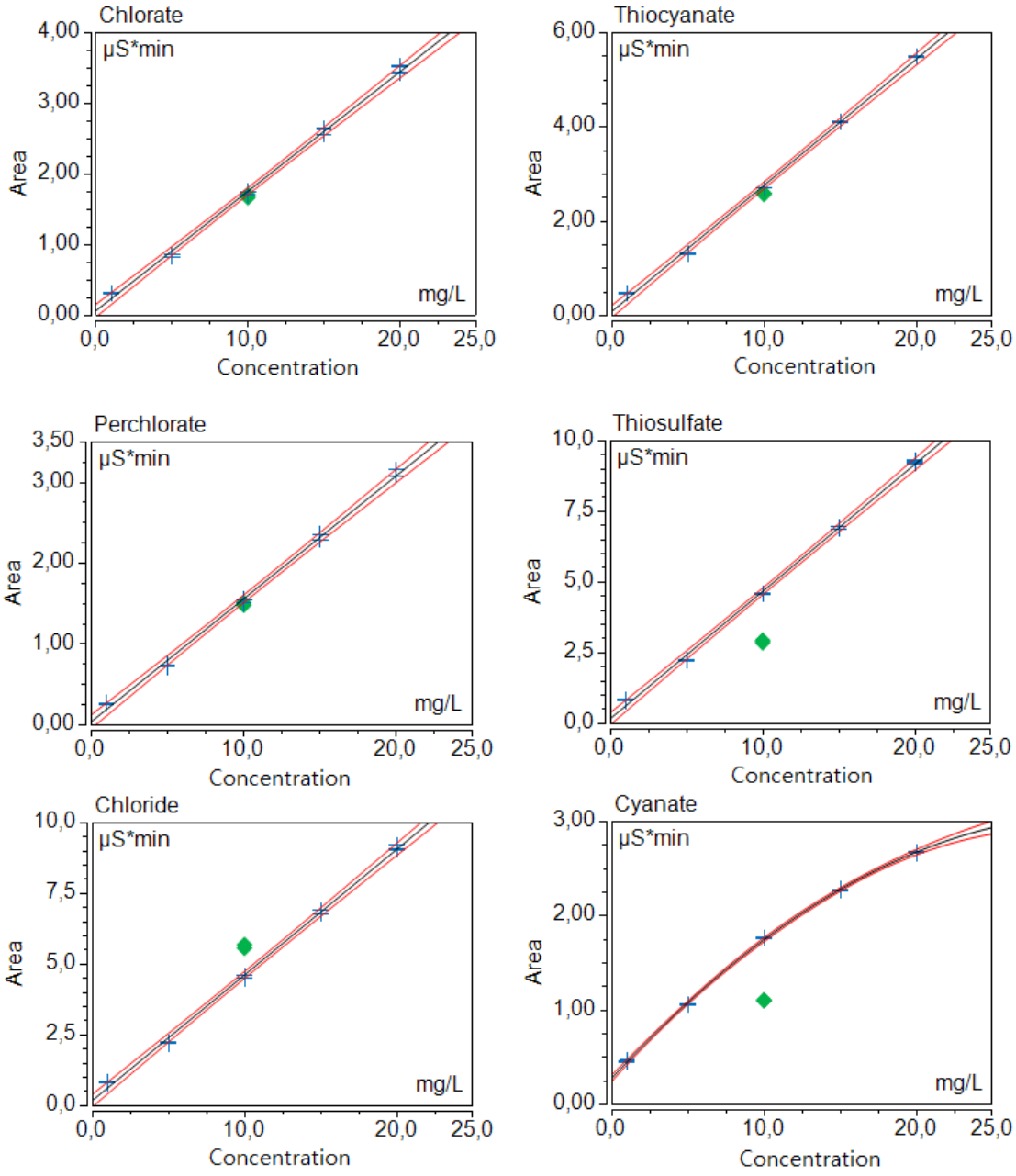

Figure S5.9. Calibration curves with their 99.9% confidence intervals (red lines) and the results, for each analyte of interest, obtained for the standard solutions prepared at the beginning of the study and used to adjust the results of the samples analyzed monthly (each analyte was evaluated using the "check standard" option of the Chromeleon® software set to its initial concentration (green square).

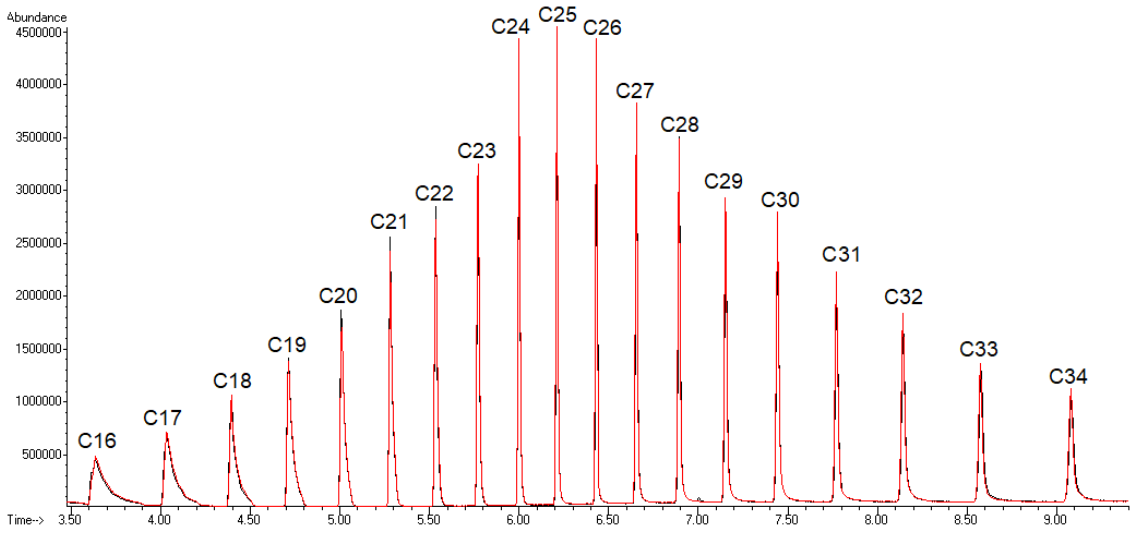

Figure S5.10. Representative overlapping chromatograms of the ten replicates of the standard n-alkane solution prepared at the end (red) and at the beginning (black) of the study, depicting the elution order of n-alkanes C_{16} to C_{34}, revealing the stability of the analytes (confirmed by Student's t-test).

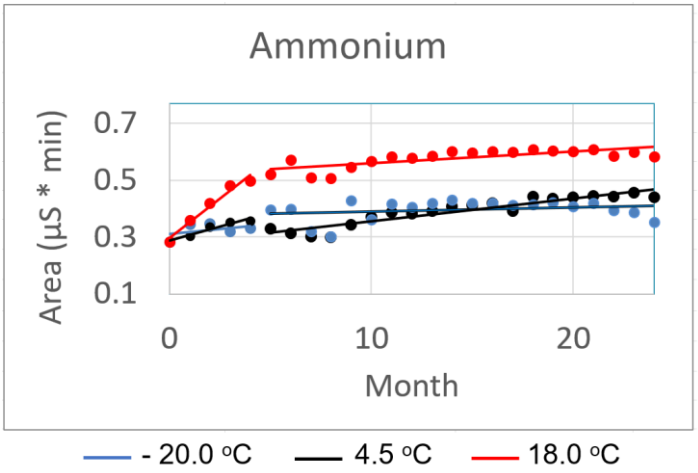

Figure S5.11. Monthly monitoring of target ammonium ions for black powder afterburning residue extracts for 24 months.

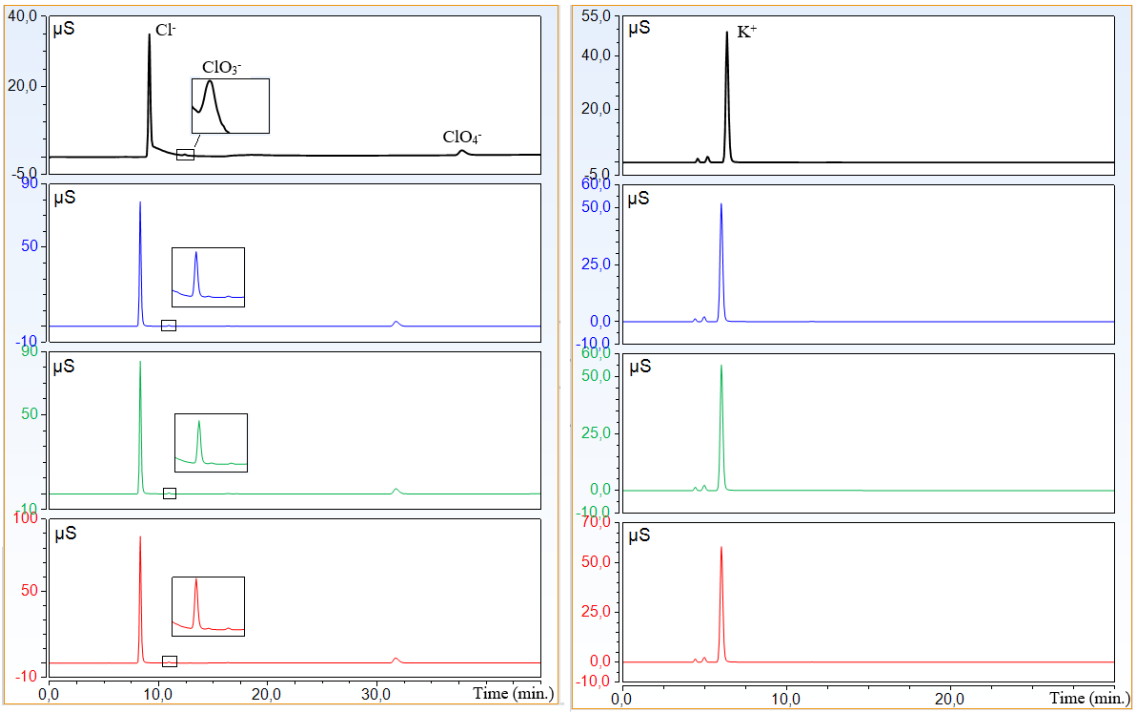

Figure S5.12. Anion (left) and cation (right) exchange chromatograms of post-burning residues of flash powder freshly extracted (black lines) and after 24 months at -20.0 ºC (blue lines), 18.0 ºC (green lines) and 4.5 ºC (red lines). The observed small variations in the retention times between the fresh extract chromatogram and the others are due to column degradation.

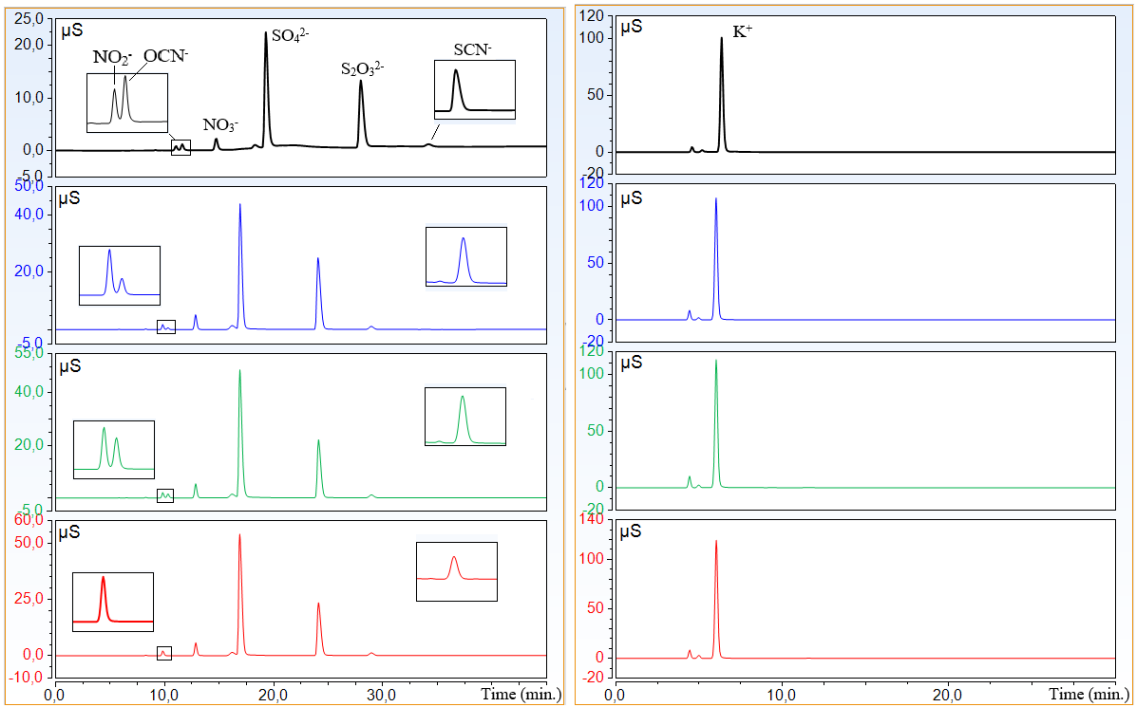

Figure S5.13. Anion (left) and cation (right) exchange chromatograms of post-burning residues of black powder freshly extracted (black lines) and after 24 months at -20.0 ºC (blue lines), 18.0 ºC (green lines) and 4.5 ºC (red lines). The observed small variations in the retention times between the fresh extract chromatogram and the others are due to column degradation.

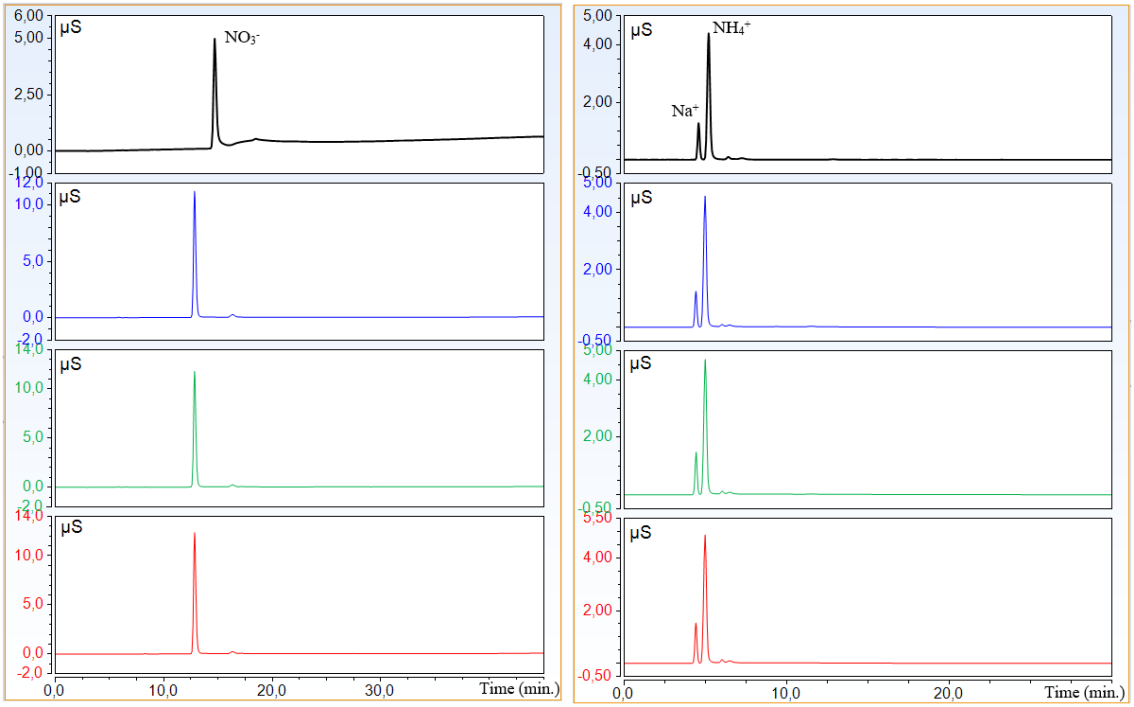

Figure S5.14. Anion (left) and cation (right) exchange chromatograms of post-burning residues of explosive emulsion freshly extracted (black lines) and after 24 months at -20.0 ºC (blue lines), 18.0 ºC (green lines) and 4.5 ºC (red lines). The observed small variations in the retention times between the fresh extract chromatogram and the others are due to column degradation.

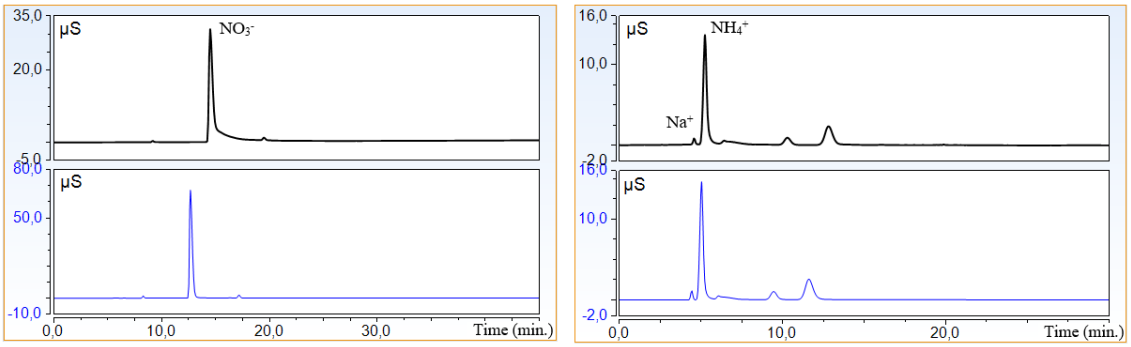

Figure S5.15. Anion (left) and cation (right) exchange chromatograms of post-explosion residues of explosive emulsion from a real sample freshly extracted (black lines) and after 23 months at -20.0 ºC (blue lines). The observed small variations in the retention times between the fresh extract chromatogram and the others are due to column degradation.

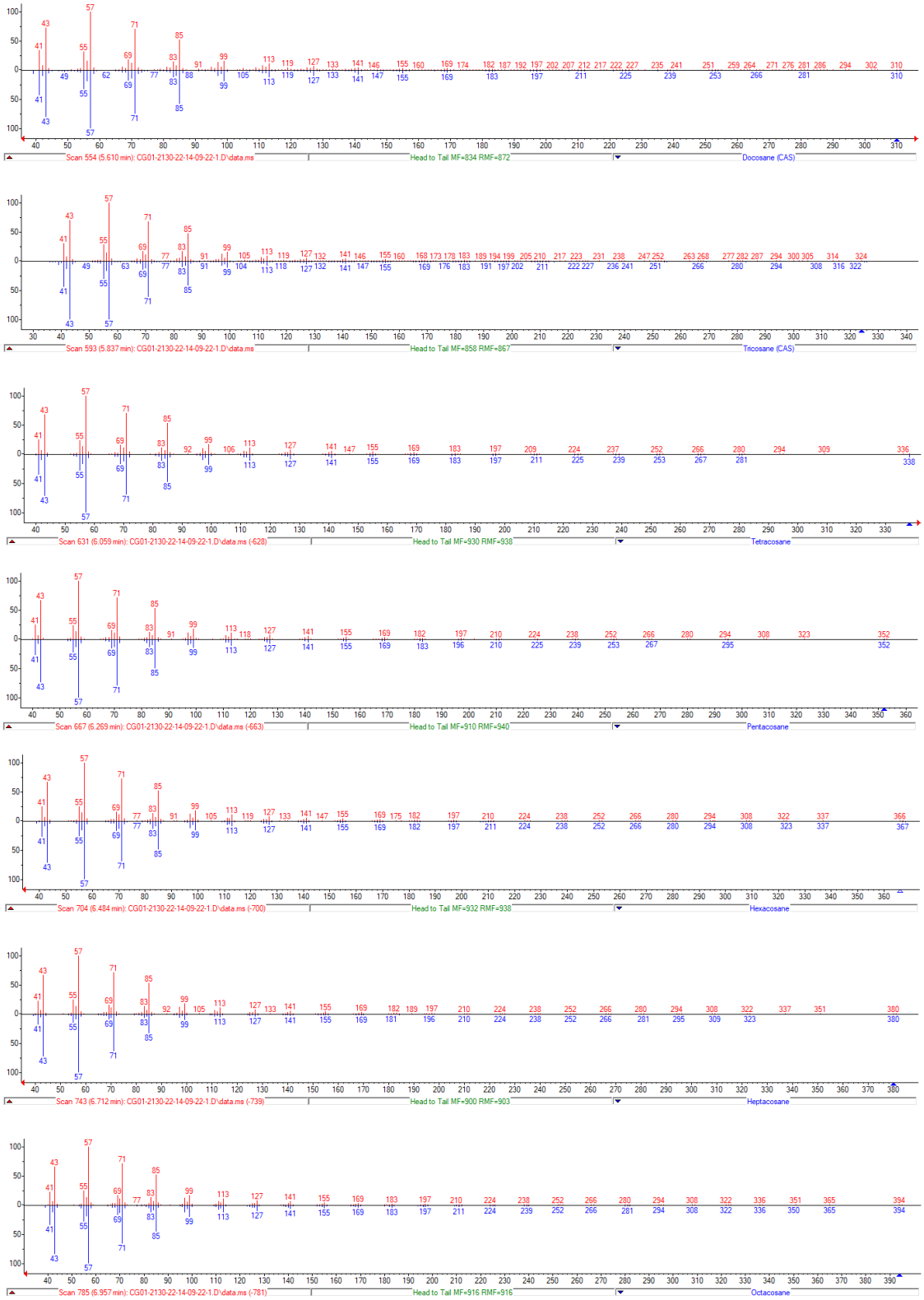

Figure S5.16. Comparison of mass spectra obtained from the explosive emulsion sample (red lines) and NIST 2.3 mass spectral library (blue lines) of C_{22} to C_{28} n-alkanes. The identity of each of them was confirmed by comparison with the retention time of n-alkane standards.

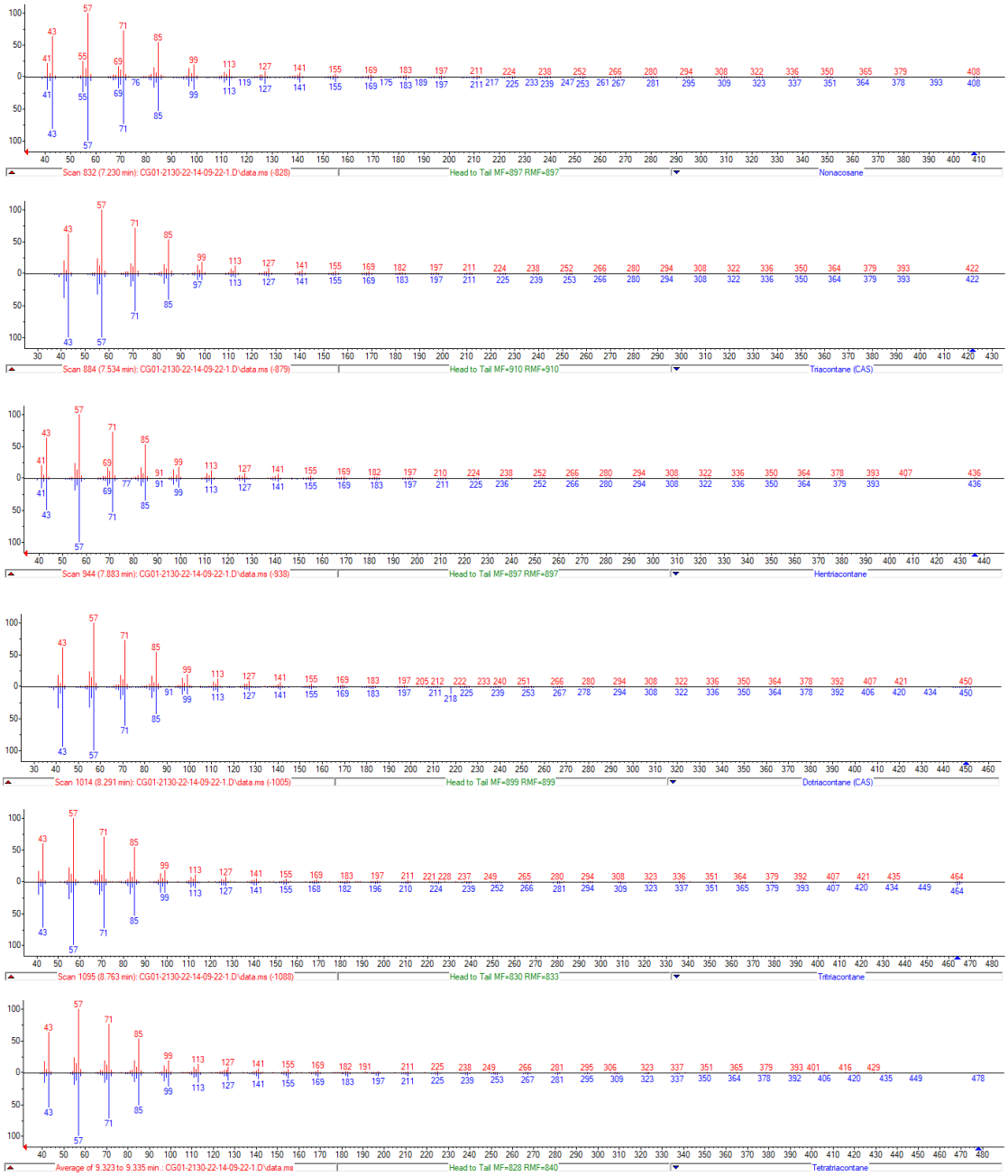

Figure S5.17. Comparison of mass spectra obtained from the explosive emulsion sample (red lines) and NIST 2.3 mass spectral library (blue lines) of C29 to C34 n-alkanes. The identity of each of them was confirmed by comparison with the retention time of n-alkane standards.

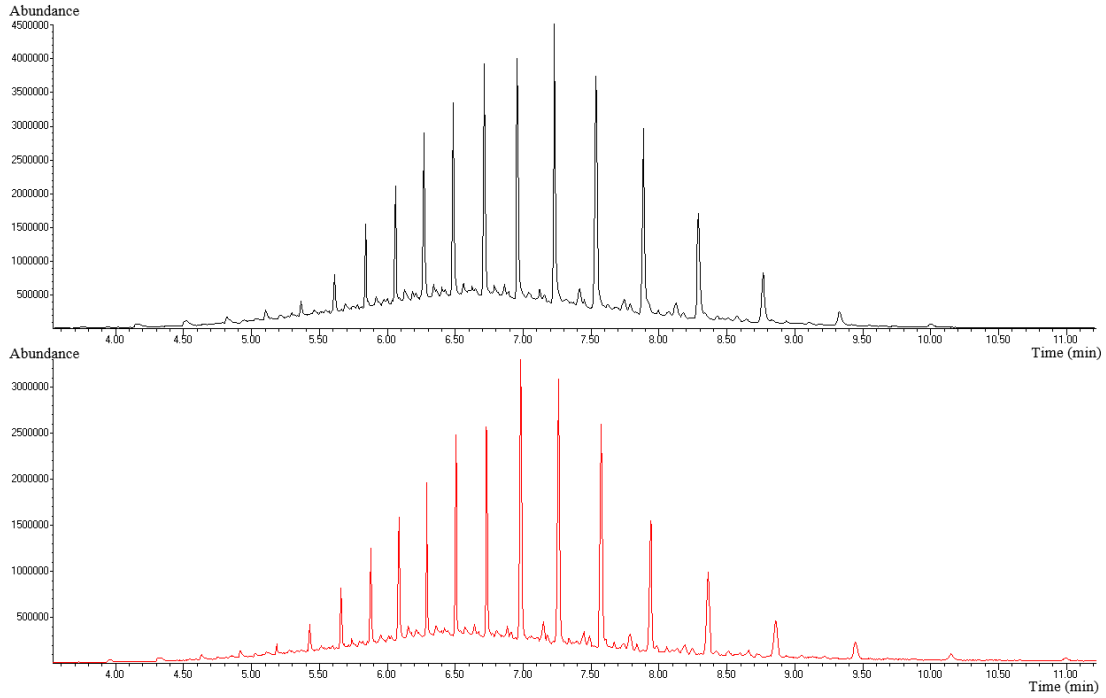

Figure S5.18. Chromatogram of the n-hexane extract of explosive emulsion post-explosion residues from a real case freshly extracted (black lines) and after 12 months at -20.0 ºC (red lines). The observed small variations in the retention times between the fresh extract chromatogram and the others are due to column degradation.

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Brasília, 17 de novembro de 2023.

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Título do Trabalho: ANÁLISE DE EXPLOSIVOS E RESÍDUOS PÓS-EXPLOSÃO: PERFIL QUÍMICO, INTERFERENTES E ESTABILIDADE POR CROMATOGRAFIA IÔNICA, CROMATOGRAFIA GASOSA COM DETECÇÃO POR ESPECTROMETRIA DE MASSAS E QUIMIOMETRIA

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