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Multicomponent characterization and differentiation of flash bangers — Part II: Elemental profiling of plastic caps

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A B S T R A C T

This study builds on the multicomponent analysis strategy for flash bangers which was previously introduced and where a representative sample set has been collected of a certain type of flash bangers. To expand the forensic strategy, elemental analysis of the plastic caps which are present in these items was performed. Both X-ray fluorescence (XRF) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis was performed to explore the possibilities for differentiation. The inherent inhomogeneity of the plastics resulted in high variations, especially for LA-ICP-MS trace analysis. In addition, due to the lack of suitable reference materials the LA-ICP-MS results can only be used for qualitative comparisons. Although XRF is less sensitive it allows for semi-quantitative analysis and the effect of inhomogeneity is significantly reduced due to the larger sample areas. Therefore, XRF is the method of choice for elemental analysis of intact plastic caps. In this scenario initial differentiation based on visual examination is combined with elemental analysis to obtain the highest degree of discrimination. In post-explosive scenarios, using XRF is not as straightforward due the irregular shapes of the burned plastic cap residues and contamination by explosive residues. For the analysis of these post-explosive caps, LA-ICP-MS proved to be useful for characterization and differentiation. Overall, it was found that blue caps contain a considerable higher amount of elements than the white caps, mainly due to additives related to the coloring process. This limits differentiation for the flash bangers containing white caps. Therefore, isotope ratio mass spectrometry (IRMS) analysis was performed to increase the differentiation potential. Based on carbon and hydrogen isotope ratios additional sets could be distinguished, both for flash bangers containing white and blue caps, that otherwise have similar visual and elemental characteristics. With the elemental and isotopic analysis of the plastic caps, an analysis strategy has been introduced that is not based on the pyrotechnic charge and therefore provides a unique opportunity to perform characterization and differentiation of flash bangers in pre- and post-explosive casework.

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1. Introduction

In the Netherlands, consumer fireworks are available to the general public under strict regulations\textsuperscript{1}. However, the demand for more powerful professional fireworks is high among individuals. Although these items are mainly used for recreational purposes and most incidents are associated with irresponsible behavior, there is a serious risk of misuse by individuals with criminal or terrorist motives. Flash bangers containing tens to hundreds of grams of very powerful flash powder can easily and almost anonymously be obtained. Beyond identification, the development of profiling methods to provide information for batch differentiation is important for law enforcement agencies in the Netherlands in order to counteract criminal activities involving fireworks. We have previously described a unique collection of flash bangers created from fireworks confiscated by the Dutch police. Furthermore, initial differentiation was reported based on features obtained through visual examinations of all components [3].

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\textsuperscript{1} The strict rules regarding consumer fireworks are recorded in the Dutch regulation consumer fireworks and the EU directive on pyrotechnic articles [1,2].
In addition to straightforward visual examination a wide variety of analysis techniques can be explored to expand the multicomponent analysis strategy of flash bangers. For instance, capillary electrophoresis (CE) and ion chromatography (IC) can be used to separate and identify inorganic ions present in intact charges, fuses or post-explosive residues [4,5]. Inductively coupled plasma-mass spectrometry (ICP-MS) or x-ray fluorescence (XRF) analysis could be performed to determine the elemental composition of different components, e.g. fuse, label, cardboard, charge and caps [6,7]. Isotopic information can be acquired by isotope ratio mass spectrometry (IRMS) [8]. Many more analytical techniques, including scanning electron microscopy (SEM) and mass spectrometry based methods could be considered to characterize the pyrotechnic mixtures and additional components in fireworks [9–11].

For profiling of fireworks possibilities will mainly exist pre-explosion, due to the random and destructive nature of explosive reactions. Additionally, in post-explosion scenarios most visual characteristics have disappeared. An interesting possibility for post-explosive characterization and differentiation is however feasible through the analysis of plastic caps. Although slightly burned and deformed these caps can usually be recovered reasonably intact from post-explosion scenes as illustrated in Fig. 1. The reason for this is that the caps are propelled from the cardboard container upon explosion.

Determining the trace-elemental composition of the plastic caps present in flash bangers could potentially enable differentiation of manufacturers and production batches. Plastic materials, such as polypropylene (PP) and polyethylene (PE) are produced by complex polymerization processes. During manufacturing many additives are used, including stabilizing agents, antioxidants, pigments, neutralizers, plasticizers and lubricants. Traces originating from these additives are introduced into the final plastic product, together with residues of catalysts, raw materials and side products [12].

Applications of plastic analysis are mostly related to the food industry to determine contaminations or migrations of (toxic) elements from packing plastics to foods [12,13]. Multi-elemental compositions at trace levels can be measured using ICP-MS. Typically samples are introduced into the plasma as liquids. Methods for the dissolution of solid plastics have been described using microwave digestion [12,14]. However, efficiency problems have been encountered for polymeric digestion, which differs between elements depending on digestion media and sample matrix. To avoid plastic digestion methods, direct analysis of solid samples is preferred. This can be achieved using laser ablation (LA) to introduce samples into the plasma. LA-ICP-MS analysis has successfully been applied to many forensic evidence types, such as glass [15,16], paint [17], document paper [18], cotton fibers [19], art [20,21], bone, teeth [22] and explosives [23].

One of the major limitations of plastic analysis by LA-ICP-MS is the lack of suitable standard reference materials for accurate quantification [24]. In most studies, external calibrations are realized through quantitative analysis by XRF or NAA analysis [25,26]. Quantitative elemental concentrations can be obtained by XRF, but this technique has limited sensitivity, especially for low atomic number elements [14]. In this study, both LA-ICP-MS and XRF have been used to determine qualitative and quantitative elemental compositions in plastics by direct solid analysis to investigate whether the plastic caps originating from flash bangers can be classified in different groups based on their elemental profiles. This could provide important information in forensic casework. Isotopic analysis using IRMS has been performed to further increase the differentiation potential. In addition, several flash bangers were ignited under controlled conditions to test the suitability of the analytical methods for linking post-explosion cap residues to intact items.

2. Materials and methods

2.1. Sample set of plastic caps

All plastic caps analyzed in this study originate from Cobra 6 and Cobra 6 2G flash bangers that have been confiscated by the Dutch police between December 2015 and December 2016. Details of the forensic collection of confiscated flash bangers can be found in Part I of this study [3]. Unfortunately, information of flash banger production in Europe is not easy to obtain. Using the terminology batch could incorrectly infer knowledge of the production process and associated inter- and intra-variability [27], therefore items that are collected in a single seizure by the police are referred to as (seized) sets of flash bangers rather than batches.

A plastic cap is present in all Cobra 6 flash bangers to seal off the cardboard cylinder containing the flash powder. The Cobra 2G items contains an additional plastic cap at the fuse end to avoid flash powder leakage. This cap is not present at the Cobra 6 items where the fuse side is sealed off with a plug of black powder as shown in Fig. 2. Due to their popularity and thus the financially lucrative illegal market of these Cobra 6 flash bangers, multiple imitations have been encountered by the Dutch police and are also included in this sample set. These imitations use similar components to mimic the appearance of a Cobra 6, including one plastic cap. However, the chemical load usually differs containing mixtures of flash powder with sawdust, gravel and clay plugs.

In total, the sample set of plastic caps includes caps from 161 flash bangers originating from 30 seized sets. The majority of flash bangers (125 items) were disassembled and resulted in the collection of 159 intact plastic caps, of which 34 were 2G fuse side caps. The remaining intact items were used for post-explosion experiments. In this study, a cap type refers to all caps having similar visual characteristics and the terminology group defines a selection of caps or flash bangers that share a specified number of (chemical) features.

**Fig. 1.** Examples of plastic caps originating from flash bangers encountered on post-explosion scenes.
2.2. LA-ICP-MS analysis

All plastic caps were scanned for the presence of 53 elements: Li, C, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Rh, Sr, Y, Zr, Nb, Mo, Rh, Ag, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Nd, Hf, Ta, W, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U. The analyses were performed at the Netherlands Forensic Institute (NFI) using an iCAP Q ICPMS (Thermo Scientific) instrument coupled to a laser ablation system with a NWR 193 nm laser (New Wave Research). Samples were analyzed using both spot and line ablation. A sample time of 70 s was used for spot sampling with spot size of 150 μm at a 10-Hz repetition rate and a dwell-time of 45 s. For line sampling, 2.5–3.5 mm line scans were performed in triplicate with a scan speed of 25 μm/s and a sample time of 100–140 s. For both ablation types the laser energy was set at approximately 3 J/cm² and sampling was preceded by a pre-ablation step (150 μm spot size, 5-Hz repetition rate). Helium was used as carrier gas to transfer the ablated particles to the plasma at a flow rate of 800 mL/min. The ICP-MS instrument used an ICP RF power of 1550 W with an argon plasma flow of 14 L/min. The argon nebulizer and auxiliary flows were set at approximately 1.0 L/min and 0.8 L/min, respectively. The dwell-time per amu was 10 ms. Carbon intensities (13C signals) have been used for normalization of the raw data within an analysis sequence to correct for potential system fluctuations. The cut-off value for an element to be identified as present was set at an intensity of 500 cps which corresponds to a signal that is roughly three times the standard deviation of the blank. Disc samples of 3 mm diameter and 1 mm thickness were prepared for analysis with the use of a single-hole puncher. A sample grid contained a maximum of 140 samples, as is shown in Fig. 3.

2.3. XRF analysis

Elemental concentration levels were measured at the Netherlands Forensic Institute (NFI) using an energy dispersive x-ray fluorescence spectrometer (Xepos, Spectro) equipped with a Vitus silicon detector. The concentrations of 35 elements were determined, at a limit of detection of 300 μg/g (Mg, Al and Si), 100 μg/g (P, S, K, Ca and Ti), 50 μg/g (Ce), 40 μg/g (La), 30 μg/g (V and Pr), 20 μg/g (Co), 10 μg/g (Cl and Mn), 5 μg/g (Cr, Cu, Zn, Ga, Ge, As, Se, Br, Zr, Mo, and Hg) and 2 μg/g (Rb, Sr, Y, Tl, Pb, Bi, Th and U). High background levels of Fe, Ni, Ag, Cd, Sn, Sb and Ba prevented the inclusion of these elements in the XRF measurements. The majority of elements included in the XRF analysis overlaps with the LA-ICP-MS analysis, except for Ge, Se and Pr which are only measured with XRF. In contrast, 21 elements are exclusively analyzed with LA-ICP-MS (Li, C, Na, Fe, Ni, Nb, Rh, Ag, Cd, In, Sn, Sb, Cs, Ba, Nd, Hf, Ta, W, Ir, Pt and Au).

Fig. 2. Pictures of a Cobra 6 2G (left) and Cobra 6 (right) flash banger, both intact (a) and showing the interior construction (b).

Fig. 3. Picture of a LA-ICP-MS sample grid (top) and two microscopy pictures with a magnification of 200× which show the laser ablation spots and lines in the plastic samples (bottom).
The Xeps instrument measured the samples under helium using multiple targets to excite the sample elements: Compton Molybdeen target (40 kv, 0.88 mA, 200 s), Barkla scatter aluminium oxide target (49.5 kv, 0.7 mA, 600 s), Barkla-scatter HOPG target (17.5 kv, 2.0 mA, 200 s) and Kobalt target (35 kv, 1.0 mA, 200 s). The plastic caps were placed in XRF sample cups (39.4 mm O.D., Chemplex Industries) on top of pre-cut Prolene thin-film circles (4.0 µm, 63.5 mm, Chemplex Industries). A maximum of 12 samples can be placed in the XRF sample tray. One plastic cap (sample A1) was used as control sample and was included in every sequence.

2.4. IRMS analysis

Isotopic compositions of the plastic caps were measured using continuous-flow isotope ratio mass spectrometry, CF-IRMS (Delta V Advantage; Thermo Fisher Scientific, Waltham, MA, USA). The IRMS system was equipped with a high-temperature conversion elemental analyzer (HTC-EA) for hydrogen measurements and with a flash EA 1112 for carbon measurements. Both elemental analyzers used a ConFlo IV for coupling to the IRMS. Samples (150 µg) were prepared in 3.3 x 5-mm tin and silver capsules for carbon and hydrogen respectively and introduced into the system using a MAS 200 R auto sampler. For carbon measurements, the oxidation reactor was set at 1020 °C and the reduction reactor at 650 °C. The oven temperature was held constant at 35 °C. For hydrogen measurements, the reactor and oven temperatures were set at 1400 °C and 65 °C, respectively. Helium was used as the carrier gas at a flow rate of 300 ml/min for carbon and 100 ml/min for hydrogen isotope ratio measurements. All samples and standards (NBS-22 oil, IAEA-CH-7 PEF and USGS-24 graphite) were measured in quadruplicate and normalized against the VPDB-scale (carbon) and VSMOW-scale (hydrogen).

2.5. Post-explosion experiment

In addition to the intact plastic caps, 36 flash bangers (3 items per set) were ignited to obtain representative post-explosive samples. Ignition occurred under strict safety guidelines and under supervision of the Dutch Explosive Ordinance Disposal Squad (EOD). A special cap was used to efficiently collect the post explosive residues of the plastic caps. In total, 45 samples (including 9 white cap residues) were collected after explosion. The burned and deformed cap residues originated from seven regular Cobra 6 sets (set F, H, J, K, N, Qb and Y), three Cobra 6 2G sets (set D, L and Z) and two Cobra 6 imitation sets (set C and M).

2.6. Data analysis

Principal component analysis (PCA) was performed on the elemental profiles obtained with LA-ICP-MS using STATISTICA (version 13). Factor analysis of the normalized signal intensities for both white and blue caps was executed with principal components as the extraction method.

3. Results and discussion

3.1. Visual examination and interpretation

Initial visual examination of the intact plastic caps already showed a wide variety of colors and molds. Fig. 4 provides a schematic overview of the sample set of plastic caps, which contains 13 different cap types. Most caps have a blue color (94 of 159 caps) and were collected from 18 seized sets. These blue caps are divided in 10 cap types of which two groups are 2G caps. The blue colors of cap type 1 and 2 are almost indistinguishable, only direct comparison shows a minor color difference. In 9 sets of flash bangers, white caps were encountered divided in three cap types. The remaining three sets (set D, L and H) consisted of a mixture of two cap types (cap type 3 and 11).

Based on visual examination of the interior of the flash bangers, items within sets C, M, P and R are classified as imitation flash bangers containing three distinct types of blue caps (cap type 6–8) as shown in Fig. 4. Since the origin of all items is unknown it cannot be stated that these are the only imitation sets, additional imitations could be present that do not contain clay plugs. However, no visual distinctive indications have been found within the seized sets that support this.

Rapid analysis using a portable RAMAN spectrometer (First-Defender, Thermo Scientific) indicated that most caps are polyethylene based. An exception was found for cap type 6 that is present in the imitation items of set C and P and which consist of poly(propylene-co-ethylene).

It is difficult to determine a common manufacturing origin for Cobra 6 flash bangers solely based on their plastic caps. Deduction from visual characteristics, such as color and mold, results in the linkage of almost all items, except the imitation flash bangers as illustrated in Fig. 4. This supports the assumption that there is one manufacturer of the regular Cobra 6 and Cobra 6 2G items that most likely obtains caps as precursors of the plastic caps from various suppliers, which results in the existence of multiple cap types in flash bangers from a single manufacturing facility. In addition, Fig. 4 shows that regular Cobra 6 items with similar language and production years on their labels are encountered in combination with different plastic caps. For example, label UK 2014 is encountered in combination with cap types 1, 3 and 11, and flash bangers containing label IT 2009 were found together with cap types 4 and 5. Conversely, cap type 1 is encountered in flash bangers that contain labels with different production years and languages (e.g. DE 2011, UK 2014, IT 2013 and DE 2011 2G). Therefore, a manufacturer might not only use various suppliers for plastic caps, but also assembles both Cobra 6 and Cobra 6 2G flash bangers and produces batches with different label language and year.

An advantage of all these variations is the forensic potential to perform differentiation, irrespective of their origin. Initially, Cobra 6 and Cobra 6 2G items can be discriminated based on the presence of an additional plastic cap at the fuse side of the Cobra 6 2G flash bangers (cap type 12 and 13). Therefore, all sets of flash bangers containing cap types 1–4 and 11 could already be subdivided in groups with and without an additional 2G cap. Based on additional visual cap features (mold and color) the 30 sets in this study can already be divided into 16 different groups.

Although visual examinations of intact plastic caps provide valuable information to distinguish between groups, elemental analysis is very promising for additional profiling. Firstly, because this adds objective information to the subjective visual observations. Secondly, elemental profiles could differ between visually indistinguishable plastic caps. Thirdly and most importantly, in some scenarios (e.g. post-explosion) visual features might be less easily obtained or even completely absent.

3.2. Elemental detection, correlation and selection

3.2.1. LA-ICP-MS

Initially, 202 plastic cap samples originating from 16 sets of flash bangers (set A, B, C, D, E, F, G, H, Ia, Ib, J, K, L, M, Qa and Qb) were screened with LA-ICP-MS for the presence of 53 elements using spot ablation (minimal of 2 samples per cap). The cut-off value for an element to be identified as present was set at an intensity of 500 cps which corresponds to a signal that is roughly three times the standard deviation of the blank. For the blue caps, 13 elements were detected in all samples (C, Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Cu and Sr).
and an additional 26 elements were present in at least one sample (Li, P, Cl, V, Fe, Co, Ni, Zn, Br, Rb, Y, Zr, Nb, Sn, In, Sb, Cs, Ba, La, Ce, Hf, Ta, Pb, Bi, Th and U). Compared to the blue caps, the white caps contained considerable less elements and on average at lower levels. Only 8 elements were detected in all white caps (C, Na, Al, Si, S, K, Ca and Cr) together with the presence of two elements in at least one cap type (Mg and Sr). These 10 elements are also present in all blue caps, indicating that these elements are not exclusively related to the coloring process. Copper and cobalt, which are absent in the white caps, are known to be frequently encountered in blue pigments. In addition, traces of iron, titanium and zirconium could originate from blue color additives [28–30]. An overview of the detected elements and associated intensities for the blue and white caps is given in Tables S1 and S2 of the Supplementary information.

Correlation coefficients have been determined to investigate if an increase (or decrease) in the intensity of one element is linearly related to an increase (or decrease) in the intensity of another element. Fig. 5 shows all elemental correlation coefficients of the elements present in the blue and white caps based on LA-ICP-MS analysis. Substantial correlation (r > 0.70) was found for 58 out of the 528 elemental combinations within the blue caps and for 4 out of the 21 elemental pairs in the white caps. Significant correlation (r > 0.90) was observed for 12 elemental combinations in the blue caps (Mg–Ni, Mg–Si, Si–Ni, Ti–Ta, Ti–Nb, Nb–Ta, Zn–Hf, Zn–Zr, Zr–Hf, La–Ce, P–Zn and V–Cr) and for only one elemental combination in the white caps (Ca–Al). Some individual graphs of elemental combinations in the blue caps that have a significant correlation are given in Fig. S1 of the Supplementary information. The La–Ce combination results from its natural correlation. Interestingly, the significant correlations within the blue caps also show multiple tri-element correlations. An example of the correlation analysis between Ti–Ta–Nb is shown in Fig. 6. No conclusive evidence is found for these tri-element correlations, but some of them could be catalytic residues from the plastic production process, e.g. production of ethylene using nickel-based catalysts or polymerization of ethylene using metal oxide and metallocene catalysts [31,32]. The absence of these elements and
correlations within the white caps might indicate a different plastic production process between the blue and white caps. However, it is more likely that the elemental residues in the blue caps originate from the coloring process. Concentrated mixtures of color pigments and additives are prepared in master batches and added to the colorless plastic granules [33]. These master batches might include pigment mixtures containing metal oxide mixtures of silicon, titanium, zirconium, zinc and/or chromium [34]. Furthermore, fillers (e.g. silica) and metal additives (e.g. tantalum and niobium) could also be added to a master batch [35].

Precious time and effort can be saved by measuring a limited number of elements. Based on elemental presence and correlation results of this initial spot analysis a total of 22 elements have been selected for further analysis as listed in Table 1. Elements that are not taken into account are either not present in the samples, have a high correlation with at least one selected element or exhibit substantial variation within a sample.

3.2.2. XRF

In addition to LA-ICP-MS, XRF analysis has been performed. Although this technique is less sensitive, it allows for semi-quantitative elemental analysis and measures the entire plastic cap which might reduce the effect of inhomogeneity on the analysis results. A total of 89 blue cap samples and 39 white cap samples have been measured (originating from all 30 sets of flash bangers) and the samples were analyzed for the presence of 35 elements. For the blue caps, 19 elements were detected of which only 5 elements were found in all samples (Si, S, Ca, Ti and Cu). An additional 7 elements were detected in the majority of samples (Al, P, Cl, Cr, Mn, Zn and Sr) and the concentrations of 6 more elements could be determined in at least one sample (Mg, K, Br, Rh, Zr, Pr and Pb). In the white caps, no elements were detected in all samples and the concentration of only 6 elements were measured in at least one cap type (Al, Si, S, Cr, Cu and Pb). Tables S3 and S4 in the Supplementary information give a summary of the detected concentration ranges per element for the blue and white caps using XRF.

The limited number of elements detected with XRF is a direct result of the reduced sensitivity compared to LA-ICP-MS. Part of the detected elements were only present in a limited number of blue samples at or close to the detection limit, thereby hampering comparison interpretations. These elements (K, Br, Rh, Sr, Zr, Pr and Pb) have therefore not been considered for further comparison analysis. In addition, aluminum is excluded due to possible contamination embedded in the plastic caused by the aluminum powder present in the active charge of the flash bangers. This results in a final selection of 11 out of the 19 elements detected with XRF.

Correlation coefficients have also been determined for the selected elements based on the XRF results as illustrated in Fig. 7. Significant correlation (r > 0.90) was found for 6 out of the 55 elemental combinations for the blue caps, including Mg–Si, Mg–Cr, Cr–Si, Mg–Zn, Mg–Mn, and Cr–Mn. Both XRF and LA-ICP-MS correlation graphs for these six combinations are given in Fig. S2 of the Supplementary information. It should be mentioned that although the LA-ICP-MS results did not show significant correlations with chromium, the observed substantial correlations are actually very close to this significant boundary, being r = 0.85, 0.77 and 0.86 for chromium combinations with magnesium, silicon and nickel, respectively. This suggests a tetra-elemental correlation between Mg, Si, Cr and Ni, which could possibly originate from residues of the master batches containing concentrated mixtures of blue color pigments and additives [33–35]. For the manganese combinations within the blue caps considerable lower correlation was encountered by LA-ICP-MS. A reason for this could be that the elements of these combinations are not detected in all blue samples using XRF and the concentration range of Mn is narrow. No significant correlations were found for the elements in the white caps with XRF.

3.3. Sample variation and analysis optimization

3.3.1. ICP-MS (spot ablation versus line ablation)

One of the challenges in measuring the elemental composition of plastics is presented by the inhomogeneity of the samples. During polymer production it is difficult to homogeneously disperse all additives into the plastic, mostly due to incompatibility of inorganic polar substances with the nonpolar polymer material [26]. Therefore, it is important to investigate the elemental inhomogeneity in the plastic caps. Because small LA-ICP-MS samples are prepared (3 mm diameter) and even smaller spot areas are measured (150 μm spot size) it is especially important to
Table 1
Sample, cap and set variations for 18 of the 22 selected elements measured by LA-ICP-MS (Cs, Ce and Bi were not present in these specific caps and carbon intensities were used for normalization). The blue, blue 2G and white samples originated from Set H, L and G, respectively.

| RSD (%) | Li | Na | Mg | Al | Si | P | S | K | Ca | Cr | Fe | Co | Cu | Sr | Zr | Ba | Ta | Pb |
|---------|----|----|----|----|----|---|---|---|----|----|----|----|----|----|----|----|----|
| Spot vs. line ablationa | | | | | | | | | | | | | | | | | | |
| Blue cap sample | x | 6 | 3 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 |
| Blue 2G cap sample | x | 6 | 3 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 |
| White cap sample | x | 6 | 3 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 |
| Cap inhomogeneityb | Li | Na | Mg | Al | Si | P | S | K | Ca | Cr | Fe | Co | Cu | Sr | Zr | Ba | Ta | Pb |
| Blue cap | x | 6 | 3 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 |
| Within vs. between setsc | | | | | | | | | | | | | | | | | | |
| Within blue cap set | x | 6 | 3 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 |
| Between blue cap sets | 348 | 234 | 137 | 125 | 76 | 96 | 114 | 173 | 123 | 81 | 261 | 153 | 53 | 72 | 134 | 186 | 60 |
| Ratio/between/within | 44 | 6 | 4 | 3 | 4 | 4 | 5 | 12 | 3 | 4 | 7 | 9 | 2 | 2 | 5 | 4 | 2 |
| Within white cap set | x | 6 | 3 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 | 6 | 3 |
| Between white cap sets | x | 28 | x | 12 | 10 | x | 24 | 26 | 6 | 1 | x | x | x | x | x | x |
| Ratio/between/within | 4 | x | 8 | 2 | x | 4 | 2 | 5 | 1 | x | x | x | x | x | x |

*R Eight measurements per sample, using both spot and line ablation, of n=1 sample from a blue (set H), a blue 2G (set L) and a white (set G) plastic cap.

<Figure 7. Correlation coefficients of the elements present in the blue plastic caps based on the XRF results.>

**Table 1**

The within sample variation of three cap samples (originating from one white, one blue and one 2G blue cap) has been investigated in detail. Each sample was measured 8 times to determine the relative standard deviations (RSDs) of each element as shown in Table 1. In total, RSD could be determined for 18 out of the 22 selected elements. Three elements (Ce, Cs and Bi) were not present in these specific caps and carbon intensities were used for normalization. Using spot ablation, as applied in the screening method, RSDs in excess of 20% were found for 13 elements in at least one of the samples which clearly shows that these elements are inhomogeneously distributed in the polymer matrix.

Instead of ablation, laser ablation of a whole line is possible which can correct for some of the heterogeneity by measuring a larger proportion of the sample resulting in a more representative average value of the elemental intensity. A disadvantage of this method is the increased preparation time since each ablation line must be defined manually to correct for height differences in the sample. Using line ablation indeed resulted in less within sample variations and RSDs decreased for almost all elements as demonstrated in Table 1. Therefore, line ablation was chosen as preferred ablation type for further analysis of the plastic caps in this study.

In addition to within sample variation also the within variations of multiple caps originating from one seizure set were investigated. As expected this resulted in higher variations compared to within sample variations. Especially, the within variation of set H containing blue cap type 3 is relative high, compared to the other two investigated cap types (set L and G) and compared to the significantly lower within sample variation. The variation between multiple samples from one cap of set H was similar to the relative high within variation of the entire set H, indicating that the inhomogeneous dispersion inside a cap is the main contributor to the within variation of a set. However, for all elements the variations between sets are significantly higher compared to their within variations. This shows that there is potential to differentiate flash bangers based on elemental analysis of their plastic caps using LA-ICP-MS, especially for elements with a higher ratio of between versus within variation.

3.3.2. XRF

As indicated, an advantage of XRF is that the entire surface of the plastic cap is measured which reduces the effect of...
Table 2
Within and between variations of 11 selected elements measured by XRF analysis.

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<th>RSD% Elements</th>
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<td>Mg  Si  P  S  Cl  Ca  Ti  Cr  Mn  Cu  Zn</td>
</tr>
<tr>
<td>Within sample variation</td>
<td>5  3  4  3  3  4  5  3  1</td>
</tr>
<tr>
<td>Within set variation</td>
<td>x  10  x  18  25  24  x  x  22  22</td>
</tr>
<tr>
<td>Between sets variation</td>
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<tr>
<td>Ratio between/within sets</td>
<td>11  6  5  6  5  3  3  18  5  4  4</td>
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</tbody>
</table>

\( *= \text{RSD < 20\%, \( \neq \) = RSD > 20\%}

\(^{1}\) Measurements of one blue cap from set A (cap type 2).
\(^{2}\) One measurement of 5 blue caps from set H (cap type 3).
\(^{3}\) One measurement of 89 blue caps from 21 sets.

inhomogeneity on the analysis results. Indeed, within variations were significantly lower for the individual elemental concentrations using XRF analysis compared to LA-ICP-MS analysis as can be seen from Table 2. For all elements, the within sample variations did not exceed 10%. The variations within a set are slightly higher for most elements, but do not exceed 25%. Similar to the LA-ICP-MS results, the significantly higher variations between sets provides an opportunity to discriminate between flash bangs based on the elemental composition of their plastic caps.

3.4. LA-ICP-MS versus XRF analysis

For all overlapping elements, except phosphor, the LA-ICP-MS intensities were in good agreement with the concentrations obtained by XRF analysis. The correlation figures are given in Fig. S3 of the Supplementary information. Significant correlations (r > 0.8) were found for magnesium, silicon, sulfur, calcium, chromium and copper. This shows that both techniques produce reliable results and support the combined use of LA-ICP-MS and XRF for the elemental analysis of plastic caps. The concentration of phosphor in the blue caps is around or below the XRF detection limit, which explains the poor correlation (r = 0.5) with the LA-ICP-MS results.

Due to the lack of suitable standard reference materials the measured intensities obtained with LA-ICP-MS cannot be used for comparisons between elements, since ablation efficiencies differ between elements. The results can therefore only be used for qualitative comparisons of elemental profiles within different samples. For the small number of overlapping elements with significant correlations XRF could be used for external quantification of the LA-ICP-MS signal intensities. Although XRF is less sensitive, this technique does allow for semi-quantitative elemental analysis and results in significant lower sample variations. In addition, sample preparation and analysis using LA-ICP-MS is much more time-consuming compared to XRF. LA-ICP-MS sample preparation is very labor intensive, which includes placing small samples on a grid and defining ablation lines for each sample as illustrated in Fig. 3. In contrast, XRF directly measures the intact plastic caps with virtually no sample preparation. Therefore, XRF analysis is the method of choice to determine the elemental compositions of intact plastic caps for forensic investigations of flash bangs. However, these plastic caps can also be encountered on post-explosion scenes after ignition of a flash banger. These post-explosive plastic caps are usually only slightly burned, but can be highly deformed or fragmented. Examples are shown in Fig. 1. In these post-explosion scenarios XRF analysis is not as straightforward due to the irregular shapes and lower sample amounts. Fortunately, LA-ICP-MS does have the potential to measure small samples of these deformed caps and the laser can be used to remove surface contaminations by pre-ablation of the samples. Therefore, LA-ICP-MS is the preferred technique for the analysis of plastic cap residues in post-explosion investigations.

3.5. Elemental analysis of intact plastic caps

3.5.1. Elemental profiling of blue caps

Based on visual examination, 10 different blue caps types are distinguished in the sample set as illustrated in Fig. 4. For intact caps, the elemental composition has been determined using XRF analysis. The average elemental concentrations of the different cap types are listed in Table 3. Cap type 2 and 12 are divided in two sub-groups that clearly have distinctive elemental profiles, whereas they could not be visually differentiated based on color and mold. Cap type 2a (set A and J) and cap type 2b (set QA) can be easily distinguished on the basis of their magnesium, sulfur and titanium concentrations, but significant differences were observed for more elements. In addition, the 2G caps of cap type 12a (set A, D and L) and cap type 12b (set U, Z and AD) can also be separated based on multiple elemental concentrations. Similar elemental profiles were found for cap type 2a and cap type 12a which corresponds to the visual examination showing a similar blue color for both cap types. The blue color of cap type 1 is almost indistinguishable from that of cap types 2 and 12, but the elemental profiles are significantly different.

Most cap types are encountered in multiple sets of flash bangers. Variations within cap types 1, 4 and 6, and subgroups 2a and 12a correspond to the within variations of cap types 5 and 7 that only contain plastic caps from a single set. Detailed analysis of individual elemental levels indicate that the sets of flash bangers containing these cap types cannot be differentiated further. On the other hand, the higher variations in elemental compositions of the caps from cap type 3 and subgroup 12b give an indication that some sets within these groups could be further distinguished based on a selected number of elements. Fig. 8 shows the differences in elemental concentrations of calcium, titanium, copper, and zinc between the individual sets of flash bangers containing cap type 3. Caution has to be taken in drawing conclusions from single elemental concentrations, but similar relative profiles are observed for sets E, D and H, for sets L and S, and for the single set N. In subgroup 12b, the 2G caps present in the flash bangers of set U can be discriminated from those of sets Z and AD based on sulfur, titanium, chloride, potassium and zinc as shown in Fig. 8b. An overview of all elemental concentrations per seized set containing blue caps is given in Table S5 of the Supplementary information.

3.5.2. Elemental profiling of white caps

The flash bangers containing white caps can be divided into three groups (cap types 9, 10 and 11) based on visual inspection as shown in Fig. 4. The restricted elemental presence in combination with substantial inhomogeneity is a limiting factor for differentiation of the white caps. Cap type 9 can be separated from cap type 10 based on sulfur and silicon. Fig. 9 shows the sulfur concentrations versus the silicon concentrations for all white cap samples. Cap types 9 and 11 can only be distinguished based on the silicon concentration. The elemental overlap between cap types 10 and 11 illustrates the limiting profiling potential for the white caps. Detailed analysis of the multiple sets of flash bangers that contain cap type 11 give an indication for subdivision of set O and set AA as illustrated in Fig. 9. The sulfur concentration in these plastic caps is higher compared to plastic caps of other sets within this cap type 11, but this subdivision cannot be conclusively stated based on results of an individual element. In Table S6 of the Supplementary information an overview is given of all elemental concentrations per set of flash bangers containing white caps.

3.6. Analysis of post-explosive plastic cap residues

The previous section clearly demonstrates the additional value of elemental analysis for differentiation of intact plastic caps.
However, in most forensic explosive casework these intact caps will probably be encountered as part of an intact flash banger. Therefore, thorough elemental analysis of the caps could prove to be redundant due to the presence of several other components and features, e.g. labels artwork, cardboard and pyrotechnic charges. Previous characterization and differentiation based on visual examination of all intact components indeed already showed a high potential to differentiate between flash bangers [3]. However, in post-explosion casework most typical visual characteristics have disappeared or are difficult to assess. Small parts of burned cardboard can be encountered and under favorable circumstances a characteristic piece of label might still be visible. In addition, post-explosion residues of the active charges cannot be used for differentiation, due to the random and destructive nature of explosive reactions. Especially in post-explosion cases where the caps are burned and deformed in such a way that molds and color differences are difficult to establish, there is a need for additional

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### Table 3

<table>
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<th>Cap type</th>
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**Fig. 8.** Elemental profiles of selected elements for different seized sets of flash bangers within (a) group 3 and (b) group 12b.

**Fig. 9.** Sulfur and silicon concentrations (μg/g) in the white plastic caps. (△ indicates samples from set O and AA of cap type 11)

However, in most forensic explosive casework these intact caps will probably be encountered as part of an intact flash banger. Therefore, thorough elemental analysis of the caps could prove to be redundant due to the presence of several other components and features, e.g. labels artwork, cardboard and pyrotechnic charges. Previous characterization and differentiation based on visual examination of all intact components indeed already showed a high potential to differentiate between flash bangers [3]. However, in post-explosion casework most typical visual characteristics have disappeared or are difficult to assess. Small parts of burned cardboard can be encountered and under favorable circumstances a characteristic piece of label might still be visible. In addition, post-explosion residues of the active charges cannot be used for differentiation, due to the random and destructive nature of explosive reactions. Especially in post-explosion cases where the caps are burned and deformed in such a way that molds and color differences are difficult to establish, there is a need for additional
chemical analysis. In these scenarios elemental analysis of the post-explosive cap residues can be very useful.

As mentioned previously, XRF analysis will be problematic due to the irregular shapes and surface contaminations of the plastic residue due to the destructive nature of the explosion. With LA-ICP-MS only a very small piece of the cap needs to be recovered to enable elemental analysis and potential surface contaminations are removed by pre-ablation of the samples.

3.6.1. Elemental profiling of blue caps

Initially, a selection of 80 intact samples originating from 21 sets containing blue caps have been measured in triplicate using line ablation to determine their elemental profiles. Due to the high variations resulting from inhomoogeneity and the lack of reference materials for quantification no conclusion should be drawn from single elemental intensities. Therefore, the multi-elemental profiles were studied. Principal component analysis (PCA) of the elemental intensities has been performed to visualize clustering of the blue caps based on LA-ICP-MS data of 9 elements. As shown in Fig. 10 and similar to the XRF results, cap types 2 and 12 are divided in two subgroups which significantly differ in elemental composition. In addition, samples from cap types 1, 6, 12b and 13 are represented as single clusters. However, not all visually distinguishable cap types can be separated into single clusters. Cap types 3, 4, 7 and 8 have overlapping elemental profiles as well as cap type 5 and subgroup 2b. The similar profiles of subgroups 2a and 12a are in line with the results reported in the previous section.

Some additional differentiation is feasible when looking at the measured elements that were not included in the PCA dataset. For instance in the biggest cluster, the caps present in the imitation flash bangers (cap types 7 and 8) have high intensities for barium, cerium and lead whereas the intensities of these elements are below or close to the limit of detection in the samples of cap types 3 and 4. No significant differences in elemental intensities are observed between cap type 3 and 4 and similar for cap type 7 and 8. In the other cluster only the presence of tantalum differs between cap type 5 and subgroup 2b, which was only detected in the latter group. An overview of all elemental intensities per cap type can be found in Table S7 of the Supplementary information.

To investigate the post-explosive effect on the LA-ICP-MS analysis results, flash bangers of multiple seized sets have been ignited. The plastic cap residues were collected and analyzed. The results of these samples are included in Fig. 10 and can be recognized by a thick border around the sample point. This figure clearly shows that no effect is observed on the elemental composition of the cap residue after an explosion. The use of LA-ICP-MS thus provides a unique opportunity for post-explosion differentiation of Cobra 6 and Cobra 6 2G flash bangers on the basis of elemental composition of their plastic cap residues.

3.6.2. Elemental profiling of white caps

A total of 23 intact samples have been selected from 13 seized sets of flash bangers containing white plastic caps. Statistical analysis of the elemental intensities using PCA visualizes clustering of the three different white cap types, but with some overlap between samples as illustrated in Fig. 11. The low amount of element present in the white caps together with substantial measurement and sample variations is a limiting factor for differentiation of flash bangers containing white caps. Especially, for sodium very high relative standard deviations are found in the samples. All elemental intensities per white cap type can be found in Table S8 of the Supplementary information. The elemental profiles of cap types 9 and 10 differ in the presence of strontium and magnesium, whereas flash bangers containing cap type 11 can only be significantly differentiated based on one element, either strontium (vs. cap type 9) or magnesium (vs. cap type 10). This corresponds to the previous findings using XRF, where cap types 9 and 10 could be differentiated on multiple elements and cap type 11 only showed a difference for a single element in the profile. Similar as for the blue caps, samples from post-explosive cap residues were analyzed, which again yielded consistent elemental compositions compared to the intact cap samples from the same seized set of flash bangers.

3.7. IRMS analysis

Elemental analysis of the blue caps showed additional potential to distinguish between sets of flash bangers which cannot be separated based on visual examination of the plastic caps. However, for the white caps additional differentiation was limited, due to the restricted number of elements present in these caps. Therefore, the carbon and hydrogen isotopic compositions of the white caps were studied with isotope ratio mass spectrometry (IRMS) to investigate if differences in isotopic ratios could provide additional differentiation potential. The isotopic data depicted in Fig. 12 shows that in addition to their visual characteristics and elemental profiles the white cap types 9, 10 and 11 can also be differentiated based on the carbon and hydrogen isotopic compositions of the plastic caps. Additionally, the suggestion on basis of the XRF data that within cap type 11 the sets O and AA can be differentiated is confirmed by the IRMS results. Interestingly, the remaining sets of flash bangers containing cap type 11 which could not be separated by visual or elemental analysis are divided in two subgroups (set D, Ib and L, and set B, G.

![Fig. 10. PCA results of the blue caps using LA-ICP-MS analysis based on 9 elements (Al, Si, P, Ca, Fe, Zr, Na, K and Cs). PC1 accounts for 31% and PC2 for 21% of the total variance. Thick border around sample points indicates the post-explosion samples.](image1)

![Fig. 11. PCA results of the white caps using LA-ICP-MS analysis based on 7 elements (Na, Al, K, Ca, Sr, Si and S). PC1 accounts for 41% and PC2 for 22% of the total variance. Thick border around sample points indicates the post-explosion samples.](image2)
H and AB) on the basis of a significant difference in the carbon isotope ratio.

Following the fruitful IRMS analysis of the white caps, isotope ratios have also been determined for the blue cap types 1 and 3 which are present in multiple sets of flash bangers. All items containing blue cap type 1 (set I, K, Y, Z and AD) have similar carbon and hydrogen isotopic ratios as illustrated in Fig. 12b. For cap type 3, the caps present in set H and S can be distinguished from the caps in the other sets of flash bangers (set D, E, L and N) based on both the hydrogen and carbon values. Furthermore, set H can be differentiated from set S on the basis of their carbon isotopic ratios. This subdivision of sets containing cap type 3 differs from the one suggested in Section 3.5.1, which could be due to the high variations in those elemental profiles.

For all cap types discussed in this section additional samples from post-explosive cap residues have been analyzed to investigate if the isotope ratios of the plastic caps are unaffected by the explosion and, therefore, comparable to the intact samples. As shown in Fig. 12, similar carbon and hydrogen isotopic values were observed for both the intact and post-explosive samples originating from the plastic caps of the same seized set of flash bangers. This also enables the use of IRMS analysis in scenarios where post-explosive cap residues are encountered.

4. Forensic relevance

For the classification of intact plastic caps, a sequential approach is proposed that starts with visual examination of the caps (e.g. color and mold) and an assessment of the flash banger type (one cap for the Cobra 6 and two caps for the Cobra 6 2G types). This resulted in 16 different groups as discussed in Section 3.1. Elemental analysis using XRF provides objective information that confirms the initial visual distinction and shows additional variation for certain visually indistinguishable blue caps. In addition, IRMS analysis further increases the degree of differentiation of some selected cap types, also enabling further classification of sets of flash bangers containing white caps. Application of all these steps results in the differentiation of 23 out of the 30 sets of confiscated flash banger fireworks as depicted in Fig. 13a.

In practice, for forensic comparison of an intact flash banger from one case to an intact flash banger from a second case visual examination could prove to be sufficient, especially when visual differences are observed. In this case of exclusion, further analysis is redundant under the assumption that a single purchase of Cobra 6 flash bangers consists of similar items. This assumption is supported by the police seizures with the exception of 3 (out of 30) seizures which consisted of flash bangers containing two different cap types (visually similar items but with either cap type 3 or 11). To strengthen the link between visually identical flash bangers, additional elemental and isotopic analysis of their plastic caps can increase the evidential value and thereby the support for the common origin hypothesis.

Analysis of post-explosive cap residues provides a unique opportunity to perform characterization and differentiation after an explosion occurred. Visual examination is greatly limited, but a general color distinction, white or blue, is usually still possible. In this scenario, elemental analysis using LA-ICP-MS provides the major contribution for differentiation. Additional IRMS analysis of some selected cap types increases the degree of differentiation to a total of 15 groups as depicted in Fig. 13b. Although the differentiation potential is less compared to intact cap analysis, using elemental analysis of plastic cap residues can be considered as one of the first methods to perform post-explosive profiling in the field of forensic explosives investigations involving pyrotechnics. For both intact and post-explosive analysis additional IRMS analysis of caps from all sets could increase the number of distinguishable groups.

The question that now remains is how this information can be used in forensic investigations. What does it mean in terms of
evidential value when (intact/post explosion) flash banger caps of
two different crime scenes belong to the same group or when the
same holds for a flash banger cap from a crime scene and a flash
banger cap confiscated from a suspect? This is related to the
relative frequency of the items within a given group in the overall
population of illegal Cobra flash bangers in the Netherlands. For
several reasons our work does not allow for an accurate estimation
of group occurrence. Firstly, we do not know whether the seized
sets are representative for the illegal Cobra market in the
Netherlands. Seizures may be biased as police priorities vary from
region to region and over time. Furthermore, the success of police
investigations might also be a function of modus operandi of the
perpetrator which can also bias the sample collection. One is also
never sure whether all items in possession of the suspect are
confiscated during a seizure. In addition, our sample set was
constructed with the deliberate aim to include seizures from all
Dutch police regions and to cover the entire range of Cobra types
with respect to label language and year of production. Hence our
sample set contains a collection bias and is therefore not
representative for the overall sample collection, inhibiting the
use for frequency estimations.

In general, as the number of overall items in a group increases, the
evidential value related to a matching group type will decrease. The
reverse situation applies for “rare” groups, i.e. groups consisting of
only a limited number of items. The data in this study does indicate
that some groups include multiple seized sets or sets containing a
relatively large number of items, i.e. 289 indistinguishable original
items confiscated in 5 different seizures (set B, D, E, L and N) and
2400 original items from the single seizure (set H). In addition, 10
groups consist of only one set with a limited number of items of
which set R and T are the most extreme examples containing only
one original flash banger each. When considering these most
extreme conditions for intact items an evidential value in the range
of 10–1000 is expected. In the verbal scale, as used by forensic
experts of the Netherlands Forensic Institute, this corresponds to
the following statements (for intact items):

- Prosecution Hypothesis: The flash banger found at the crime
  scene and the flash banger confiscated from the suspect
  originate from the same manufactured batch.
- Defense Hypothesis: The flash banger found at the crime
  scene and the flash banger confiscated from the suspect originate
  from different manufactured batches.
- Evidence: The visual features, elemental profiles and isotopic
  values of the plastic caps from the two flash bangers are
  identical within the measurement uncertainty.
- Expert statement: The evidence is more likely (10–100)/much
  more likely (100–10,000) when the prosecution hypothesis is
  true than when the defense hypothesis is true.

In post explosion cases the average evidential value is
somewhat reduced as the differentiation is less by the restriction
of investigative options, but the range in similar to that of the intact
items.

5. Conclusions

This study reports a strategy to differentiate between flash
bangers that is not based on analysis of the active charge, but
instead, analyzes the plastic caps that are present in the items.
Elemental profiles of the caps were obtained by XRF and LA-ICP-
MS. The elemental concentrations obtained with XRF were in good
agreement with the LA-ICP-MS signal intensities. For comparison
of intact caps, visual examination in combination with elemental
analysis using XRF proved to be the optimal method. Characterization
and differentiation of flash bangers based on their plastic
caps provides a unique opportunity for comparison in post-
explosive scenarios. In this case, elemental analysis using LA-ICP-
MS is able to differentiate between certain cap types and
subgroups. The blue caps present in the flash bangers contain a
considerable higher number of elements and with that a higher
differentiation potential based on elemental analysis, compared to
the white caps. In both intact and post-explosion cases IRMS
analysis of carbon and hydrogen isotopic values of some selected
cap types increased the degree of differentiation by distinguishing
caps, both from flash bangers sets containing blue and white caps,
with shared visual and elemental characteristics. A more detailed
IRMS analysis of caps from all seized sets could further increase the
differentiation potential. Overall, the intact analysis strategy in this
study can differentiate 23 out of the 30 seized sets of flash bangers
and the post-explosion strategy can differentiate 15 sets. Although
the analysis of intact caps has a higher differentiation potential to
our knowledge this work for the first time introduces a
methodology for post-explosion pyrotechnics profiling for forensic
explosives casework and intelligence.

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Appendix A. Supplementary data

Supplementary data associated with this article can be
found, in the online version, at https://doi.org/10.1016/j.forensi-
cint.2018.06.012.

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