#### ADVANCED REVIEW

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## Chlorate-based homemade explosives: A review

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#### Abstract

Chlorates and perchlorates, inorganic salts known for their potent oxidizing properties, find utility in various products such as pyrotechnics, matches, and disinfectants. Their chemical properties also make them suitable for homemade explosives, resulting in their extensive use by criminals. Hence, the forensic analysis of these compounds is vital for investigating crimes involving their utilization. A wide array of analytical techniques is available for detecting and quantifying these substances, offering forensic investigators an extensive toolkit to effectively analyze and identify chlorates and perchlorates in various samples. Recent research highlights the potential for leveraging the information obtained from analyzing these materials, including for intelligence purposes. The future of forensic analysis in this domain lies in extracting additional information, such as source attribution, through methods like chemometrics, thereby enhancing forensic intelligence capabilities.

This article is categorized under:

Forensic Chemistry and Trace Evidence > Explosive Analysis

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#### KEYWORDS

chlorates, forensic analysis, homemade explosives, perchlorates, source attribution

#### 1 **INTRODUCTION**

Homemade explosives (HMEs) are increasing in use by criminals due to the availability of precursors that can be used to create the required explosive materials (Nazarian & Presser, 2014). HMEs are used in improvised explosive devices (IEDs), which are estimated to have caused over 137,000 casualties in the past 20 years (Collett et al., 2021). The forensic detection and chemical analysis of HMEs are of profound importance in many different areas, such as criminal investigations, transportation security, border protection and overall counterterrorism efforts (Collett et al., 2021; Forbes et al., 2020).

Chemical explosions result from the rapid conversion of solid or liquid material into reaction products with a much greater volume than the originating mixture (Akhavan, 2011; Goodpaster, 2015). Two main components make up chemical explosives: an oxidizer (electron-deficient compound) that reacts with heat to generate oxygen gas, and a fuel

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(electron-donating compound) that reacts with oxygen to produce heat (Conkling & Mocella, 2018; Goodpaster, 2015). Once initiated, the oxidizer and the fuel produce a rapid chain reaction, creating a large volume of gas and heat, usually in a contained vessel, resulting in an explosion. Other components, such as binders, stabilizers, thickeners, plasticizers, and retardants, can be added to an explosive mixture to alter the explosion's properties (Goodpaster, 2015; Mohanty, 2011). Chemical explosives are the most common type currently used for military and commercial purposes. Therefore, unsurprisingly, most explosives used in criminal activity are chemical rather than mechanical or nuclear (Goodpaster, 2015).

For an explosion to detonate successfully, there is a requirement for sufficient oxygen to be released from the oxidizer (Goodpaster, 2015). Oxidizers in HMEs are commonly present in amounts greater than 70% of the explosive mixture's composition to ensure complete combustion. Thus, the high proportion of oxidizer in explosive mixtures explains the importance of detecting oxidizers, as they will be present in larger amounts. A wide range of materials can be used as fuel in HMEs, including many organic and inorganic materials, further evincing the importance of oxidizers in the forensic detection of HMEs, as there is a smaller range of suitable materials typically present in larger amounts.

Chlorates (ClO<sub>3</sub><sup>-</sup>) and perchlorates (ClO<sub>4</sub><sup>-</sup>) are inorganic salts that exhibit high oxidizing power, making for a suitable material for preparing HMEs. Ammonium, potassium, and sodium chlorate, and ammonium, magnesium, potassium, and sodium perchlorate are examples of these powerful oxidizers that can be used in the preparation of HMEs (Aziz & Hatzinger, 2009; Crespo Cajigas et al., 2019; Trumpolt et al., 2005; Yeager, 2011). Chlorates and perchlorates are frequently employed in the creation of homemade explosives for several reasons. Firstly, their utilization is facilitated by the abundance of readily available precursor substances. Furthermore, commercial chlorates and perchlorates can be easily accessible in specific regions across the globe, enhancing their widespread usage.

#### 2 | CHLORATES AND PERCHLORATES

#### 2.1 | Chlorates and perchlorates background

Chlorates were first discovered in 1788 by Claude Louis Berthollet by introducing elemental chlorine to aqueous potassium hydroxide before evaporation (Berthollet, 1788; Lemay & Oesper, 1946). Berthollet was impressed with the explosive properties of the chlorate, so much so that it was manufactured in larger quantities after preliminary testing, ultimately resulting in the accidental death of the superintendent and another worker at the mill where the powder was being manufactured (Lemay & Oesper, 1946). This accident highlighted the dangers of chlorates but did not result in the discontinuation of manufacturing and testing this product (Lemay & Oesper, 1946). Today, the main synthesis pathway of chlorates is via industrial electrolysis of chloride salts. Chlorates have extensive applications across various industries. They are commonly utilized as nonselective herbicides, additives in agricultural products, and dyes for textile and fur dyeing. Additionally, chlorates play a crucial role in uranium refining, pyrotechnics, disinfectants, production of matches, toys (gun caps), oxygen masks, pharmaceuticals, cosmetics, and serve as a versatile oxidizing agent (Vogt et al., 2000).

Chlorates, such as sodium chlorate, potassium chlorate, and ammonium chlorate, are common oxidizers used in preparing HMEs (Crespo Cajigas et al., 2019; Yeager, 2011). They are potent oxidizers, especially potassium chlorate, and are relatively accessible to the general public (Crespo Cajigas et al., 2019). Chlorates were once a common component in propellants such as fireworks and colored smoke bombs; however, they are highly reactive and lead to many industrial incidents, resulting in decreased use (Yeager, 2011). Due to the high number of industrial incidents involving chlorates, safety restrictions and regulations have been established on chlorate salts, along with many other explosives precursors, increasing the difficulty in sourcing the materials (National Code of Practice for Chemicals of Security Concern, 2016). Chlorates are still commercially available through pyrotechnics chemical distributors, especially in the United States, or alternatively can be easily synthesized via electrolysis of accessible salts, such as sodium chloride or potassium chloride (US Bureau of Mines, 1929; Yeager, 2011). Chlorates can also be synthesized relatively easily through the decomposition of sodium hypochlorite, which is found in commercial bleach (Adam & Gordon, 1999). The high sensitivity of chlorates paired with the ease of synthesizing from household materials results in a highly dangerous explosive material that is readily accessible.

Perchlorates were first discovered in the 1800s as impurities in nitrates mined from the Atacama Desert in Chile (Dafert, 1908; Snyder et al., 2009). Perchlorates have many legitimate uses as an oxidizer in fireworks, flares, rocket propellants, blasting agents, airbag initiators, and explosives (Aziz & Hatzinger, 2009; Oxley et al., 2009; Trumpolt et al., 2005). Perchlorates are generally more stable than chlorates, being less prone to accidental detonation due to

decomposing at higher temperatures and being less sensitive toward friction and impurities (Conkling & Mocella, 2010; Trumpolt et al., 2005). Due to this increased stability, perchlorates were chosen to replace chlorates in most pyrotechnic products to decrease industry incidents (Conkling & Mocella, 2010). However, in some countries, such as China, potassium chlorate is still used in local pyrotechnic products (Conkling & Mocella, 2010). Similar to chlorates, perchlorates are also a common oxidizer used in the preparation of HMEs (Aziz & Hatzinger, 2009; Zapata & García-Ruiz, 2018). Examples of perchlorates that can be used include potassium perchlorate, sodium perchlorate, ammonium perchlorate, and magnesium perchlorate (Aziz & Hatzinger, 2009; Trumpolt et al., 2005; Vogt et al., 2000). Perchlorates are commercially available through chemical distributors, but they can also be synthesized through the electrolysis of chloride or chlorate salts, the decomposition of chlorate salts or synthesized from bleach and some fertilizers (Conkling & Mocella, 2010; Trumpolt et al., 2005; Yeager, 2011).

The accessibility of chlorates and perchlorates to create HMEs results in the frequent use of these materials in criminal activities. Therefore, it is essential that chlorate and perchlorate salts can be properly identified and discriminated on the basis of their starting materials to provide as much information as possible to aid in forensic intelligence purposes.

#### 2.2 | Criminal incidents involving the use of chlorates and perchlorates

When ignited with fuel, chlorate and perchlorate compounds can create sizeable explosions. Common fuels that are currently used with chlorate and perchlorate are outlined in Table 1 (Yeager, 2006). A significant example of the use of chlorates in a criminal incident was in 2002 when approximately 1000 kg of potassium chlorate mixed with aluminum and sulfur was detonated by terrorists in a high-traffic nightclub area in Bali, resulting in the deaths of 202 people (Beveridge & Benson, 2009; Oam, 2013; Royds et al., 2005; Yeager, 2011). Two years after this event, a small delivery van loaded with an approximate 200 kg charge of similar composition was detonated at the Australian Embassy in Jakarta, Indonesia, killing 11 people and injuring many more (Oam, 2013). Within ten hours of the event, it was confirmed by forensic chemists that chlorate was present in the explosive mixture, along with TNT (Oam, 2013). In 2005, there was another terrorist attack in Indonesia, this time three simultaneous attacks around Bali that resulted in the deaths of 20 people (Oam, 2013). Chlorate was once again detected in the composition of the explosives used in these attacks, highlighting the prevalence of chlorate in HME attacks. Other cases that have involved the use of chlorates and perchlorates in HMEs and IEDs include devices deployed by the Irish Republican Army in the early 1970s and some of the later and more deadly devices made by Ted Kaczynski, the Unabomber, between 1978 and 1995, the United States (Yeager, 2011).

#### 3 | FORENSIC ANALYSIS

The forensic detection of explosive residue (ER) is an integral step in the investigation of forensic casework. ER detection begins with an assessment of a debris exhibit via visual and vapor examination (Beveridge, 1998). If small remnants of explosive material, or intact explosives, are found, direct analysis is undertaken using various techniques. The next step involves performing organic and water extractions on the collected material and exhibits that may not have observable material on them in preparation for further analysis (Beveridge, 1998). Many analytical techniques can be used to detect and identify explosive materials collected from crime scenes, as outlined in the Technical Working Group for Fire and Explosions (TWGFEX) guidelines (Technical Working Group for Fire and Explosion, 2007).

Name	Mixture
Improvised Plastic Explosive/Poor Man's C-4	Chlorate and/or perchlorate + vaseline
Armstrong's Mixture	Chlorate and/or perchlorate + red phosphorus
Flash Powder	Chlorate and/or perchlorate + aluminum, magnesium, sulfur, or antimony trisulfide
Rack-a-Rock	Chlorate and/or perchlorate + nitrobenzene
Chlorate-Sugar Mixture	Chlorate and/or perchlorate + powdered sugar

TABLE 1 Improvised chlorate and perchlorate explosive mixtures (Yeager, 2006).

Techniques used to analyze and detect ERs included chemical spot tests, separation techniques, spectroscopic techniques, electrochemical techniques, or alternative methods such as canine detection (National Institute of Standards and Technology, 2007a). Methods used include ion chromatography (IC), infrared (IR)/Raman spectroscopy, mass spectrometry (MS), high-performance liquid chromatography (HPLC), and gas chromatography (GC) (Dicinoski et al., 2006; National Institute of Standards and Technology, 2007b). GC paired with MS (GC–MS) is one of the more common analytical techniques used for the analysis of organic ERs, however, for the analysis of inorganic chlorates and perchlorates, GC–MS is typically not utilized. Many current methodologies for the analysis of chlorates and perchlorates involve an aqueous extraction of a sample as preparation for capillary electrophoresis (CE) or IC (Dicinoski et al., 2006; Zapata & García-Ruiz, 2018). However, CE and IC are not the only methods available for the detection and quantification of inorganic ERs such as chlorate and perchlorate, as there is ever-growing research into improving and inventing analytical techniques for the analysis of explosive materials.

#### 3.1 | Spot tests

Presumptive spot tests can provide qualitative confirmation of the presence of chlorates and perchlorates. Spot tests may be used in the field in a similar manner to presumptive drug tests. Sanger (1973) explored the detection of chlorates in the presence of sugar, a common fuel used with chlorates, using a spot test that was developed by Feigl and Anger (Feigl & Anger, 1954; Sanger, 1973). This spot test involves the formation of a violet color manganese (III) phosphate complex when a chlorate-containing sample is reacted with a 1:1 mixture of manganese sulfate and syrupy phosphoric acid (Feigl & Anger, 1954; Sanger, 1973). Another spot test, which can confirm the presence of chlorate within a mixture of chlorate, bromate and iodate, was developed by Jungreis & Ben-Dor (Jungreis & Ben-Dor, 1964). For this spot test, a drop of sample in an aqueous solution is mixed with a drop of concentrated sulfuric acid and then heated in a water bath. A diphenylamine reagent solution made up of 0.5 g of trichloroacetic acid in 10 mL of saturated diphenylamine in ethyl acetate is used to moisten a filter paper, which is then placed over the test tube, with a green fleck indicating a positive result for the presence of chlorate (Jungreis & Ben-Dor, 1964). For perchlorates, there is a methylene blue spot test, which occurs as perchlorates form violet precipitates with the methylene blue cation, with the aid of zinc sulfate and sodium nitrate if the sample is dilute (Benedetti-Pichler, 1964). Additional presumptive spot tests exist that can detect the presence of chlorates and perchlorates in a sample, some of which have been developed into forensic test packs for explosive materials, available by forensic service providers. After a presumptive test verifies the presence of a chlorate or perchlorate residue, samples must be sent to a forensic laboratory for quantitative chemical analysis.

#### 3.2 | Ion chromatography

Ion chromatography is a common laboratory analytical technique that separates and detects anions and cations from an aqueous sample. This method is particularly well suited for the forensic detection of chlorates and perchlorate, which are readily separated from the metal counter ion in aqueous solutions. Kolla's research into the use of IC for ER analysis high-lights the importance of utilizing IC for the analysis of homemade mixtures of chlorates and other pyrotechnic mixtures (Kolla, 1994). Thus, it becomes evident why extensive research is conducted in this field. McCord et al. identified the use-fulness of IC in detecting and identifying chlorate and perchlorate salts in ERs and provided improved procedural conditions that give investigators the best chance of correctly determining the ions present in a sample (McCord et al., 1994). Improvements in the capabilities and applications of this technique in the analysis of explosive materials are reviewed by Dicinoski et al. and Barron and Gilchrist (Barron & Gilchrist, 2014; Dicinoski et al., 2006).

In 2008, Johns et al. investigated the IC analysis of post-blast residues to identify homemade inorganic explosives, which would yield outcomes that more accurately reflect real explosive cases (Johns et al., 2008). This study analyzed many inorganic explosive materials using an optimized IC method. To obtain post-blast samples, various explosive mixtures were created and detonated, including chlorate/sugar, perchlorate/sugar and chlorate/perchlorate/sugar mixtures, before the collection of soil and witness plate samples (Johns et al., 2008). Chlorate was detected with a limit of detection of 7.2  $\mu$ g/L and perchlorates to 8.4  $\mu$ g/L (Johns et al., 2008). The low limit of detections acquired with this method confirms the sensitivity of this technique for detecting chlorates and perchlorates. In the same year, Meng et al. conducted a study into the simultaneous determination of inorganic anions and cations in ERs via IC using a non-suppressed IC method where both an anion and cation exchange column were connected directly into the column (Meng et al., 2008).

Chlorate and potassium were successfully detected and quantified in a simultaneous run, resulting in a limit of detection of  $300 \ \mu g/L$  for both ions. This research allows for the simultaneous determination of common anions and cations in ERs in the field, as the instrumentation used in this study was a portable IC instrument (Meng et al., 2008).

Perchlorate and nitrate are the main oxidizers used in black powder substitutes, which then combust to form products such as chloride, chlorate, and nitrite. Therefore, for the analysis of black powder substitutes and the post-blast residues, IC would be suitable. Lang and Boyle, for example, investigated the analysis of black powder substitutes by IC paired with mass spectrometry (MS) (Lang & Boyle, 2009). In their studies, six black powder substitutes containing potassium perchlorate were used to create pipe bombs. Due to insufficient resources, only two powders were detonated, and the collected data showed that perchlorate and chlorate were present in both post-blast residues. This study further indicates the capability of IC as a detection method for chlorates and perchlorates. The capability of IC is also expressed in the review by Klassen et al., which describes the IC methods in use at the explosive component facility at Sandia National Laboratories (Klassen et al., 2002).

#### 3.3 | Electrophoresis techniques

Capillary electrophoresis allows for the rapid and efficient separation of ions in small sample volumes, with the separation of ions based on differences in the electrophoretic mobilities of ions in electrophoretic media inside small capillaries (Li, 1992). This separation method is suitable for detecting chlorates and perchlorates due to its simplicity, speed, small amount of sample needed, and ease of automation (Kishi et al., 1998). Kishi et al. demonstrated the application of CE to determine inorganic ions in trace explosives and explosive residues (Kishi et al., 1998). In this study, a homemade chlorate explosive, with potassium chlorate and fuel set up in a pipe bomb, and a cotton glove that had been contaminated with firework residues, were analyzed. CE was able to detect chlorate and chloride ions in the chlorate explosive and perchlorate from the contaminated glove. Further analysis via x-ray fluorescence on the glove confirmed that it was ammonium perchlorate that had been the source of the perchlorate detection.

More recent research by Sarazin et al. further delves into the analysis of extracts from pre- and post-blast explosive residues by CE (Sarazin et al., 2010). The study involved the analysis of real pre- and post-blast residues for 19 anions in under 20 min, with chlorate and perchlorate having a limit of detection of 0.33 and 0.43 mg/L, respectively (Sarazin et al., 2010). Applying this method to real samples resulted in chlorate being detected at approximately 30 mg/L (Sarazin et al., 2010). Matrix effects were also investigated in this study, as the detection of the inorganic ions from soil, glass, cloth, plastic, paper, cotton and metal were all tested, with no significant matrix effects occurring (Sarazin et al., 2010). The collected results were confirmed through a comparison to the same samples being analyzed via IC, which showed comparable and consistent results.

Research by Martín-Alberca et al. involved the analysis of six types of consumer fireworks, including firecrackers, rockets, pyrotechnic fountains, pyro batteries, sparklers and smoke bombs, both pre- and post-blast (Martín-Alberca et al., 2014). Perchlorate was detected in approximately 90% of the samples (with the exclusion of one of the pyrotechnic fountains and sparklers) in both the pre-blast charge, fuse, and post-blast residues. Detection of chlorate in some of the firecrackers and pyro-battery's pre- and post-blast residues was due to possible contamination or unreported use in the production of the products, as chlorates have been largely replaced by perchlorates in this industry due to safety issues (Conkling & Mocella, 2010). This research not only shows that perchlorates and sometimes chlorates can be detected in post-blast firework residues but also demonstrates the detection capabilities of CE.

Improvised incendiary devices are similar to IEDs, however, their primary function is to start a fire rather than cause an explosion. Incendiary devices such as a chemical-initiated Molotov cocktail often require the presence of an oxidizer to initiate the reaction that will start a fire. Martín-Alberca et al. investigated the qualitative determination of inorganic anions in incendiary device residues by CE (Martín-Alberca et al., 2012). This study investigated a chemical-initiated Molotov cocktail made up of petrol and sulfuric acid surrounded by a potassium chlorate and sugar mixture. As the chlorate mixture comes into contact with the sulfuric acid, a small explosion will ignite the petrol, causing a fire to spread. Both in vitro and in vivo experiments were run, with the device detonated in a laboratory environment and outdoors, to assess the potential information available from the analysis of remaining residues. Chlorate, perchlorate, sulfate, and chloride were detected via CE from samples of glass, soil and other environmental materials. Perchlorate et al., 2012). This research further demonstrates the capability of CE to detect chlorates and perchlorates, as well as provide potential target anions for the detection of chlorates in chemical-initiated Molotov cocktails.

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Hutchinson et al. developed a novel CE method in 2008 on portable instrumentation adapted to accommodate a capacitively coupled contactless conductivity detector to analyze inorganic post-blast ERs (Hutchinson et al., 2008). This study is an example of the ever-growing advancements in technology, with the achievement of making CE portable for detecting chlorates and perchlorates in the field. A limit of detection of 0.069 mg/L was achieved for chlorate and 0.084 mg/L for perchlorate. Two IEDs containing chlorate and a chlorate/perchlorate mixture were set up and detonated for the post-blast analysis of residues collected from witness plates and soil samples. Chlorate and perchlorate were successfully detected in the residues of the IEDs containing each component. IC was then used as a confirmatory analysis for these results, resulting in agreement with the CE values.

Isotachophoresis (ITP) is a technique similar to CE whereby charged analytes are separated based on ionic mobility. ITP can preconcentrate dilute samples and limit the target species through careful selection of the chosen electrolytes (Prest et al., 2008). Prest et al. conducted research into the use of ITP for the analysis of post-blast ERs, as this had not been investigated prior (Prest et al., 2008). This investigation consisted of determining chlorine-containing species in ERs using chip-based ITP. Separations performed using a miniaturized poly(methyl methacrylate) chip device, with the intention of being able to analyze samples in a portable manner, resulted in a limit of detection of 1.75 mg/L for chlorate and 1.40 mg/L for perchlorate. These values are higher than those achieved when using CE; however, they are sufficient for the research (Prest et al., 2008). This method was then used to analyze several inorganic ERs provided by a forensic explosives laboratory, resulting in the success of detecting chlorate and perchlorate in the samples that contained them. However, confirmatory analysis with IC showed that ITP detected the analytes at a lower concentration. This study demonstrated the ability to analyze chlorates and perchlorates using ITP, which with improvements, provides a potential alternative pathway for their analysis, which is encouraged in forensic science.

Prest et al. later investigated the analysis of the potassium content of ERs using miniaturized ITP (Prest et al., 2010). There is interest in the analysis of potassium in ER, as it indicates the use of chlorate and perchlorate when found in high concentrations. Prest et al. used similar instrumentation as they used in 2008 to achieve a detection limit of 0.5  $\mu$ g/mL for potassium cations (Prest et al., 2010). A forensic explosives laboratory once again provided eight post-blast ER samples, to which this method was able to detect and quantify potassium in all but one of the samples. IC confirmatory analysis was also conducted, which showed that the ITP results were slightly less. Prest et al. have demonstrated proficiency in developing and applying ITP for the analysis of common ions found in inorganic ER on miniaturized instrumentation, which further increases the number of potential portable analytical methods in this area.

#### 3.4 | Vibrational spectroscopic techniques

Vibrational spectroscopic techniques, such as ATR-FTIR and Raman spectroscopy, are more commonly utilized for organic materials but can also be used to analyze inorganic ions in both laboratory and field environments. Vibrational spectroscopic techniques measure the vibrational motions of molecules when specific light is absorbed by molecules, providing details on the molecular structure of samples. Martín-Alberca et al. used ATR-FTIR to analyze five commercial pyrotechnic products, both pre- and post-blast (Martín-Alberca et al., 2016). Potassium perchlorate was detected in all five of the products' post-blast residues, with potassium chlorate being detected in only one of the post-blast residues. The pre-blast analysis then confirmed these post-blast results. In a similar study, Castro et al. analyzed confiscated fireworks using Raman spectroscopy assisted with scanning electron microscopy paired with energy dispersive x-ray spectroscopy (SEM-EDS) and FTIR (Castro et al., 2011). Raman spectroscopy was successful in the detection of common inorganic analytes found in fireworks residues, including chlorate and perchlorate. The same was achieved for FTIR, although Raman was said to achieve better results for all the target analytes. SEM-EDS can provide structural and trace elemental chemical information for samples and was used to identify the source of perchlorate in the firework as ammonium perchlorate (Castro et al., 2011).

Zapata and García-Ruiz investigated the detection of four different types of chlorates, including barium, potassium, silver, and sodium, along with 22 perchlorates via Raman and IR spectroscopy (Zapata & García-Ruiz, 2018). After analysis of the samples, Pearsons correlation coefficients were calculated to evaluate the unequivocal identification of the salts (Zapata & García-Ruiz, 2018). For Raman spectroscopy, all chlorates and five of the perchlorates were correctly identified. For IR spectroscopy, only two chlorates and four perchlorates were correctly identified. When combining both Raman and IR spectroscopic data, it was found that all the chlorates and seven of the perchlorates were correctly identified. The unidentified perchlorates did not go undetected yet were only unable to be distinguished from other species of perchlorates in the study. This research shows the

robustness of work involved in the analysis of chlorates and perchlorates via vibrational spectroscopic techniques and the accuracy that can be achieved in identifying specific species.

#### 3.5 | Mass spectrometry

Mass spectrometry is a well-established laboratory technique in the analysis of chlorates and perchlorates, which is often used in conjunction with other techniques, such as IC. Mass spectrometry involves the ionization of an analyte which is then passed through a mass analyzer, which separates compounds through a magnetic field based on their mass-to-charge ratio before passing on to the detector (Glish & Vachet, 2003). Mass spectrometry has been used for the detection of explosives since the introduction of desorption electrospray ionization (DESI) and direct analysis in realtime (DART) ionization techniques (Forbes & Sisco, 2018). Sokol et al. investigated the trace detection of inorganic oxidants using DESI mass spectrometry, which provided a sensitive and selective method for the analysis of inorganic salts, including chlorates and perchlorates (Sokol et al., 2011). In particular, sodium chlorate and perchlorate were analyzed, along with samples of fireworks, using this method that requires no sample pre-treatment. It was established that this technique could detect sodium chlorate at concentrations as low as 120 pg on a high porosity polytetrafluorethylene (PTFE) surface and between 0.7 and 50 ng on more common surfaces such as aluminum foil, glass, wood, and cotton fabric (Sokol et al., 2011). For sodium perchlorate, the limit of detection was as low as 50 pg on a high porosity PTFE surface and between 0.5 and 20 ng on more common surfaces (Sokol et al., 2011). A real sample analysis of paper tubes that contained fireworks was conducted, in which perchlorate was found in both samples and chlorate in one. This research highlights mass spectrometry's ability to analyze chlorates and perchlorates, with a technique that allows for instant unambiguous determination directly from surfaces (Sokol et al., 2011).

Similar research by Zhao and Yinon investigated the forensic identification of explosive oxidizers by electrospray ionization mass spectrometry (Zhao & Yinon, 2002). Pure sodium and potassium chlorate and sodium and ammonium perchlorate were studied in this research. Results showed that chlorates and perchlorates formed different cluster ions during the analysis, allowing the detection of each species (Zhao & Yinon, 2002). Samples of match heads that had been reported to be used in IEDs were analyzed, resulting in the detection of potassium chlorate (Zhao & Yinon, 2002). More recent work by Kelley et al. used thermal deposition, atmospheric-pressure chemical ionization ion mobility spectrometry (TD-APCI-IMS) to assess the effectiveness of acidic reagents for enhanced trace detection of chlorates and perchlorates (Kelley et al., 2016). Sodium and potassium chlorate, and perchlorate, in the presence of sulfuric acid, were analyzed, resulting in a limit of detection of 8 ng for all analytes but sodium chlorate, with a limit of detection of 1.6 ng. Detection of chlorates and perchlorates at concentrations this low is sufficient for forensic analytical processes. This research highlights that improvements for established methods are constantly sought after for analytical capabilities in this area.

Mass spectrometry is often paired with a separation technique, such as IC, for the analysis of analytes after separation. Barron and Paull investigated the simultaneous determination of trace oxyhalides and haloacetic acids using suppressed IC paired with electrospray mass spectrometry (Barron & Paull, 2006). Chlorate and perchlorate were analyzed using this technique, resulting in a detection limit of 9  $\mu$ g for chlorate and 10  $\mu$ g for perchlorate. This study shows how mass spectrometry can be utilized in conjunction with other separation techniques to obtain more in-depth information than from the separation techniques alone.

#### 3.6 | Electrochemical techniques

Electrochemical analysis is a recent technique that is being utilized for the analysis of ERs. It is a desirable technique for analyzing ERs as it is fast, inexpensive, and a more viable option for portable analysis, as the instrumentation is smaller and lighter than other available portable analytical instruments (Yu et al., 2017). Electrochemical analysis relies on an analyte's induced reduction or oxidation at an electrode through the input of an electric current. The reduction and oxidation of an analyte can be detected using cyclic voltammetry, which can then be used to identify an analyte, as the produced reduction peaks are specific to each analyte. Trammell et al., for example, investigated the statistical evaluation of an electrochemical probe for the detection of chlorate (Trammell et al., 2017). In this study, a multilayer film prepared via layer-layer deposition of cationic para-rosaniline acetate dye and the vanadium-containing Keggin-type polyoxometalate anion on an indium tin oxide electrode was used for the detection of chlorate (Trammell et al., 2017).

This technique provided insensitivity to oxygen and common explosives such as TNT, which commonly exhibit electrochemical signatures in the same region as chlorate reduction (Trammell et al., 2017). The limit of detection for chlorate using this technique was reported as 220  $\mu$ M, which proves the sensitivity of such techniques. This study highlights the possibility of electrochemical analysis to detect chlorates and potentially perchlorates, further demonstrating the varying analytical techniques available for these processes.

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The existing literature demonstrates a substantial body of research focused on detecting, identifying, and quantifying chlorates and perchlorates using diverse analytical methods. However, there is a notable gap in the literature on the full potential of information that can be gathered through the analysis of explosive materials, such as source-attributing information. Source attribution is an area of research and practice that is well-established in the forensic analysis of illicit drugs and encompasses the detection and identification of compounds indicative of the production of an illicit substance (Mayer et al., 2016). Source attribution in explosives and arson evidence holds promise for improving forensic investigations and intelligence purposes. Recent studies on the source attribution of inorganic explosive evidence have yielded promising results, highlighting its potential value in this particular application (D'Uva et al., 2020). D'Uva et al. investigated the source attribution of party sparklers using trace elemental analysis and chemometric methods (D'Uva et al., 2020). Eight different brands of party sparklers were investigated, resulting in a classification model that matched 100% of the samples to the specific brand of sparkler (D'Uva et al., 2020). However, it must be noted that this study only involved the analysis of pre-blast material. Further research by D'Uva et al. looked into the characterization of homemade urea nitrate from commercial urea sources (D'Uva et al., 2021). This study used five urea sources to synthesize urea nitrate before being analyzed using varying analytical techniques. The information of particular characteristics apparent from specific starting materials contributes to forensic intelligence, such that it provides key differences that could be used in identifying potential starting materials (D'Uva et al., 2022). The information gained throughout D'Uva et al.'s research, when applied to the analysis of chlorates and perchlorates, would be a tremendous aid in future investigations, intelligence, and research.

Forensic intelligence can be defined as the use of collected forensic information to provide solutions and insight into forensic processes to support proactive and preventative approaches (Bruenisholz et al., 2016; Ribaux et al., 2006). Currently, countries including Australia, Canada, the United States and the United Kingdom have implemented strategies involving the collection of information from improvised explosive devices (IEDs), forensic analysis of explosives, device exploitation, analysis of insurgent tactics, and more to form forensic intelligence suitable for use by counter-IED task forces (Legrand & Vogel, 2012). Bishop et al. detail how there is a challenge in recognition of potential intelligence by bomb squad management as there is a tendency for specific types of evidence, such as DNA, to be regarded in a higher manner, leaving evidence such as explosive evidence in disregard (Bishop et al., 2022). Bishop et al., however, go on to say that security services and the military, contrarily, have been gathering intelligence such as placement locations, designs and compositions of IEDs for years (Bishop et al., 2022). Therefore, it is evident that forensic intelligence holds the potential to aid in future investigations of explosive cases involving chlorate and perchlorate substances. This potential could be further enhanced if source attribution information is incorporated into the process.

Research by Logrado et al. provides a great example of the possible applications of forensic intelligence concerning explosives (Logrado et al., 2022). This work involved profiling the use of explosives in ATM/cash-safe robberies in Brazil. It was shown that only a small percentage of the crimes were subjected to chemical analysis for explosive identification, therefore revealing a need for improvements in post-blast crime scene processing (Logrado et al., 2022). It was noted that information on the local characteristics of each state, such as the possible firework industries, types of stores, and mining or civil construction activities, is relevant in providing intelligence for future investigations (Logrado et al., 2022). For example, it was found that there is a possible direct relation between the use of explosive mixtures containing chlorates and perchlorates and the abundant presence of fireworks manufacturers in certain states. The use of intelligence in this example could restrict the number of investigative possibilities. The research into the possible intelligence from ERs, such as chlorates and perchlorates, is imperative for continual improvements in the investigation of explosive events.

Forensic intelligence applied in the area of explosives mainly relates to the activity and physical characteristics of explosives. Chemical profiling can provide a wealth of information that can be applied to forensic intelligence purposes,

such as the source attribution studies previously mentioned. Source attribution involves two key aspects. First, it necessitates the use of suitable chemical methods to detect multiple impurities within a compound. Second, it requires an appropriate framework for interpreting complex data. This was exemplified in work conducted by D'Uva, which utilized chemometric analysis for source determination of homemade ammonium nitrate using ATR-FTIR spectroscopy and trace elemental analysis (D'Uva et al., 2022). Chemometrics is a discipline that models chemical data using well-established statistical methods to reveal variance and correlation between analyzed samples. Chemometric methods are composed of varying multivariable data treatments, such as modeling, unsupervised exploration and supervised classification, that can be used for differing research approaches. Such methods include principal component analysis (PCA), linear discriminant analysis (LDA), partial least squares regression (PLSR) and central composite design (CCD), which are utilized in forensic research to aid in potential pattern recognition, calibration, and experimental design (Brereton, 2007). Due to the possible outcomes of applying chemometric methods throughout forensic research, it has been increasingly used in investigations into the analysis of explosive materials to provide forensic intelligence. During D'Uva et al.'s research, nine ammonium nitrate products were sourced and prepared, both pure and homemade forms. PCA was performed on collected IR data before subsequent LDA, correctly classifying 100% of the pure forms and 80% of the homemade products (D'Uva et al., 2022). The traceelemental data collected via ICP-MS underwent a similar chemometric approach, resulting in the correct prediction of all samples. The results from this type of research provide essential information that can be utilized in forensic intelligence applications. Therefore, employing chemometric approaches for the source attribution of chlorate and perchlorate substances emerges as a promising avenue for future research. By utilizing advanced analytical techniques and conducting chemometric data analysis, it may be possible to attribute chlorates based on their starting materials, such as different brands or scented bleach products, thereby enhancing the investigative capabilities in this field.

Beyond source attribution, there is the potential for chemical analysis of chlorates and perchlorates to overlap with various other forensic processes. These may include fingermark detection, DNA extraction, and numerous other procedures involved in the examination of forensic evidence, presenting possibilities for potential interference. An example of research into a scenario such as this is Love et al.'s investigation into the detection of anionic energetic material residues, such as chlorates and perchlorates, in enhanced fingermarks on both porous and non-porous surfaces using IC (Love et al., 2013). Love et al. were interested in the possible effects of fingermark development techniques on the detection of ERs that had been transferred from a fingertip to a surface. The experiment involved participants handling Pyrodex<sup>®</sup> before depositing fingermarks onto a glass and paper surface. The analysis of chlorate and perchlorate within the fingermark matrix was found to have a decreased recovery rate of 40%-80%, compared to a 90%-110% initial recovery rate, which proves that chlorates and perchlorates can indeed be detected in fingermarks (Love et al., 2013). For aluminum-developed fingermarks, the recovery of chlorate and perchlorate stayed above 70%, whereas ninhydrindeveloped fingermarks resulted in a further loss in the recovery of chlorate and perchlorate. This study expresses the importance of ensuring that the analytical processes being implemented are compatible with other necessary procedures. Research of this nature holds significant importance as it aims to maximize the detection of chlorates and perchlorates, particularly in scenarios where other activities may have taken place prior to the detection process. This type of research also ties into the importance of investigations into the transfer and persistence of explosive materials.

One interesting challenge in forensic explosives research is the detection of post-blast residues. This presents a unique difficulty as it involves the detonation of samples to gather crucial data, however, this approach comes with numerous issues. These include safety concerns associated with handling explosives, the difficulty of recreating realistic explosion scenarios in controlled environments, and the complex analysis required to identify and interpret the resulting material. Resolving these challenges is essential for advancing our understanding of post-blast forensics and improving investigative techniques in cases involving explosive incidents.

### 5 | CONCLUSION

This review provides a comprehensive overview of the historical and current use of chlorates and perchlorate, both legally and illegally, and summarizes significant global criminal incidents involving these compounds. The review has identified the current analytical techniques for their forensic detection and ongoing research into improving such techniques. Forensic intelligence and its potential in explosive investigations were highlighted, with examples of how chemical information can be applied in an intelligence context. Forensic intelligence is gaining, however, a distinct lack of research into the potential intelligence available from explosives compared to other fields is evident, even more so for chlorates and perchlorates specifically. It was determined that there is a gap in the field of source attribution,

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highlighting the necessity for further research in this area. Such research has the potential to provide additional information that can greatly benefit both forensic investigations and intelligence purposes. Also highlighted was the need for research into the analysis and fundamental principles encompassing the transfer and persistence of chlorate and perchlorate evidence, particularly in conjunction with other types of evidence present, such as DNA and fingermarks.

#### AUTHOR CONTRIBUTIONS

**Aaron J. Horrocks:** Conceptualization (equal); writing – original draft (lead); writing – review and editing (equal). **David DeTata:** Conceptualization (equal); supervision (supporting); writing – review and editing (equal). **Kari Pitts:** Conceptualization (equal); supervision (supporting); writing – review and editing (equal). **Simon W. Lewis:** Conceptualization (equal); project administration (lead); supervision (lead); writing – review and editing (equal).

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#### CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

#### DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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