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Emerging techniques for the detection of pyrotechnic residues from seized postal packages containing fireworks

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ABSTRACT

High volume screening of parcels with the aim to trace the illegal distribution and selling of fireworks using postal services is challenging. Inspection services have limited manpower and means to perform extensive visual inspection. In this study, the presence of solid pyrotechnic residues collected from cardboard shipping parcels containing fireworks was investigated for direct in-field chemical detection. Two emerging trace detection techniques, *i.e.*, capillary electrophoresis (CE)-based inorganic oxidizer detector and infrared thermal desorption (IRTD) coupled with direct analysis in real time mass spectrometry (DART-MS), were investigated for their potential as screening tools. Detection of non-visible pyrotechnic trace residues from real-case seized parcels was demonstrated using both screening techniques. However, the high nitrate background in the commercial CE system complicated its screening for black powder traces. IRTD-DART-MS allowed differentiation between flash and black powder by identification of the molecular inorganic ions. Compared to the portable CE instrument, rapid screening using IRTD-DART-MS is currently limited to laboratory settings. The capabilities of these emerging techniques established solid particle and trace residue chemical detection as interesting options for parcel screening in a logistic setting.

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1. Introduction

Strict regulations in various countries around the world currently exist for the handling of fireworks by the general public. For example, in the Netherlands, flash banger fireworks containing flash powders may not be used and possessed by persons without the appropriate license. Firework items containing solely black powder can be used by consumers. However, restrictions exist for the size and weight for possession [1]. Nevertheless, there exists a high desire among part of the general public for obtaining powerful pyrotechnic materials containing flash and black powders for recreational use. Although the illegal use of these items is largely in the context of reckless amusement, these powders are also misused to commit crimes such as blowing up ATM machines, extortion and intimidation. The ease and relative anonymity with

which these powerful fireworks can be obtained, mostly through the Internet, pose a serious security risk in the Netherlands. In 2018, over 56,000 kg of illegally traded fireworks were confiscated by the Dutch police [2]. Unfortunately, it is well-known that these seizures only represent the proverbial tip of the iceberg. Postal companies and inspection agencies have limited means to check whether parcels contain fireworks.

Currently, postal inspection in the Netherlands mainly consists of visual examinations of the outer packaging. Parcels raising suspicion, *e.g.*, through the use of large amounts of tape or unusual labels, are reported to the inspection authority. The Transport Inspectorate will then perform a visual examination of the suspicious parcel content and if the presence of fireworks is confirmed the materials will be seized by the police. Occasionally, random checks are carried out by the Transport Inspectorate with sniffer dogs and X-ray screening techniques. These detection tools, especially X-ray inspection, are well-known and effective in airport security and customs. However, the practical feasibility for high volume screening of parcels is limited. X-ray screening performed at airports is too slow and too expensive for the significant number

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of packages that parcel carriers have to process daily and would seriously disrupt the national and international distribution chain. Additionally, applying indirect detection methods based on visual inspection or X-ray screening raises debates between parcel carriers and customers concerning privacy policies.

For the trace detection of explosives, ion mobility spectroscopy (IMS) is generally the method of choice for high throughput direct chemical detection [3–5]. This technique is routinely used in airport security for trace detection of drugs and explosives on luggage and persons by analyzing wipe-based sample collections. Although IMS is very effective and sensitive for organic explosives, the detection of pyrotechnic compositions including black and flash powders is not as straightforward. A typical black powder formulation contains 75:15:10 wt% of potassium nitrate, charcoal and sulfur, respectively [6,7]. Flash powder compositions usually consist of potassium perchlorate (70 wt%) as inorganic oxidizer and dark pyro aluminum (30 wt%) as fuel component [8]. The low vapor pressures of the inorganic oxidizers of interest in pyrotechnic compositions (e.g., KNO_3 , KClO_4 and KClO_3) at thermal desorption temperatures traditionally used in IMS ($\leq 280^\circ\text{C}$) make it difficult to detect these species [9]. In forensic explosive casework, ion chromatography (IC) with conductivity and ultraviolet (UV) detection or coupled to electrospray ionization (ESI) mass spectrometry (MS) is predominantly used for identification of inorganic ions [10–12]. However, complex sample preparation procedures, relatively long analysis times and the use of aqueous samples are undesirable for high volume, on-site trace detection of flash and black powder residues on parcels [9].

In the field, colorimetric tests and portable handheld detectors are frequently used for general screening of explosives due to their ease-of-use. Multiple colorimetric tests are available for detecting pyrotechnic compositions in fireworks and, more specifically, to screen for the presence of nitrate, chlorate, and perchlorate anions. Typical colorimetric reactions are the methylene blue test for perchlorate, the aniline sulfate test for chlorate and a modified Griess test for nitrate, with positive color changes from blue to purple, clear to green, and clear to orange/red, respectively [13,14]. However, these color tests are generally not sensitive enough for trace detection. Fluorescence and luminescence-based handheld detectors are also used for ultra-trace explosives detection [15,16]. Amplifying fluorescent polymers (AFP) are used for fluorescence quenching in the presence of target explosive analytes resulting in an amplified signal response of the sensor [17–22]. However, sensor sensitivities and detection mechanisms related to the detection of inorganic oxidizers are not yet understood nor completely developed.

Recent efforts to tackle challenges with inorganic explosive trace detection have mainly focused on improving currently used IMS strategies [5,9,23–25]. In traditional IMS instruments, detection of black powder is based on the presence of sulfur. However, the detection of sulfur is challenging due to restricted ionic sulfur formation by dopants and peak overlap with reactant ions. Liang et al. [23] proposed a strategy to increase the sensitivity for sulfur detection by introducing a separate titration region. In this way the formation of sulfur ions in the ionization region is no longer inhibited by the reagent [23]. Another effort by Peng et al. [9] and Kelley et al. [24] focused on the use of acidic reagents with IMS to enhance the evaporation of chlorate and perchlorate salts by transforming them into their acid analogs. Acidified wipes using phosphoric or sulfuric acid solution and solid acidic salts showed significant increases in signal intensities by indirect detection of the chloric and perchloric acids [9,24]. However, introducing acidic reagents in the IMS instruments can lead to detrimental effects on the apparatus and the detection capabilities for other components of interest, e.g., organic explosives [24]. High temperature thermal desorption methods have also been previously implemented to

improve ionization of less volatile inorganic oxidizers. This method is challenging with the current IMS technology. However in one example, Forbes et al. [26] coupled a resistive Joule heating thermal desorption component to direct analysis in real time (DART)-MS enabling ionization and detection of inorganic oxidizers. In addition, the application of in-source collision induced dissociation (CID) in this work enhanced the detection of inorganic explosives by controlling adduct formation and reducing organic contaminants [26]. In more recent work, infrared thermal desorption (IRTD) was combined with DART-MS for the sensitive detection of inorganic oxidizers, resulting in detection limits within the low nanogram range [27–29].

Alternatively, capillary electrophoresis (CE) has been utilized for the identification of explosives as a solvent-based method that does not require thermal desorption of target analytes by means of vaporization for detection. CE-based techniques offer advantages in robustness, sensitivity and selectivity as an analytical method with unique characteristics towards portability [30]. CE-based methods for the detection of organic and inorganic explosive compounds has been performed using UV detection [31–34], electrochemical methods [35,36], and indirect and direct fluorescence [37]. Conductivity detection methods have been the most widely used detection modality for inorganic ions, with capacitively coupled contactless conductivity detection (C^4D) extensively used for portability considerations and ease-of-use [38–42]. Challenges in the detection of inorganic compounds using CE-based techniques arise due to the similarities in electrokinetic mobilities of the ions. Foundational work towards the detection of inorganic oxidizers was performed by Blanco et al. using a sequential injection CE instrument with C^4D , built in-house using commercial components, for the separation of 10 inorganic ions relevant for explosives detection within 90 s [43]. Later, Gaudry et al. developed a dual-capillary sequential injection CE instrument with C^4D for the simultaneous separation of 12 cation and 11 anions from a single sample within 3.5 min [44].

In this study, two emerging trace detection techniques, portable CE with C^4D detection and IRTD-DART-MS, were investigated for direct chemical screening of pyrotechnic residues on parcels. The main objectives were to investigate the potential for detecting and characterizing the chemical composition of trace pyrotechnic residues from parcels seized by the Dutch police. The capabilities to detect and differentiate between flash bangers composed of either purely flash powder or a mixture of black and flash powders from wipe-based collections from packaging bags and tubes was also investigated. Here, we report the successful detection of inorganic oxidizers using both emerging techniques by simply wiping across postal shipping boxes and associated packaging materials collected from Dutch police seizures and performing direct chemical analyses. Both platforms allowed for rapid analyses and no manual sample preparation as required for high-volume screening in mail facilities.

2. Materials and methods

2.1. Seized pyrotechnic samples

A total of four cardboard boxes confiscated by the Dutch police in 2018 were interrogated by wipe sampling for the characterization of emerging analytical techniques for the trace detection of pyrotechnic residues. These seized packages included a factory labeled box that originally contained a large number of flash bangers, packed in plastic bags in sets of three items (Fig. 1a). The remaining three cardboard parcels, originating from Dutch casework, were related to the illegal trade of fireworks and consisted of miscellaneous non-sealed firework items repackaged by non-licensed individuals (Fig. 1b–d). In addition to these seized



Fig. 1. Images showing the content of the confiscated parcels: (a) original factory box; and three repacked parcels for the illegal dispatching of fireworks (b) Box 1, (c) Box 2, and (d) Box 3 as referred to in the text.

cardboard boxes, a selection of the packaging materials (*i.e.*, plastic packaging bags and individual flash banger tubes) from flash banger pyrotechnics confiscated by the Dutch police were sampled [45,46]. These pyrotechnic samples consisted of flash bangers that either contained solely flash powder or a mixture of flash powder and black powder. The black powder ($\text{KNO}_3/\text{C/S}$) and flash powder (KClO_4/Al) compositions of these flash bangers were confirmed by direct analysis using X-ray fluorescence, X-ray diffraction and IC.

2.2. Capillary electrophoresis

A portable GreyScan ETD-100 CE instrument (GreyInnovation, Melbourne, Australia)† was utilized for the targeted screening of nitrates, chlorates and perchlorates [47]. The portable CE instrument was 48.8 cm × 38.6 cm × 22.9 cm (width × depth × height) in size and weighed 13.1 kg. The instrument was equipped with a battery supply capable of 1–8 h of operation and, alternatively, was configurable for 100 V–240 V AC outlet power. Initial powering on of the instrument required a 10 min startup.

Samples were collected by swiping with dry single-use disposable acetate paper wipes (Smiths Detection, Edgewood, MD, USA). Manual swipe sampling (*i.e.*, no wand) was conducted from target locations on packages (*e.g.*, labels, seams, surfaces, and observed soiled areas). Total surface areas sampled varied from package-to-package based on overall size and user-observed areas of interest. Sample wipes (88 mm × 26 mm) were incorporated into the system through a wipe-introduction port on the front side of the instrument. Samples were extracted from an approximately 2 cm² area of the wipe and then pressure-injected into the separation capillary (25 μm i.d., 30 cm in length) for separation and detection of the inorganic ions using C⁴D. The targeted nature of this portable CE instrument for inorganic anions allowed for 40 s run times. However, an additional time of 2–3 min was necessary to rinse the capillary after positive target analyte detection. Peak identification and normalization were achieved using three internal standard species (proprietary composition) and the system firmware with proprietary algorithms.

2.3. IRTD-DART-MS

Dry polytetrafluoroethylene (PTFE)-coated fiberglass weave wipes (DSA Detection, LLC, Boston, MA, USA), roughly 72 mm × 25 mm, were used for collection of sample residues from all packaging materials of interest to be analyzed by IRTD-DART-MS. Details of the IRTD and IRTD-DART-MS platform and operation can be found in recent literature [27,29]. The glass-mica bottom plate of the IRTD-unit (Hereaus-Nobelight America, LLC, Buford, GA, USA) was heated to a quasi-steady-state temperature of 200°C by a series of preliminary 15 s emission intervals. Wipe-based samples were inserted into the unit and by manual activation of the infrared emission (100% power for 15 s) the temperature was

ramped up to 500–550°C, allowing for high temperature thermal desorption. Sample collections were thermally desorbed from an approximately 1.5 cm² to 2 cm² area of the wipe with a radial thermal gradient descending from the infrared focal point. Following thermal desorption, analytes were transported through a T-junction for ionization by a DART SVP source (Ionsense, Saugus, MA, USA) and finally for mass analysis by a time-of-flight mass spectrometer in negative ion mode (AccuTOF, JEOL USA, Peabody, MA, USA) [29]. Mass spectra were collected under two sequential sets of conditions, switched every 0.5 s, between low (–20 V orifice 1 voltage) and high (–60 V orifice 1 voltage) in-source CID. At high in-source CID, fragmentation of larger inorganic clusters and organic species was achieved [29,48].

3. Results and discussion

The strict regulation of fireworks, propellants, and other pyrotechnics in the Netherlands requires the investigation of emerging techniques and capabilities for the trace detection of these powders from parcels transiting the postal system. Here, we examined two emerging analytical techniques for the high-throughput chemical detection of pyrotechnic residues from confiscated parcels.

3.1. Capillary electrophoresis pyrotechnic screening of seized parcels

The portable CE system used in this study enabled rapid screening of packages with individual sample run times of less than a minute. The seized parcels exhibited in Fig. 1 were sampled by acetate paper wipes using standard swipe sampling procedures [49]. The seized original factory box was completely filled with hundreds of flash bangers, packaged in sets of three within plastic bags. The confiscated repacked parcels, Boxes 1 and 2, contained a large amount of different firework items (*e.g.*, flash bangers, signal rockets, and shells), many of which lacked plastic packaging, often due to subdivision of the original number of items over multiple boxes. Contrarily, confiscated Box 3 only contained two large batteries (cakeboxes), each individually packaged.

The portable CE system was designed for the targeted detection of nitrate, chlorate, and perchlorate. Fig. 2 demonstrates a series of representative electropherograms that include peaks, in order of elution time, for chloride (a component of the extraction buffer), nitrate, chlorate (no peak shown), acetate (from the acetate paper wipes), perchlorate, internal standard 1, carbonate (from the atmosphere) and internal standard 2. In this example, nitrate and perchlorate were detected from sampling of the confiscated Box 1 (Fig. 1b). However, it is important to note the presence of nitrate from the sampling of a control cardboard box, which had no prior exposure to pyrotechnics, and from the blank wipe.

The Greyscan ETD-100 system firmware was used for peak searching/identification and peak height determination. The

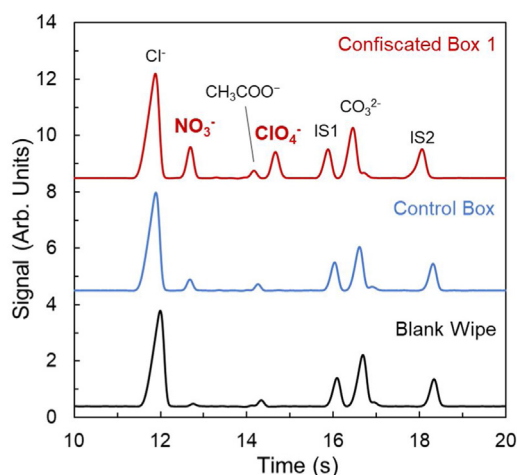


Fig. 2. Representative CE electropherograms for a blank wipe, control cardboard box (no pyrotechnics), and a sample from confiscated Box 1.

measured conductivity signal and peak heights were also normalized to the internal standards and reported in digital units (du). Under traditional operation, the system was run through a user-directed interface that provided alarm indication based on firmware defined thresholds. For this study, the processed data was exported and manually compiled. Eight to ten samples were collected from each of the four packages and analyzed using the portable CE. The resulting nitrate, chlorate, and perchlorate signals were compiled as box plots in Fig. 3. In addition, a series of control samples were taken from ten control boxes, which had no known prior exposure to pyrotechnics or related materials, for comparison. Wipe samples were taken from all over each parcel and often resulted in widely varying signal intensities. The box plots were utilized to capture this variability, enable visualization of outliers, and identify statistically significant differences across parcel and control samples. Here, the median is displayed in red, the bottom and top edges of each blue box represent the lower (Q1: 25th percentile) and upper (Q3: 75th percentile) quartiles, and the “whiskers” display $1.5\times$ the interquartile range ($Q3-Q1$). In addition, Fig. 3 displays outliers (black circles) defined as values out of the whisker range, as well as red triangular markers displaying the 95% confidence intervals.

The results most notably demonstrated the detection of perchlorate, a common flash powder oxidizer, from all four confiscated boxes (Fig. 3c). The median signal from each confiscated box was also greater than the near zero levels measured on the control boxes (95% confidence medians were different than controls). The results also demonstrated a significantly higher perchlorate signal from confiscated Box 2 relative to the others. For some items, the original packaging material was missing due to subdivision of the original number of items over multiple boxes. It is evident that in this scenario the transfer of traces to the outside of the parcel, directly or *via* the person handling the fireworks, is more likely, as demonstrated by the wide coverage and strong signal intensity of target species. In addition, some samples yielded “Inconclusive” results from the system firmware, resulting in zero signals for the three target species (*i.e.*, nitrate, chlorate and perchlorate). However, upon further inspection, those samples were overloaded (*i.e.*, contained a very high concentration of the target analytes) and the significant signal and change in buffer conductivity shifted the target peaks out of the detection windows (Fig. S1). In some instances, this significant change in conductivity shifted other analyte peaks well outside of their respective target elution time windows. For example, the

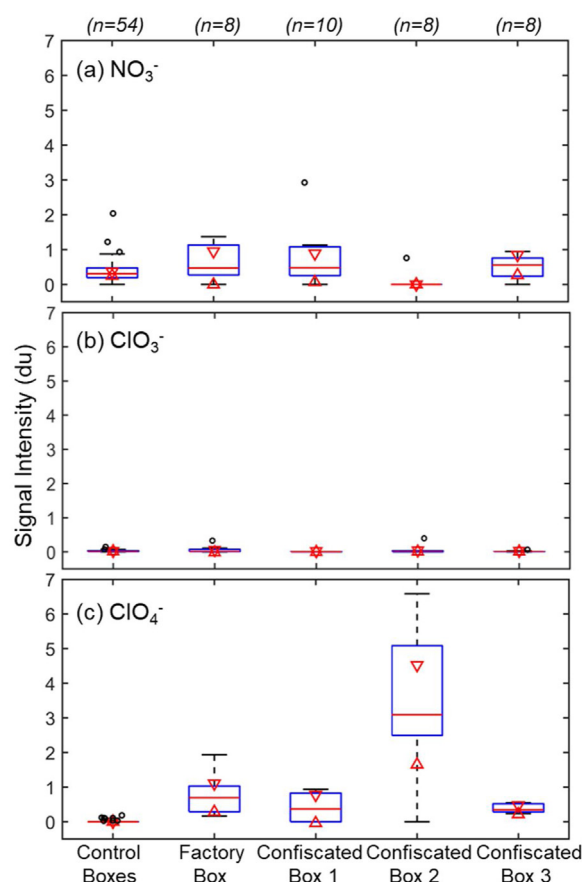


Fig. 3. CE signal intensity box plots for (a) nitrate: NO_3^- , (b) chlorate: ClO_3^- , and (c) perchlorate: ClO_4^- , across the four confiscated parcels and control packages. Boxes represent the median with lower (Q1) and upper (Q3) quartiles, whiskers represent $1.5\times$ the interquartile range (length of the box), outliers (o) represent values out of the whisker range, and triangular markers represent 95% confidence intervals ($\text{median} \pm 1.57(Q3 - Q1)/\sqrt{n}$).

elevated perchlorate signals observed from confiscated Box 2 shifted the nitrate peaks well outside of the target window.

Chlorate, another firework and pyrotechnic oxidizer, was not observed at substantial levels from any of the confiscated parcels or control boxes (Fig. 3b). Interestingly, nitrate was detected on samples from three of the four confiscated boxes, but also from samples of the control boxes. The median non-zero detection from the factory box and confiscated Boxes 1 and 3 was not significantly different than that of the control samples. While nitrate-based oxidizers are found in black powders and a range of fireworks, without further chemical analysis of the packaged pyrotechnics and control box samples, we cannot conclusively attribute the nature of these nitrate signals. The results demonstrated here also provided preliminary indications for thresholds necessary for the detection of these species above background or baseline signal levels.

The screening for common pyrotechnic oxidizers by CE successfully identified the presence of perchlorate-based oxidizers on all confiscated packages containing firework items. The significant incidence of nitrate detection in all samples, presumably from high environmental nitrate, hindered the identification of potentially present nitrate-based oxidizers. Further characterization of background levels of nitrate from relevant sampling scenarios would enable appropriate alarm thresholds to be determined. Yet, the portable system employed here exhibited appealing SWaP parameters, *i.e.* size, weight and power, to facilitate field deployment [28]. Next, trace residues present on

these confiscated packages were further investigated by a recently developed thermal desorption technique coupled with a more powerful laboratory-based mass spectrometer [29,48].

3.2. IRTD-DART-MS pyrotechnic screening of seized parcels

The successful detection of the inorganic oxidizers present on black powder and flash powder laden wipes using IRTD-DART-MS has previously been demonstrated, providing the foundation for this application [29,48]. Unlike the portable CE system, which used acetate paper wipes, the IRTD-DART-MS platform incorporated PTFE-coated fiberglass weave wipes due to their ability to withstand relatively high temperatures, their low chemical background, and their ability for transmission of the emitted near infrared irradiation. Relative to the commercial CE system described above, the IRTD-DART-MS platform also provided rapid analysis times (less than a minute). However, manual data processing of the resulting signals is required. In addition, the high specificity of mass spectrometry and potential ion distributions provided a wide range of target ions for monitoring. Fig. 4 displays a representative IRTD-DART-MS mass spectrum from confiscated Box 1. The IRTD-DART-MS yielded additional information beyond the anion detection provided by the CE-based analysis above. Here, in addition to the perchlorate anion (m/z 99 ClO_4^-), the ion distribution exhibited intact salt adducts of potassium perchlorate with nitrate (generated by the DART ion source) and free perchlorate anions (m/z 200 $[\text{KClO}_4+\text{NO}_3]^-$ and m/z 237 $[\text{KClO}_4+\text{ClO}_4]^-$). The observation of intact salt structures provided the cation information from the pyrotechnic oxidizer in use, potassium in this case. As introduced above, high in-source CID parameters were also incorporated to simplify the large cluster and adduct ion distributions created by these mixtures when necessary or beneficial for analysis. Under these conditions, the distribution of potassium perchlorate adducts were predominantly fragmented down to the perchlorate anion.

The four confiscated parcels displayed in Fig. 1 were all sampled and analyzed using IRTD-DART-MS. The DART ion source created an abundance of nitrate anions when interacting with atmosphere, which formed adducts with compounds of interest [26]. However, the nitrate anion peak was not useful as a target channel for nitrate-based pyrotechnic oxidizers. The ability to detect intact salts by IRTD-DART-MS provided an alternative avenue that will be discussed further below. A preliminary screening of the derived mass spectra and associated extracted ion chromatograms (selected ion or m/z value as a function of time) from the confiscated parcel samples found predominantly potassium perchlorate. Largely, no

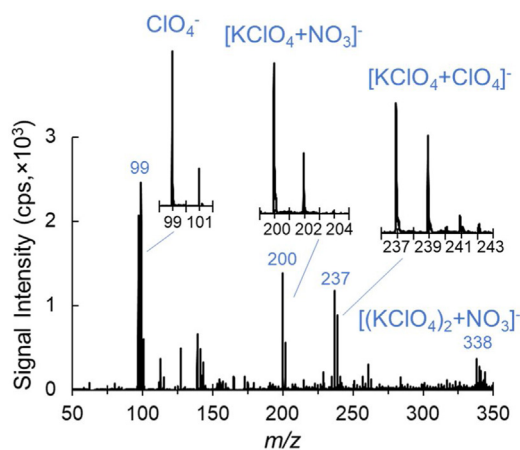


Fig. 4. Representative IRTD-DART-MS mass spectrum of a wipe-based sample from confiscated Box 1 displaying a wide ion distribution from potassium perchlorate.

significant peaks for chlorates, sulfur, or sample-based nitrates were observed. However, potassium nitrate adducts were observed on two individual samples from Confiscated Box 2 (Fig. S2). Given the very localized detection, individual items from the assorted mixture from the parcel (Fig. 1) may have contained potassium nitrate. Due to the limited detection, potassium nitrate was excluded from the summarized data below.

Fig. 5 displays the compiled results for two of the observed potassium perchlorate ions, specifically the intact salt adduct of potassium perchlorate with nitrate and the perchlorate anion. The perchlorate anion was measured from the high in-source CID parameters as specified in the Materials and Methods section. For the IRTD-DART-MS data, peak areas from the extracted ion chromatograms of each ion or specific m/z value were measured. Similar to the CE analysis, wipe samples were collected from numerous locations across each parcel yielding a range of peak areas. The characteristic potassium perchlorate peaks were detected on all four of the seized parcels. The measured median peak areas for each seized parcel was significantly greater (95% confidence) than the control box samples. Contrary to the CE results (Fig. 3), confiscated Box 2 did not yield the highest IRTD-DART-MS perchlorate signals. However, the presented results are only semi-quantitative and these differences in relative signal were likely a result of the slight differences in sampling. Specifically, due to the sensitivity of mass spectrometry, heavily loaded samples (i.e., those resulting in clear darkening or visibly “dirty” wipes) were swiped with a secondary wipe to reduce the amount of analyzed material. A couple of the confiscated box samples yielded no peaks for the adduct of potassium perchlorate with nitrate, demonstrating the importance of the sampling process, i.e., surface area coverage. For a high-throughput screening environment, each parcel may only be sampled with a single wipe, for which the maximum area should be covered.

Though both emerging techniques detected perchlorate-based flash powder oxidizers from the confiscated parcels, the limited

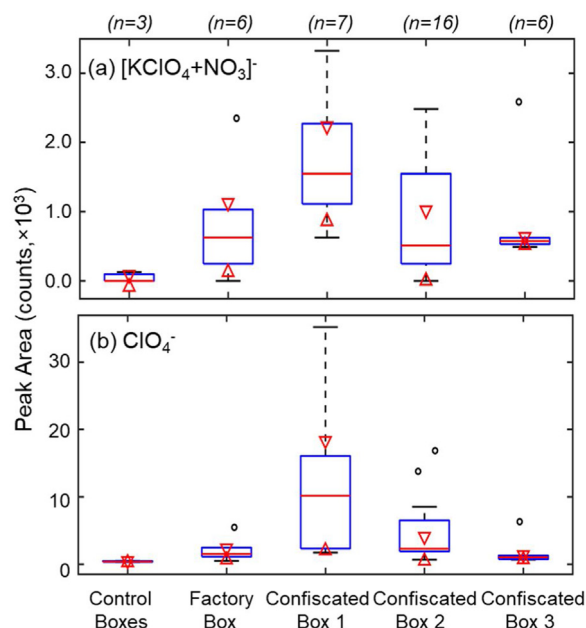


Fig. 5. IRTD-DART-MS extracted ion chromatogram peak area box plots for (a) the adduct of potassium perchlorate with nitrate: $[\text{KClO}_4+\text{NO}_3]^-$ and (b) the perchlorate anion and high in-source CID: ClO_4^- , across the four confiscated parcels and control packages. Boxes represent the median with lower (Q1) and upper (Q3) quartiles, whiskers represent $1.5\times$ the interquartile range (length of the box), outliers (o) represent values out of the whisker range, and triangular markers represent 95% confidence intervals ($\text{median} \pm 1.57(\text{Q3} - \text{Q1})/\sqrt{n}$).

specificity of the CE system simply enabled the identification of the perchlorate anion, while the use of mass spectrometry as the detection scheme for the IRTD-DART front-end provided additional information about the cation composition of the oxidizer – potassium perchlorate. The superior performance and direct identification of ions of interest by the IRTD-DART-MS platform comes at the price of portability, currently limited by the detection unit, a laboratory-based high-resolution time-of-flight mass spectrometer. While the IRTD-DART configuration has been demonstrated with a more portable single quadrupole mass spectrometer [29], future developments in sensitive portable mass analyzers could benefit the mobility of this technique. However, for parcel screening in a logistic environment the specific concept of operations could incorporate a stationary detection technique within distribution centers of the postal companies. Still, the methodology needs to be sufficiently robust and operational by laymen to successfully be employed. This will require user-friendly interfaces, automated (standardized) sampling and data analysis in addition to instrumental developments.

3.3. Pyrotechnic composition differentiation

Both emerging techniques demonstrated the capability to detect trace levels of perchlorate-based oxidizers from parcels seized by the Dutch police. Here, we considered the ability of each technique to detect and differentiate between wipe-based samples collected from packaging materials of two different flash bangers (Fig. 6), one containing solely flash powder and the other a mixture of flash and black powders. The black powder was present as a compressed plug on the fuse side of the flash banger. Compositions were confirmed by elemental analysis using X-ray fluorescence to be a common flash powder composition containing the inorganic oxidizer KClO_4 mixed with metal aluminum as the fuel (Fig. S3) [50]. Similarly, black powder traditionally contains charcoal, potassium nitrate and sulfur [51].

The exterior of multiple individual flash banger tubes and associated plastic bags were sampled for analysis by both the portable CE and IRTD-DART-MS systems. Wipe-based samples were taken at different locations on each side of the bag (bottom, top, and cardboard label) and from the bottom, top and length of the tubes. Fig. 7 displays the CE signals obtained for the sampling of bags and tubes from flash bangers containing solely flash powder or a mixture of black and flash powders. Similar to the screening of seized packages, perchlorate was detected on the packaging bags and at elevated levels from the tubes. Control bags and tubes (those not exposed to pyrotechnics) were not available, so blank wipes were used for background measurements. The blank wipe yielded nearly no perchlorate signal, but again similar to the cardboard boxes, exhibited nonzero nitrate signal. Samples collected from bags containing both powder compositions did not demonstrate

nitrate above background (Fig. 7a(i)). Tubes from both compositions revealed significantly higher nitrate than blank wipes. No differentiation was observed between those tubes containing solely flash powder and those containing the mixture with black powder, suggesting an unknown nitrate source other than the potassium nitrate from the black powder. Unfortunately, given the limited target scope of the commercial CE system (*i.e.*, only nitrate, chlorate, and perchlorate), peaks for sulfur-related species (usually a main component of black powders) were not observed, yielding limited discriminative capabilities.

The superior resolution of mass spectrometry as an analytical technique provides additional capabilities for differentiation of the pyrotechnic powder samples. In addition, the combined infrared-based thermal desorption process, DART ionization scheme, and mass spectrometric detection enabled improved specificity based on the ion distributions created and their temporal profile [31,36]. The discrete nature of the infrared emission interval and resulting temperature ramp enabled temporal separation of the desorption and detection of the more volatile sulfur species from the black powder relative to the non-volatile inorganic oxidizers – potassium nitrate from the black powder and potassium perchlorate from the flash powder (Fig. S4a). Each of the compounds from the black and flash powders generated a wide distribution of ions for targeted detection schemes (Fig. S4). Similarly, the IRTD-DART-MS platform enabled the detection of the intact inorganic salts, providing additional specificity and chemical information, notably, the adduct of potassium nitrate with nitrate, $[\text{KNO}_3+\text{NO}_3]^-$, from black powder and the adduct of potassium perchlorate with nitrate, $[\text{KNO}_3+\text{NO}_3]^-$, from the flash powder.

Fig. 8 displays box plots for samples collected from the packaging bags and tubes of flash bangers containing either solely flash powder or a mixture of black and flash powders. The figure provides peak areas from three ions representative of three target compounds, specifically, the adduct of potassium nitrate with nitrate and sulfur from the black powder, as well as the adduct of potassium perchlorate with nitrate from the flash powder. Both sample compositions demonstrated potassium nitrate signals above the blank wipes. While the bags and tubes containing black powder, residues exhibited higher potassium nitrate signals, the medians were not significantly different. The presence of the potassium nitrate ion from samples containing only aluminum and potassium perchlorate was believed to result from the dissociation of the potassium perchlorate and recombination with excess nitrate in the gas phase. The sulfur component of the black powder revealed a clear and significant difference in peak areas from the two compositions, providing discrimination of these samples. However, sulfur signals are still observed, at lower peak areas, for the flash powder only samples. Both flash banger types are produced by the same manufacturer and most likely in the same production facility. Therefore it is envisioned that cross

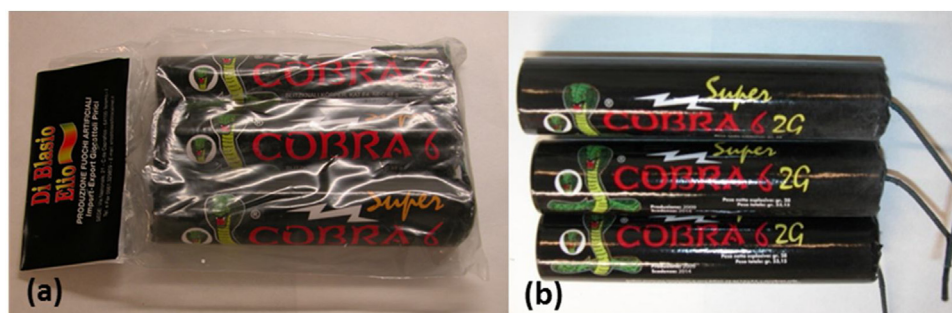


Fig. 6. Examples of the two types of packaging materials and flash bangers of different composition; (a) plastic bags with three flash bangers containing flash and black powder, and (b) three cardboard tubes of flash bangers containing only flash powder.

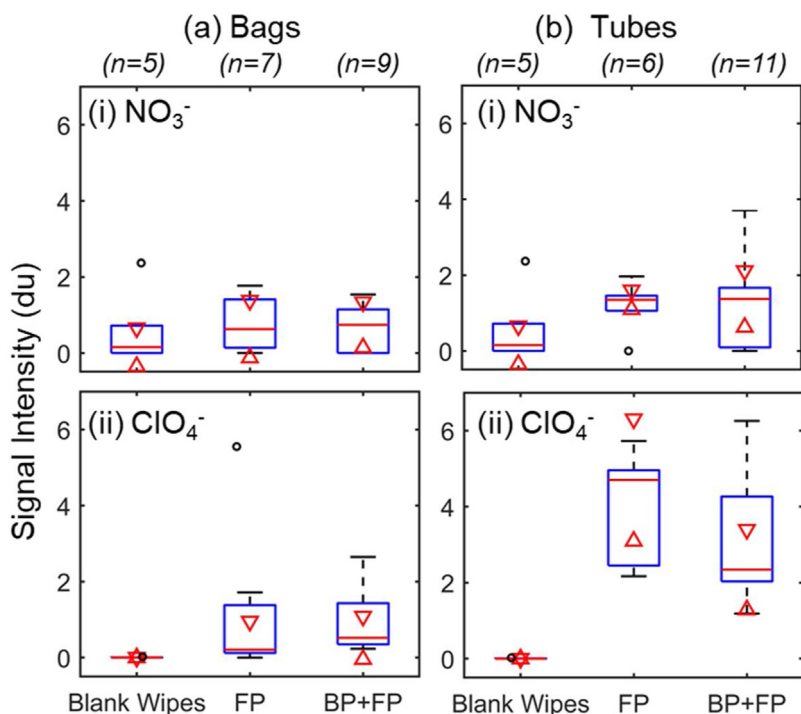


Fig. 7. CE signal intensity box plots for samples from (a) bags and (b) tubes for the detection of (i) nitrate: NO_3^- and (ii) perchlorate: ClO_4^- , from flash bangers containing either solely flash powder (FP), or a mixture of black and flash powders (BP + FP). Boxes represent the median with lower (Q1) and upper (Q3) quartiles, whiskers represent $1.5 \times$ the interquartile range (length of the box), outliers (o) represent values out of the whisker range, and triangular markers represent 95% confidence intervals ($\text{median} \pm 1.57(Q3 - Q1)/\sqrt{n}$).

contamination of black powder traces could occur during the actual production of the items, depending on the production and packaging procedures. In addition, the nonzero sulfur signal exhibited on the flash powder-only tubes could also be a result of cross contamination of samples or instrument carryover.

Finally, potassium perchlorate was detected on the bags and tubes of both sample compositions at levels significantly above the blank wipes. This demonstrates the ability of the IRTD-DART-MS technique to not only facilitate detection of both black and flash powders, but also to enable their differentiation, predominantly through identification of the sulfur ions. As both flash banger types contain flash powder, no insight is gained in possible flash powder contamination during production and packaging. From a forensic perspective this does not represent an issue as flash banger items containing flash powder are illegal (in the Netherlands when sold to consumers) and the flash bangers from this manufacturer are all flash powder-based.

The question that remains is whether IRTD-DART-MS could also be successfully used to classify flash powder-based fireworks (*i.e.*, flash powder + black powder formulations *versus* flash powder only formulations) when sampling the exterior of boxes containing these products. Unfortunately, for this study no genuine factory boxes were available containing items based on flash and black powder. It is expected that classification will be possible when sufficient amounts of residues can be collected on the wipes. This will differ from box to box depending on the overall number of items, additional packaging inside the box and the forces exerted on the boxes during transport.

The emerging techniques presented here demonstrated the potential for direct chemical screening of postal packages and both require no sample preparation with analysis times less than a minute. Yet, speed can be a crucial factor for high-throughput screening, both in sample collection and analysis times [52]. Traditionally at airports, a related high throughput setting, a total

screening time of six seconds is reserved per passenger [53]. Further, methods using wipe-based sample collection generally have longer screening times, around twenty seconds [53,54]. Recent developments that avoid swipe-sampling and use integrated sampling strategies are approaching the six second limit [53,54]. Preferably, large scale screening of packaging materials for the presence of pyrotechnic traces might be performed directly on the sample surfaces. However, for the detection of solid residues on cardboard parcels wipe-based sampling cannot be avoided. One potential avenue might be a fully-automated parcel sampling and analysis system. Nevertheless, expanding the analytical toolbox for screening in a logistic setting with direct chemical detection increases the options to track down parcels containing fireworks.

4. Conclusions and recommendations

In this article, a proof-of-concept study is presented for the direct chemical screening of postal packages containing fireworks by two emerging analytical techniques; a commercially-available portable CE system and a laboratory-based prototype IRTD-DART-MS platform. The analyzed pyrotechnic packaging materials seized by the Dutch police, showed that residues of the characteristic flash powder inorganic oxidizer (*i.e.*, potassium perchlorate) can be detected from cardboard shipping parcels. Although both screening tools detected the perchlorate components of the pyrotechnic residues of interest, they differed in portability, selectivity, and user interaction. The field deployable CE system demonstrated rapid analysis with a fully interactive user interface, peak identification firmware, and alarm algorithms. However, the limited specificity and inherently high environmental nitrate background led to difficulties identifying nitrate-based oxidizers, specifically from black powder samples. Alternatively, the IRTD-DART-MS platform

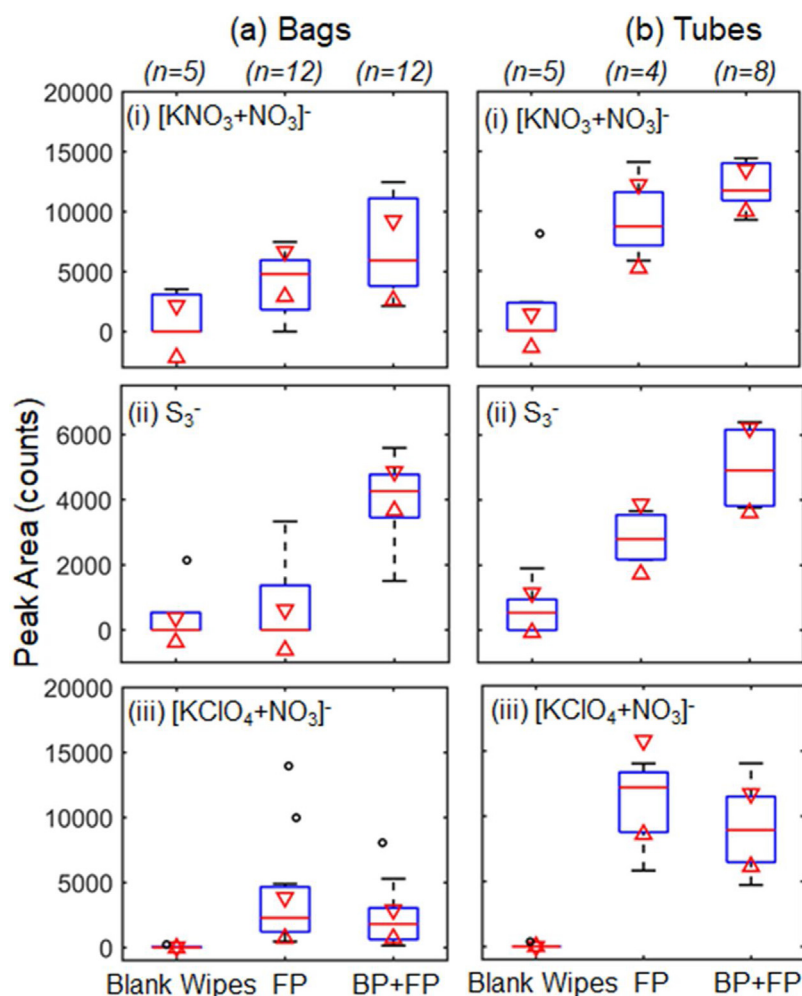


Fig. 8. IRTD-DART-MS extracted ion chromatogram peak area box plots for samples from (a) bags and (b) tubes for the detection of (i) adduct of potassium nitrate with nitrate: $[\text{KNO}_3+\text{NO}_3]^-$, (ii) sulfur: S_3^- , and (iii) adduct of potassium perchlorate with nitrate: $[\text{KClO}_4+\text{NO}_3]^-$, from flash bangers containing either solely flash powder (FP), or a mixture of black and flash powders (BP + FP). Boxes represent the median with lower (Q1) and upper (Q3) quartiles, whiskers represent $1.5 \times$ the interquartile range (length of the box), outliers (o) represent values out of the whisker range, and triangular markers represent 95% confidence intervals ($\text{median} \pm 1.57(\text{Q3} - \text{Q1})/\sqrt{n}$).

provides very selective detection of a diverse ion distribution, as well as the capability to differentiate between flash and black powder traces by identification of their molecular inorganic ions and intact salts. Nevertheless, the evolution of this technique toward more portable mass analyzers would likely reduce this overall specificity. In addition, neither technique identified the aluminum fuel of the pyrotechnic flash powder. The initial results presented in this study demonstrate the benefits chemical detection might bring for tracking the illicit shipment of pyrotechnics and fireworks. Additional research of real-case samples and parcels is needed to investigate the relationship between the firework contents of packages and the detectable traces on the exterior of such parcels and to gain insight with respect to persistency of pyrotechnic residues and secondary transfer to unrelated parcels. The suggested approach can only be effective if the extent of parcel-to-parcel cross contamination is limited during transport as this would otherwise lead to significant false-positive rates. In addition, more knowledge and data are required on background levels of target ions in the postal facility environment. As more data is gathered also the use of chemometric data analysis can be considered to extract as much information as possible to unravel the contents of packages through the chemical analysis of exterior residues. Although sufficient speed to enable comprehensive screening remains a challenge for wipe-based methods, developments in portability,

automation and targeted screening strategies may lead to the application of chemical residue analysis for pyrotechnic trace detection in a logistic setting.

CRedit authorship contribution statement

Karlijn D.B. Bezemer: Conceptualization, Investigation, Writing - original draft, Writing - review & editing, Visualization, Project administration. **Thomas P. Forbes:** Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization. **Annemieke W.C. Hulsbergen:** Conceptualization, Writing - review & editing. **Jennifer Verkouteren:** Conceptualization, Investigation, Writing - review & editing. **Shannon T. Krauss:** Formal analysis, Writing - original draft, Writing - review & editing, Visualization. **Mattijs Koeberg:** Conceptualization, Writing - review & editing. **Peter J. Schoenmakers:** Conceptualization, Writing - review & editing. **Greg Gillen:** Conceptualization, Writing - review & editing, Supervision. **Arian C. van Asten:** Conceptualization, Methodology, Writing - review & editing, Supervision.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <https://doi.org/10.1016/j.forsciint.2020.110160>.

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