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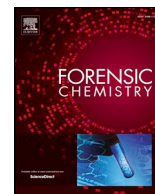
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Rapid forensic chemical classification of confiscated flash banger fireworks using capillary electrophoresis

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HIGHLIGHTS

- Rapid CE analysis of flash and black powder in Cobra 6 flash bangers.
- Characterization of both anions and cations present in pyrotechnic charges.
- Limited variation is observed between seized sets of commercial flash bangers.
- Cation traces serve as markers for Cobra 6 imitation items.

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ABSTRACT

In the Netherlands, the illegal use of powerful flash bangers is popular and as a result these items are frequently encountered in forensic casework. In collaboration with the Dutch police a representative sample set of the most frequently confiscated flash bangers, the Cobra 6 and Cobra 6 2G, has previously been collected also including imitation items. Classification of the different flash bangers was performed by analysing the pyrotechnic charge using capillary electrophoresis (CE) with indirect UV-detection. Two rapid CE methods were used to determine the anions and cations present in the pyrotechnic mixtures. Black and flash powders were easily distinguishable based on their main inorganic compositions, *i.e.*, KNO₃ and KClO₄, respectively. Differentiation of flash powders from the commercial and imitation pyrotechnic items was achieved by the identification of Ca²⁺ and Mg²⁺ cation traces in the imitation flash banger powders. Quantitative CE results were used to explore the possibilities to differentiate seized sets of flash bangers but this proved to be difficult for commercial items due to lack of impurities and uniform production processes. In addition, inherent inhomogeneity of the powders and incomplete sample extraction yielded a relative high measurement uncertainty within a set. For the imitation items potential for set-based differentiation was observed. Although the number of seized imitation sets was limited, a first step has been taken to classify pyrotechnic mixtures to provide additional information and intelligence in forensic casework of flash bangers.

1. Introduction

Pyrotechnic mixtures are classified as energetic materials, but react at a relatively slower rate compared to other types of explosives [1]. Reactions during combustion are driven by electron-transfer or oxidation-reduction mechanisms in presence of oxidizers and fuel [2,3].

Their major civil application is in fireworks, where pyrotechnic compositions are tuned to produce visible and audible effects, such as colors, smokes, sparks and sounds, for entertainment purposes. A wide variety of firework items is used during festivities and celebrations. In the Netherlands, fireworks are a vital component of the New Year's Eve traditions and citizens are allowed to ignite consumer fireworks under

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strict conditions. Specific regulations apply to the trade period, composition and load of these consumer firework items to limit the risks for public and environment. More powerful professional fireworks contain larger quantities of active charges and can only be ignited by licensed individuals [4,5].

Nevertheless, there is high demand for these more exciting professional firework items among the general population and more specific among young adolescents. One of the most often encountered professional firework items that are frequently being misused in the Netherlands are flash bangers which contain very powerful flash powder. Most incidents in the Netherlands are related to accidental injuries and destructions of public properties. However, flash bangers are also used for criminal activities, e.g. destruction of ATM machines. In addition, there is an actual threat for abuse of fireworks by individuals with terrorist motives where pyrotechnic charges originating from these items can be used to fabricate improvised explosive devices (IEDs) [3]. This is especially true since very powerful flash bangers can easily and almost anonymously be obtained via the Internet. Therefore, the analysis of intact and post-explosion residues of flash bangers is important in forensic investigations in the Netherlands.

The main pyrotechnic charges in flash bangers are flash and black powder. A typical composition of flash powder in firework items consists of potassium perchlorate (70 wt%) as oxidizer and dark pyro aluminum (30 wt%) as fuel [6]. Other types of flash powder can also contain magnalium powder, sulfur and a diversity of oxidizers. Black powders mainly consist of potassium nitrate, charcoal and sulfur, with the most common formulation of 75:15:10 wt%, respectively [7,8]. In forensic casework, quick chemical screening of intact explosives is usually performed by infrared and Raman spectroscopy. However, these screening techniques are frequently inconclusive for the identification of pyrotechnic compositions, due to the dark appearance of the powders which can result in low spectroscopic signals and/or laser induced ignition of the sample. Therefore, these inorganic mixtures are generally analyzed with X-ray techniques, such as X-ray fluorescence (XRF) and X-ray diffraction (XRD) to determine their intact chemical compositions [9]. In addition, ion chromatography (IC) with suppressed conductivity detection or UV detection is successfully and predominantly used in both pre- and post-explosive forensic casework for the separation and identification of inorganic ions [10–13]. The use of capillary electrophoresis (CE) as a complementary technique could be beneficial to obtain higher values of evidential strength and decrease the possibility of co-migrating ions due to its electrophoretic mobility based separation mechanism [12]. Additionally, CE typically allows for faster analysis compared to IC and does not require dedicated, costly columns with a limited life time. In the last 20 years, studies have shown that CE analysis with contactless conductivity detection and UV detection is suitable for parallel analysis of inorganic ions [1,3,14–16]. A very interesting and forensically relevant advantage of CE is the possibility of miniaturization in the form of portable or lab-on-a-chip devices that could allow direct analysis of inorganic explosives at a crime scene [12,14–17].

Currently, forensic analysis of pyrotechnics is limited to detection and identification of the active charges. Inorganic explosives studies using IC and CE are, therefore, mainly focused on qualitative analysis of intact and post-blast explosive samples [1,3,4,15–19]. To continue to assist law enforcement agencies in their endeavors to minimize the availability and abuse of professional fireworks, additional research is required that goes beyond identification. Classification and batch differentiation of flash bangers might provide valuable tactical information regarding composition and production origin. In a period of one year, from December 2015 to December 2016, a unique collection of Cobra 6 type flash bangers has been created from items that were confiscated by the Dutch police. Visual characteristics of these items have previously been described and showed the presence of three subtypes of which two are commercially produced items and one group of imitation items [20]. A selection of flash bangers from this collection

has been made available for analysis in this study to distinguish between different seized sets of flash bangers based on their intact inorganic pyrotechnic compositions using a quick chemical classification by CE with indirect UV-detection. Additionally, differentiation of flash bangers through quantitative analysis has been explored.

2. Materials and methods

2.1. Chemicals and standards

Ammonium nitrate, sodium sulfate, sodium nitrite and lithium nitrate were obtained from Merck (Darmstadt, Germany). Sodium nitrate, calcium nitrate tetrahydrate, barium nitrate, strontium nitrate, magnesium nitrate hexahydrate, sodium chlorate, lithium perchlorate, sodium thiosulfate, sodium cyanate, sodium thiocyanate, sodium chloride and potassium perchlorate were obtained from Sigma-Aldrich (Steinheim, Germany). Potassium nitrate was obtained from Janssen (Beerse, Belgium). All chemicals were of analytical grade with a minimal purity of 99%, except lithium perchlorate ($\geq 98\%$), sodium thiosulfate ($\geq 98\%$) and sodium cyanate ($\geq 96\%$). A self-made flash powder was created by mixing a 1:1 ratio of potassium perchlorate salt with aluminum powder obtained from Riedel de Haën/Honeywell (Seelze, Germany).

Anionic stock solutions of 1 g/L were prepared from the above mentioned sodium and lithium salts dissolved in ultra-pure water ($18.2 \text{ M}\Omega\text{-cm}$ at 25°C). A standard anion mix of 0.1 g/L was used for screening of chlorate, chloride, cyanate, nitrate, nitrite, perchlorate, sulfate, thiocyanate and thiosulfate. For calibration and quantification a standard solution of 0.1 g/L consisting of nitrate and perchlorate was used. In all intact powder samples analyzed with the anion method, cyanate was used as internal standard (0.03 g/L–30 ppm). It should be noted that cyanate can be a byproduct of black powder combustion and hence this internal standard is not recommended as internal standard for post-explosive residue studies.

Nitrate salts were used to prepare cationic stock solutions of 1 g/L. A cationic screening mix of 0.1 g/L contained ammonium, barium, calcium, lithium, magnesium, potassium, sodium and strontium ions. A solution of 0.1 g/L containing calcium, magnesium, potassium and sodium ions was used for calibration and quantification. Although barium nitrate is a common oxidizer used to produce green flames in fireworks, the absence of this oxidizer in the flash bangers of interest in this study allowed the use of barium (30 ppm) as internal standard in all calibration solutions and samples analyzed with the cationic method. Calibration lines were prepared in the range of 10–60 ppm for all anions and cations.

Sodium hydroxide obtained from Merck (Darmstadt, Germany) was used for preconditioning of the capillaries with 1 M and 0.1 M solutions. The commercial pyromellitic acid based anion background electrolyte (BGE) was obtained from Agilent Technologies (Santa Clara, CA, USA). Imidazole, 18-crown-6-ether (18-C-6), α -hydroxyisobutyric acid (α -HIBA) obtained from Sigma-Aldrich (Steinheim, Germany), and acetoneitrile obtained from Biosolve Chimi (Dieuze, France) were used for the BGE of the cation method.

2.2. Sample collection

The pyrotechnic powders analyzed in this research originate from a unique collection of Cobra 6 flash banger fireworks that have been confiscated by the Dutch police. Fig. 1 illustrates the schematic constructions of the three Cobra 6 subtypes encountered in the sample collection, i.e., the commercially available Cobra 6 and Cobra 6 2G flash bangers, and an example of a typical Cobra 6 imitation flash banger.

All flash bangers were disassembled under the appropriate safety conditions, which included but were not limited to taking precautions to avoid static discharges and collection of only small amounts of active charges (few grams) separately stored in wooden sample trays. Table 1

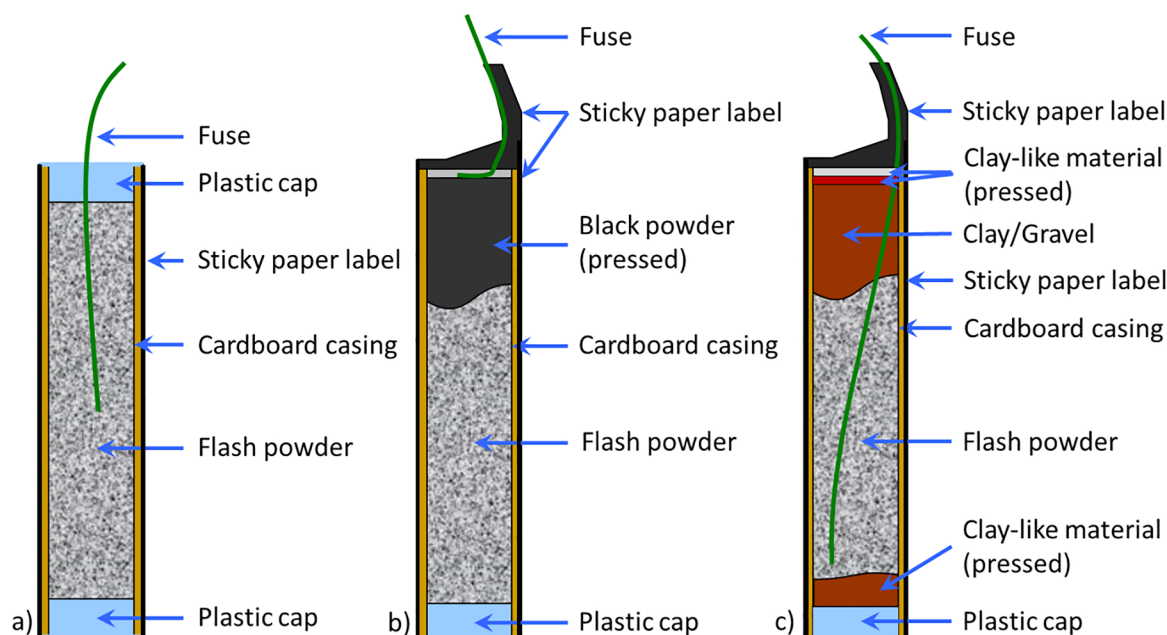


Fig. 1. Schematic illustration of a) the commercial Cobra 6 2G flash banger, b) the commercial Cobra 6 flash banger and c) an imitation flash banger.

Table 1

Overview of sample set of flash bangers, including number of items analyzed in each set (n) and production year and language depicted on the labels.

Cobra 6 flash banger				Cobra 6 2G flash banger			
Set	n	Year	Language	Set	n	Year	Language
1	1	2014	English (UK)	17	1	2011	DE
3	1	2014	Italian (IT)	18	2	2014	UK
4	1	2011	German (DE)	19	5	2014	UK
5	1	2015	UK	20	1	2009	IT
6	5	2014	UK	21	1	2009	IT
7	1	2011	DE	Imitation flash banger			
8	1	2014	UK	Set	n	Year	Language
11	2	2005	IT	2	3	2012	IT
12	1	2009	IT	9	3	2007	IT
14	2	2013	IT	10	3	2012	IT
15	1	2009	IT	13	1	2007	IT
16	1	Not specified	Polish (PL)				

lists the seized sets of flash bangers that were made available for this study, including the number of items analyzed in each set and the production year and language depicted on the labels. In total, flash powder samples were collected from 22 commercial items, originating from ten seized sets of Cobra 6 flash bangers and five seized sets of Cobra 6 2G flash bangers. Black powder was only present in the commercial Cobra 6 flash bangers and samples were collected from 18 items, originating from twelve seized sets. Additionally, flash powder samples were collected from ten imitation items originating from four seized sets of imitation flash bangers.

2.3. Sample preparation

Sample preparation of the intact pyrotechnic charges was based upon the method described by Martín-Alberca et al. [3]. Briefly, this included dispersion of 25 mg of powder in 5 mL of ultra-pure water, vortexing of the sample for 1 min. Black powder and flash powder samples were prepared separately. Since black powder was present as a compressed plug in the flash bangers gentle manual crushing was

needed to create a powder sample. No additional sample preparation was required for the loose flash powder present in the flash bangers. The sample preparation was expanded to be used for quantitative analysis by placing all samples in an ultra-sonication bath for 10 min and afterwards suspensions were filtered using syringe filters (4 mm PTFE, \varnothing 0.45 μ m).

Glass vials (1.5 mL) were used for screening and quantification of the bulk ions present in the samples at concentrations of 0.05 g/L. Additional samples of 5 g/L were prepared for the analysis and quantification of additional cation traces. In this case polypropylene vials (1 mL) were used to prevent potential sodium contamination originating from glass surfaces and to prevent adsorption of the analytes of interest. For quantification of the different intact charges, six measurements were performed for each powder by preparing three samples and analyzing them in duplicate.

2.4. CE instrumentation and methodology

All samples were analyzed using a G1600AX CE system (Agilent Technologies) equipped with a DAD detector. New fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) were conditioned by flushing with sodium hydroxide (1 M, 15 min, 1 Bar), sodium hydroxide (0.1 M, 15 min, 1 Bar), ultra-pure water (8 min, 1 Bar), and background electrolyte (BGE) (8 min, 1 Bar). Two separate CE methods and BGEs were applied for the analysis of anions and cations. Sample loading was identical in both methods using hydrodynamic injection (50 mbar) for 20 s. An additional BGE plug was introduced after the samples (5 s, 50 mbar) for sample stacking.

The anion method used was previously described by Martín-Alberca et al. [3] and Harrold et al. [21]. For this study, the original method performed on a Beckman system was adjusted for analysis on an Agilent system. Fused silica capillaries with an effective length of 48 cm (56.5 cm total length) and 50 μ m ID were used. Separation was performed at -30 kV using an initial linear gradient from 0 to -30 kV in 30 s and a constant temperature of 30 $^{\circ}$ C. The wavelength of the DAD detector was set at 250 nm with a bandwidth set at ± 10 nm. A commercially available BGE from Agilent Technologies was used, which was composed of 2.25 mM pyromellitic acid (PMA), 6.5 mM sodium hydroxide, 0.75 mM hexamethonium hydroxide and 1.6 mM triethanolamine at pH 7.7. The capillaries were flushed with BGE before each

separation (3 min, 1 Bar).

A method described by Hopper et al. [18] was used for the cation separation and adjusted for analysis on an Agilent system. Fused silica capillaries with an effective length of 40.2 cm (48.7 cm total length) and 50 μm ID were used. Separations were performed using a positive voltage of 10 kV, with an initial linear gradient from 0 to 10 kV in 30 s, at 20 °C. Indirect-UV detection was conducted at a wavelength of 208 nm (bandwidth \pm 10 nm). The BGE comprised of 17.5 mM α -hydroxyisobutyric acid, 16 mM imidazole, and 4 mM 18-crown-6-ether in ultra-pure water with 6% (v/v) acetonitrile at pH 4.7. The capillaries were flushed with BGE before each separation (2 min, 1 Bar) [18].

Agilent Technologies 3D-CE ChemStation software was used for data collection and processing. Peak areas and migration times of the analytes and internal standards were extracted from the data. The effect of observed shifts in migration times of ions on peak area was found to be minimal and no peak area correction was required. Calibration lines were computed using Excel software (Microsoft).

3. Results and discussion

3.1. Physical appearance

The schematic constructions of the different subtypes of Cobra 6 flash bangers are illustrated in Fig. 1. The commercially available Cobra 6 2G flash banger contains flash powder as active charge. In the Cobra 6 flash bangers a black powder plug is added, on top of the flash powder, which functions as a delay charge because of its reduced burning speed compared to flash powder [2]. Visual distinction between both powders can be made based on their physical appearance, especially since black powder is present as a compressed plug in the flash bangers. Due to the popularity and lucrative market of both commercial flash bangers, imitations of these items are frequently encountered. The imitations mimic the external features of the Cobra 6 flash banger, but the interior is usually clearly different. The flash powder in these items is often mixed with sawdust, gravel and clay plugs. A direct comparison of the flash powders indicates that the powder from the imitation items (after removal of the gravel and sawdust by sieving) has a bigger particle size than the powder from the commercial Cobra 6 and Cobra 6 2G flash bangers, as seen in Fig. 2a and 2b. This is confirmed by microscopic analysis, as shown in Fig. 2d and 2e. However, in forensic scenarios where active charges are removed from the firework items, and used for the fabrication of home-made explosive devices, visual and microscopic comparison of the flash powder can be difficult. Especially when black powder is mixed with flash powder the direct visual assessment is no longer feasible. Therefore, although physical appearance can already provide an initial distinction between pyrotechnic charges in some forensic scenarios, CE analysis as proposed in this study can serve as a quick identification technique to confirm the presence of black and/or flash powder in a sample. Firstly, and most importantly, because it provides chemical information that allows identification of the inorganic ions present in the pyrotechnic mixtures. Secondly, because it allows the compositional differentiation of samples that are visually indistinguishable. And thirdly, because it adds objective information to subjective visual distinctions.

3.2. CE method evaluation

To cover both the anionic as well as cationic content, two separate CE methods have been implemented using indirect UV detection. The commercially available anion BGE uses pyromellitic acid (PMA) as carrier ion, buffered with triethanolamine to allow fully ionized PMA. Hexamethonium is used to modify the electroosmotic flow [21]. For cation separations, complexing agents are often added to the BGE in order to increase electrophoretic mobility differences, and thus improve separations. In the BGE of this study, α -hydroxyisobutyric acid possesses weak complexation properties for all eight studied cations. In addition,

18-crown-6-ether is known for its ability to form a complex with potassium enabling the CE separation of this ion from sodium [22]. Separations could be achieved within an analysis time of 10 min for each method. Limits of detections (LODs) were determined as the ion concentrations yielding a detector signal equal to approximately 3 times the noise level and were around 1 ppm for all analytes. The method performances for the separation of anions and cations is in line with the previously described method developments [3,15,18]. Separations of the relevant anions and cations for the analysis of pyrotechnic mixtures are shown in Figs. 3 and 4, respectively.

Initial screening of the intact powder samples was performed to determine the presence of anions and cations in the different pyrotechnic mixtures. As expected, the main inorganic ion compositions of black and flash powder are potassium nitrate and potassium perchlorate, respectively (Figs. 3 and 4).

In this study a quick and straightforward extraction method is used for the analysis of ions present in the active charges of flash bangers. Robustness of this sample extraction method is needed to enable reliable quantitative analysis of the pyrotechnic charges. Therefore, a homemade flash powder with known compositions of potassium perchlorate and aluminum powder (ratio 1:1) was extracted using 1 min of vortex prior to 10 min of ultra-sonication. Recoveries were $86 \pm 8\%$ and $59 \pm 2.4\%$ for potassium and perchlorate, respectively. This shows that there is no complete extraction of potassium perchlorate after 10 min of sonication. The latter could be due to the relatively low solubility of potassium perchlorate in water (15 g/L at 25 °C). This significantly lower recovery of perchlorate versus potassium also leads to a lower mass ratio of perchlorate vs potassium as would be expected, 1.8 versus 2.4, respectively. Fortunately, in addition to our homemade flash powder, all flash powder samples from the flash bangers showed similar ratios (mean 1.8, RSD 7.2%) indicating constant recoveries. An artificial black powder sample with known concentrations of potassium nitrate was not available and could not easily be prepared. Various black powder compositions are reported in literature, where the most common ratio is 1.5:1:7.5 m/m for charcoal, sulfur and potassium nitrate, respectively [7,8]. The expected mass ratio of potassium and nitrate is 1.6 which is close to, but slightly higher than, the observed average ratio for all black powder samples (mean 1.4, RSD 6.8%). It should be noted that the current extraction procedure is not exhaustive, leading to limited accuracy and precision in quantitative analysis. The alternative of exhaustive extraction including complete sample destruction and dissolution would make the analysis very laborious and would nullify the benefits of the rapid CE analysis. Therefore, although the extraction procedure is not exhaustive, and therefore selective, the stability of the recoveries for potassium perchlorate and potassium nitrate demonstrate the usefulness of the practical and short extraction method.

3.3. Chemical classification

As seen in the previous section, black and flash powder can easily be differentiated based on the presence of their main inorganic ion composition, *i.e.*, NO_3^- versus ClO_4^- , respectively (Fig. 3). No additional traces of anions were detected in all black and flash powder samples, even when more concentrated samples were injected. Traces of Na^+ are visible in all samples, but the results showed that irrespective of the use of plastic or glass sample vials, Na^+ contamination was inevitable as the instrument contained several glass parts (*e.g.* buffer and cleaning vials). Therefore, Na^+ was not included as a parameter to differentiate samples. Traces of Ca^{2+} were detected in black powder when more concentrated samples were injected, as shown in Fig. 4b. The flash powders originating from the imitation flash bangers contain traces of Ca^{2+} and Mg^{2+} , whereas no additional cation traces were detected in the flash powders coming from the commercial Cobra 6 flash bangers (Fig. 4b). This enables differentiation of flash powder originating from the commercial Cobra 6 and the imitation flash bangers based on the

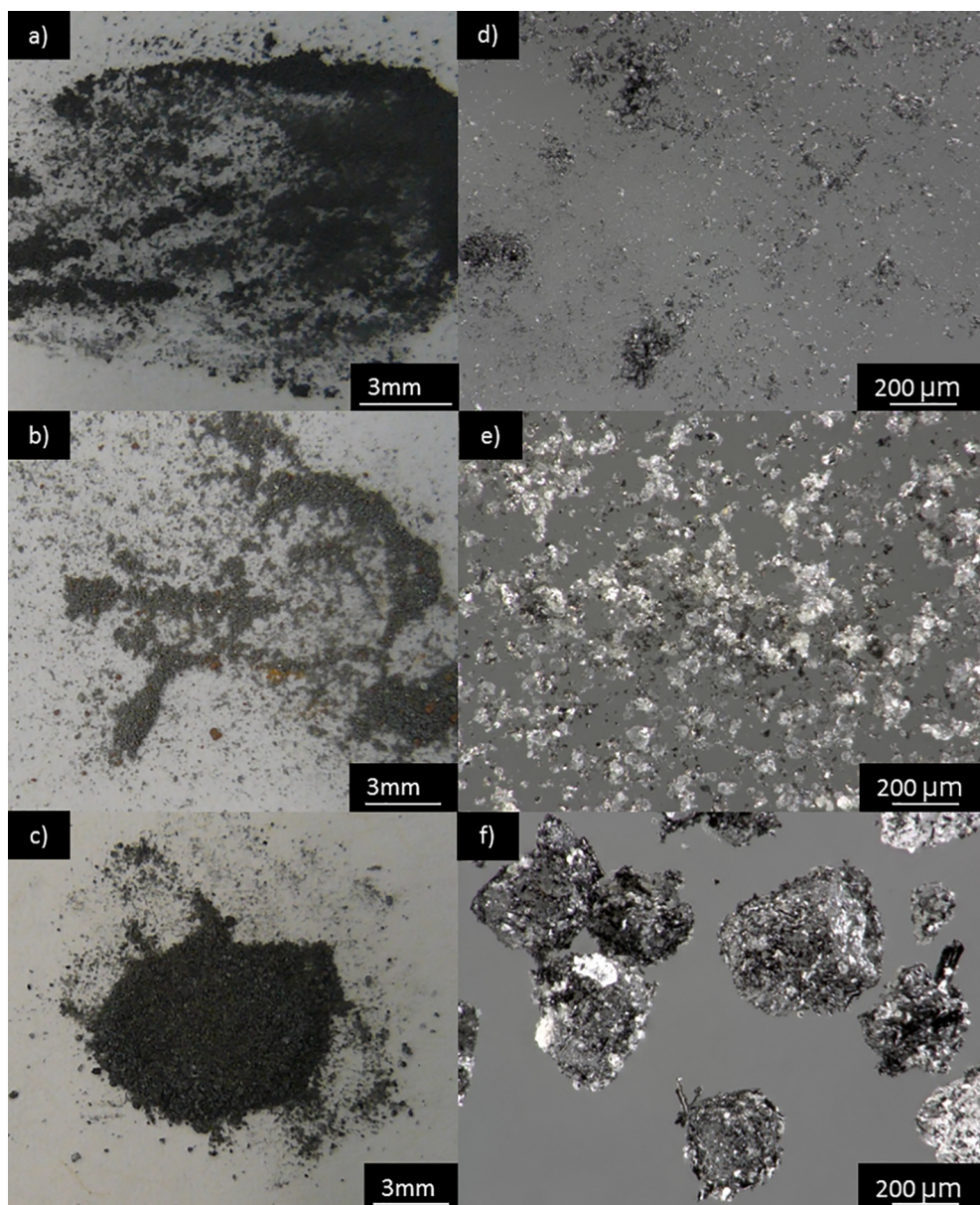


Fig. 2. Physical appearance of a) flash powder from a Cobra 6 flash banger, b) flash powder from an imitation item and c) black powder from a Cobra 6 flash banger, and corresponding microscopic images (d,e,f).

presence of cationic impurities, *i.e.*, Ca^{2+} and Mg^{2+} . In forensic scenarios where black and flash powders from Cobra 6 flash bangers are mixed, Ca^{2+} cannot be used for classification between the flash powders, since Ca^{2+} traces are also present in black powder. Fortunately, Mg^{2+} traces in the flash powder from the imitation items provide an opportunity to also distinguish between flash powder originating from commercial and imitation flash bangers in mixtures with black powder.

The graph in Fig. 5 shows the observed weight% (wt%) levels of K^+ and ClO_4^- in all flash powder samples of the different seized sets of flash powders. The amount of KClO_4 in the flash powders of the commercial items is consistently higher than in the flash powders of the imitation items. Assuming that aluminum is the only other constituent of flash powder, this shows that the flash powders from the imitation items contain considerable more aluminum. This is supported by the near perfect correlation of K^+ and ClO_4^- in the flash powder, which can only exist when there are no other sources of these ions. Although extraction is not exhaustive, as illustrated by the full vs. partial extraction correlation lines in Fig. 5, the methodology is robust and

reproducible enough to distinguish commercial from imitation flash powder based on the variation in potassium perchlorate levels in the pyrotechnic mixtures. Combining this with the previous finding that additional cationic impurities (Ca^{2+} and Mg^{2+}) only exist in imitation flash powder, a very robust, rapid and straightforward differentiation through CE analysis is achieved.

3.4. Exploring differentiation

In general, the capability of a method to distinguish batches of the same product class depends on the measurable differences between batches relative to the inherent variations in the measurements for a given batch. Therefore, the variation observed for each inorganic ion present in the pyrotechnic powders of an item (within-item variation) and corresponding seized set (within-set variation) have been compared to the overall variation of all the seized flash bangers of a given subtype (between variation). Table 2 lists the concentration ranges for all detected ions in the black and flash powders from the commercial Cobra 6

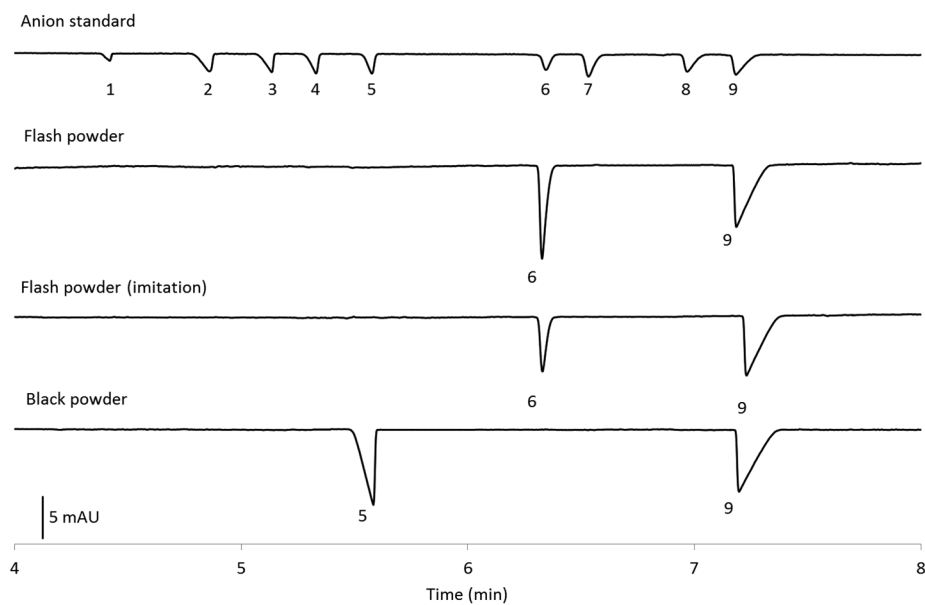


Fig. 3. Determination of anions in the different pyrotechnic powders at a sample concentration of 0.05 g/L. The anion peaks in the standard mix (5 ppm, 0.005 g/L) are identified as 1) thiosulfate, 2) chloride, 3) sulfate, 4) nitrite, 5) nitrate, 6) perchlorate, 7) thiocyanate, 8) chlorate, and 9) cyanate (IS). Flash powder (imitation) corresponds to flash powder present in the imitation flash bangers.

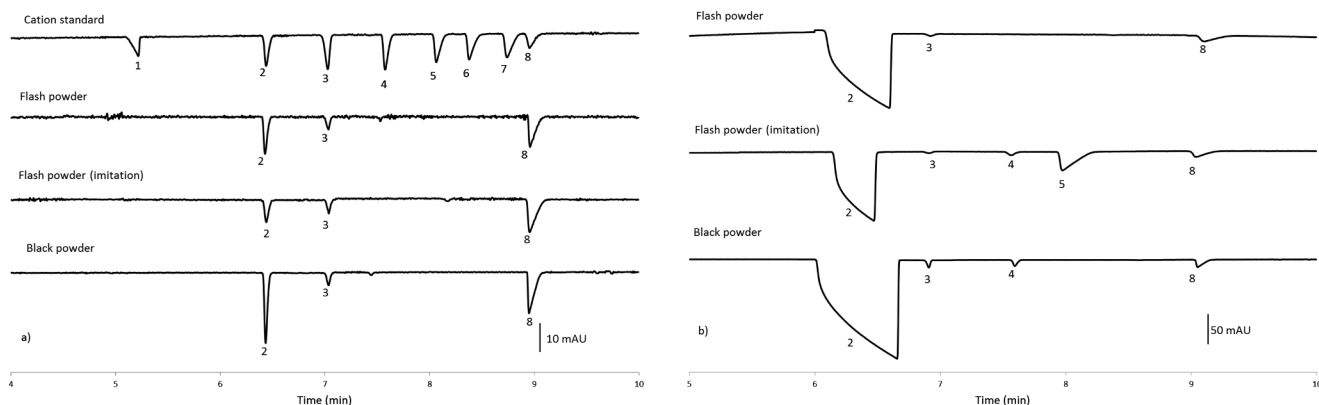


Fig. 4. Determination of cations in the different pyrotechnic powders at (a) a sample concentration of 0.05 g/L used for quantification of potassium in the sample, and (b) a sample concentration of 5 g/L to be able to detect trace amounts of additional cation impurities. The cation peaks in the standard mix (30 ppm, 0.03 g/L) are identified as 1) ammonium, 2) potassium, 3) sodium, 4) calcium, 5) magnesium, 6) strontium, 7) lithium and 8) barium (IS). Flash powder (imitation) corresponds to flash powder present in the imitation flash bangers.

and Cobra 6 2G flash bangers, and shows the total, within-set and within-items variations for each inorganic ion. The within-item variation has been determined by six measurements of powder from a single item (three individual extractions measured twice). Similarly, the within-set variation was obtained from 30 measurements, *i.e.*, the analysis of six samples from five flash banger items, originating from a single seized set. Most likely, the within-item variation is a combination of variations induced by the incomplete extraction procedure and the inherent inhomogeneity of the powder itself.

For all ions present in the black and flash powders, the within-item variation is similar to the within-set variation. This result suggests that the items in a given seized set contain pyrotechnic powder from the same main batch. To enable potential differentiation between the seized sets of flash bangers the overall variation between sets has to be considerably higher compared to the within-set variation. Unfortunately, for the main inorganic ions present in the powders, *i.e.*, K^+ , ClO_4^- and NO_3^- , the total variation between sets is relatively close to the within-set variation, as seen in Table 2. This limits the possibility for differentiation based on the main inorganic components. Since no additional trace ions were detected in the flash powder samples from the commercial items differentiation among the seized sets of Cobra 6 and Cobra 6 2G flash bangers is not feasible with the current methodology.

In the black powder samples trace amounts of Ca^{2+} were detected and a higher overall between sets variation suggests potential for differentiation. The observed levels (wt%) of Ca^{2+} in the black powder of the Cobra 6 flash bangers are depicted as function of the observed levels (wt%) of K^+ in the corresponding powder samples as depicted in Fig. 6. Indeed, items from some seized sets can be differentiated when combining the small variation in their KNO_3 concentrations with the trace-concentration of Ca^{2+} , but extensive overlap exists between most seized sets. In addition, no consistent trend was observed between powder composition and the production year of the flash bangers, as shown in Fig. 6.

Overall, differentiation among the commercially available flash bangers with the current screening method proves difficult, indicating a reasonably consistent black and flash powder composition over multiple batches and production periods of these flash bangers. This supports the hypothesis that the commercial Cobra 6 and Cobra 6 2G flash bangers in the seized sets originate from a single manufacturer.

The concentration ranges of all the detected ions in the flash powder from the imitation flash bangers are listed in Table 3. Since the origin of the imitation flash bangers and the flash powder that they contain is unknown, seized sets could originate from similar or different sources. Therefore, the within-item and within-set variation for all imitation sets

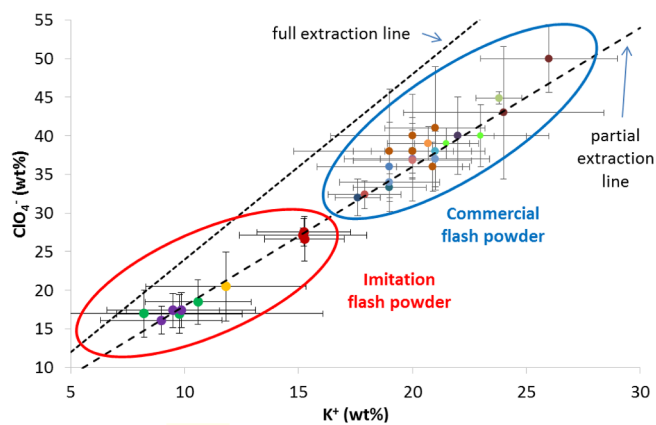


Fig. 5. Overview of the observed potassium and perchlorate ion levels with $\pm 2SD$ (wt%) in all flash powder samples, originating from both the commercial and imitation items. Each sample point represents six measurements of intact flash powder from a single flash banger item. Similar colors represent items from a single seized set of flash bangers. The fine and coarsely dashed lines in the figure respectively show the theoretical correlation between K^+ and ClO_4^- originating from $KClO_4$ at full extraction and the observed correlation for the partial extraction method used in this study.

(with exception of the single item in set 13) have also been included in Table 3. Following the results of the commercial flash bangers, the within-set and within-item variations for the main inorganic ions in the flash powders of the imitation items, *i.e.*, K^+ and ClO_4^- , are similar. Again, the within-variation of these ions is most likely the result of a combination of the incomplete extraction procedure and the inherent inhomogeneity of the powders. In contrast, the within-item variation of the trace ions (Ca^{2+} and Mg^{2+}) is considerably lower in most flash powders of the imitation sets, than the within-set variation. For example, the within-item variation of Ca^{2+} of set 9 is relatively low (2.6%), compared to the within-set variation of all three items within set 9 (21.8%).

As stated earlier, the ability to differentiate between seized sets of flash bangers increases when the measurable differences (overall or between-sets variation) are higher compared to the inherent variations in the measurements of a given set (within-set variations). For most of the ions and sets listed in Table 3, the between-sets variation is at least two times higher than the within-set variation. This suggests that differentiation might be feasible when the estimated levels of all ions are combined. Indeed, three groups of imitation flash bangers can be identified as seen in Fig. 7. Seized sets 2 and 10 have a similar ionic profile, which might suggest a common origin. This is further supported by the fact the items in these seized sets have the same production year and language depicted on their labels, *i.e.*, IT 2012. Therefore, differentiation between different production sets of imitation flash bangers based on their inorganic composition as analyzed with capillary

Table 2

Observed range of ion levels (wt%) and the associated relative standard deviation (RSD%) based on the extracted concentrations in the flash and black powder from the commercial Cobra 6 and Cobra 6 2G flash bangers. Black powder is only present in the Cobra 6 flash bangers.

		Min (wt%)	Max (wt%)	Average (wt%)	RSD (%)		
					Total/Between ¹	Within-set ²	Within-item ³
Flash powder	K^+	17.6	25.7	20.8	11.5	7.3	9.0
	ClO_4^-	31.9	51.3	38.4	12.4	8.7	6.8
Black powder	K^+	28.3	43.2	34.9	10.3	4.1	6.0
	NO_3^-	38.0	53.5	49.4	8.0	2.8	2.6
	Ca^{2+}	0.03	0.08	0.06	25.4	7.7	9.0

¹ The total or between sets variation is determined by the analysis of the powders in the items from all seized sets of commercial flash bangers, as listed in Table 1.

² The within-set variation is determined by the analysis of the powders in five items from seized set 6 and 19 for black and flash powder, respectively.

³ The within-item variation is determined by six measurements (three individual extractions measured twice) of the powders in a single item from seized set 6 and 19 for black and flash powder, respectively.

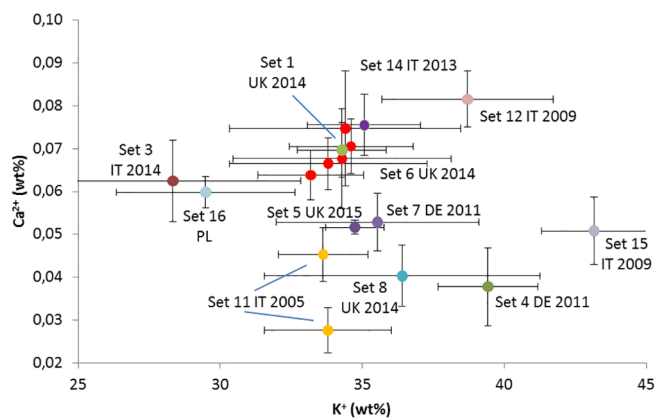


Fig. 6. Overview of the observed K^+ and Ca^{2+} levels with $\pm 2SD$ (wt%) in the black powder samples of the commercial Cobra 6 flash bangers, based on the extracted concentrations. For set 1, 3–5, 7–8, 12 and 14–16 black powder from one item has been analyzed. For set 11 and set 6 black powder from respectively two and five items have been included. Each sample point represents six measurements of intact black powder from a single flash banger item. Similar colors represent items from a single seized set of flash bangers.

electrophoresis seems feasible. However, given the limited sample size of imitation flash bangers this should be considered as a preliminary conclusion.

4. Conclusions

In this study, a quick chemical classification of pyrotechnic powders in commercial and imitation Cobra 6 flash bangers was realized using CE analysis with indirect UV-detection. This approach could be very useful in forensic explosives investigations, especially in case scenarios where the active charge has been removed from the original items and applied in home-made explosive devices.

Black powder and flash powder can easily be distinguished based on their main inorganic composition. All flash powders have a similar main inorganic ion composition, *i.e.*, $KClO_4$, but additional cation impurities (Ca^{2+} and Mg^{2+}) can be used to differentiate imitation from commercial items. In addition, the weight% of potassium perchlorate is significantly lower in the flash powder of the imitation batches.

Overall, limited classification potential was observed based on the main inorganic ions present in the pyrotechnic powders. A limiting factor is the high variation within a single item and within a seized set, most likely due to the incomplete extraction procedure and sample inhomogeneity. Additionally, for the commercial Cobra 6 and Cobra 6 2G items, the lack of impurities in the flash powder and the small between-set variations of Ca^{2+} impurities in the black powder prevented differentiation between these sets. Most likely this is the result of a uniform production process where large volumes of these type of flash

Table 3

Observed range of ion levels (wt%) and the associated relative standard deviation (RSD) based on the extracted concentrations in the flash powders from the imitation flash bangers. No black powder is present in the imitation items.

	Min (wt%)	Max (wt%)	Average (wt%)	RSD (%) Total/Between ¹	Set 2		Set 9		Set 10	
					RSD (%) Within-set ²	RSD (%) Within-item ³	RSD (%) Within-set ²	RSD (%) Within-item ³	RSD (%) Within set ²	RSD (%) Within-item ³
K ⁺	9.0	15.3	11.6	23.9	11.4	14.0	6.9	5.7	14.0	10.8
ClO ₄ ⁻	16.1	27.5	20.5	22.7	9.0	7.4	3.8	5.4	6.9	6.4
Ca ²⁺	0.03	0.17	0.08	57.5	14.9	10.4	21.8	2.6	26.7	4.3
Mg ²⁺	0.03	0.15	0.08	42.8	19.9	3.6	37.6	2.7	20.4	20.4

¹ The total or between sets variation is determined by the analysis of the powder in the items from all seized sets of imitation flash bangers, as listed in Table 1.

² The within-set variation is determined by analysis of the powder in three items from seized set 2, 9 and 10, respectively.

³ The within-item variation is determined by six measurements (three individual extractions measured twice) of the powders in a single item from seized sets 2, 9 and 10.

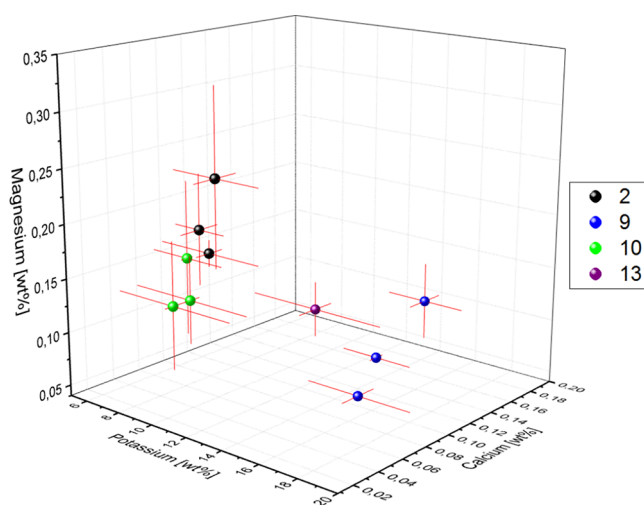


Fig. 7. Overview of the observed potassium, calcium and magnesium ion levels with $\pm 2SD$ (wt%) in the flash powder samples of imitation set 2 ($n = 3$ items, IT 2012), 9 ($n = 3$ items, IT 2007), 10 ($n = 3$ items, IT 2012) and 13 ($n = 1$ item, IT 2007). Each sample point represents six measurements of intact flash powder from a single flash banger item. Similar colors represent items from a single seized set of flash bangers.

bangers are being produced by one manufacturer. The opposite is suspected for the imitation items, which are expected to be produced in smaller, less controlled volumes. Indeed, the differentiation potential is higher for the flash powders in the imitation flash bangers when combining the concentrations of all ions. However, caution is required in extrapolating the findings of this study, since only a limited number of samples was available and the origin of the seized sets of imitation flash bangers is unknown. More research is needed to improve and expand the differentiation potential of flash bangers based on their active charge. Additional chemical analysis focusing on the aluminum powders or the clay plugs could therefore be beneficial. However, the results in this study provide a first step towards an analysis strategy that could yield tactical information on the origin of confiscated flash bangers and of intact pyrotechnic charges used in improvised explosive devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Balancing Security and Mobility



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References

- [1] J. Sáiz, M.T. Duc, I.J. Koenka, C. Martín-Alberca, P.C. Hauser, C. García-Ruiz, Concurrent determination of anions and cations in consumer fireworks with a portable dual-capillary electrophoresis system, *J. Chromatogr. A* 1372 (2014) 245–252.
- [2] J.A. Conkling, 1. Introduction, *Chem. Pyrotech. Basic Princ. Theory*, Marcel Dekker, Inc, New York, 1985, pp. 1–6.
- [3] C. Martín-Alberca, M.Á.F. de la Ossa, J. Sáiz, J.L. Ferrando, C. García-Ruiz, Anions in pre- and post-blast consumer fireworks by capillary electrophoresis, *Electrophoresis* 35 (2014) 3272–3280.
- [4] C. Martín-Alberca, C. García-Ruiz, Analytical techniques for the analysis of consumer fireworks, *Trends Anal. Chem.* 56 (2014) 27–36.
- [5] Nederlandse-Overheid, Wetten en regelgeving vuurwerkbesluit, <http://wetten.overheid.nl/BWBR0013360/2016-10-17>. (Accessed November 2018).
- [6] K.L. Kosanke, B.J. Kosanke, B.T. Sturman, R.M. Winokur, *Encyclopedic Dictionary of Pyrotechnics: (and Related Subjects)*, Pyrotechnic Reference Series No. 6, J. Pyrotechn. (2012) 493.
- [7] M.S. Russell, *The Chemistry of Fireworks*, 2nd ed., Royal Society of Chemistry, 2000.
- [8] R. Turcotte, R.C. Fouchard, A.M. Turcotte, D.E.G. Jones, Thermal analysis of black powder, *J. Therm. Anal. Cal.* 73 (2003) 105–118.
- [9] J.A. Siegel, *Forensic Chemistry: Fundamentals and Applications*, 1st ed., John Wiley & Sons Inc, 2015, pp. 175–227.
- [10] L. Barron, E. Gilchrist, Ion chromatography-mass spectrometry: a review of recent technologies and applications in forensic and environmental explosives analysis, *Anal. Chim. Acta* 806 (2014) 27–54.
- [11] G.W. Dycoski, R.a. Shellie, P.R. Haddad, Forensic identification of inorganic explosives by ion chromatography, *Anal. Lett.* 39 (2006) 639–657.
- [12] K. Hargadon, B. Mccord, Explosive residue analysis by capillary electrophoresis and ion chromatography, *J. Chromatogr.* 602 (1992) 241–247.
- [13] M. Huri, U. Ahmad, M. Omar, Determination of anionic profiling of improvised explosive devices from different types of low explosive material, *Mal. J. Fund. Appl. Sci.* 10 (3) (2014) 144–149.
- [14] A. Padaruskas, CE determination of small ions: methods and techniques, *Anal. Bioanal. Chem.* 384 (2006) 132–144.
- [15] C. Sarazin, N. Delaunay, A. Varenne, J. Vial, C. Costanza, V. Eudes, J.-J. Minet, P. Gareil, Identification and determination of inorganic anions in real extracts from

- pre- and post-blast residues by capillary electrophoresis, *J. Chromatogr. A* 1217 (2010) 6971–6978.
- [16] F. Tagliaro, F. Bortolotti, Recent advances in the applications of CE to forensic sciences (2005–2007), *Electrophoresis* 29 (2008) 260–268.
- [17] M. Pumera, Trends in analysis of explosives by microchip electrophoresis and conventional CE, *Electrophoresis* 29 (2008) 269–273.
- [18] K.G. Hopper, H. Leclair, B.R. McCord, A novel method for analysis of explosives residue by simultaneous detection of anions and cations via capillary zone electrophoresis, *Talanta* 67 (2005) 304–312.
- [19] F. Tagliaro, F. Bortolotti, Recent advances in the applications of CE to forensic sciences (2001–2004), *Electrophoresis* 27 (2006) 231–243.
- [20] K. Bezemer, R. Woortmeijer, M. Koeberg, P. Schoenmakers, A. van Asten, Multicomponent characterization and differentiation of flash bangers — part I: sample collection and visual examination, *Forensic. Sci. Int.* 290 (2018) 327–335.
- [21] M.P. Harrold, M.J. Wojtusik, J. Riviello, P. Henson, Parameters influencing separation and detection of anions by capillary electrophoresis, *J. Chromatogr.* 640 (1993) 463–471.
- [22] J.M. Doyle, B.R. McCord, Novel electrolyte for the analysis of cations in low explosive residue by capillary electrophoresis, *J. Chrom. B* 714 (1998) 105–111.