Ion chromatographic quantification of nine cationic components in pre-blast and post-blast residues of pyrotechnic samples

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ABSTRACT

An ion chromatographic method and its application have been described to quantify nine cationic components (lithium, sodium, ammonium, methylammonium, potassium, magnesium, calcium, strontium, and barium) in pyrotechnics (firecracker and firework) samples. The samples in this study were purchased from local shops in Ternate City, North Maluku. The method performed a mixed eluent with 4 mM HNO3 and 0.015 mM Na2EDTA, combined with a Metrosep C4-150/4.0 separation column for all quantification. Excellent chromatograms were achieved, and the nine cationic components were eluted in less than 18 min. The calibration graphs of the quantification were linear in the range of 1.25 – 37.5 mg L−1. The detection limit (LOD) at S/N = 3 was below 0.098 ppm (mg L−1). This method was applied to the pre-blast and post-blast residues of pyrotechnics samples, and the simultaneous quantification of the nine cationic components in these samples was achieved with satisfactory results.

KEYWORDS

ion chromatography, cationic components, pre-blast and post-blast residues, pyrotechnics, methylammonium

1. INTRODUCTION

Many criminals, vandals, and terrorist activities carry out explosive blast cases in today’s globalized world. Because of the increase in this type of illegal activity, if explosives blast, it cannot be quickly determined whether it is a criminal, vandal, or terrorist activity in the event of an explosive blasting. Therefore, it is crucial to know the explosive type used in the blasting. [1–3].

Identifying explosives or potentially explosive materials used by activists is a crucial topic for researchers in criminal acts, vandals, and terrorism. The area that requires analysis of explosives can be divided into two sub-categories: detection and identification. Before blasting, the primary material and identification of explosives blasting by collecting residues [4].

Inorganic explosives or explosives are extensively encountered in improvised homemade explosives such as pyrotechnics. Cationic components such as ammonium, methylammonium, potassium, barium, and other cations can be detected in the pre-blast and post-blast residue of
firecrackers and fireworks, mainly from oxidizer and reaction products of explosives or potentially explosives. A firecracker (cracker and noisemaker) is a potentially explosive device initially invented for creating a big noise. It has a fuse wrapped in a thick paper casing to contain explosive compounds.

The literature has stated different methods to determine cationic components in various aqueous and solid samples. Flame photometer [5], flame atomic absorption spectrometric [6], atomic emission spectroelectrochemistry [7] have been traditionally used for cations and metal determination at a time, and inductively coupled plasma-atomic emission spectrometry (ICP-AES) [8] to determine cations simultaneously. Ammonium (NH₄⁺) ion is typically determined based on solid-contact ion-selective electrode potentiometry (SC-ISEs) [9], which measures the free ammonium concentration. However, this method could not measure MeNH₃⁺ ions when they are contained in the samples. Instead, ion chromatography (IC), developed by Small in 1975, is now being offered to analyze different kinds of ions at present [10, 11]. In IC, the number of ions, especially cations, can be detected using different eluent, mixed eluent, and columns [12-14]. The capillary zone electrophoresis method has been used to complement peak confirmation in IC and applied in the quantification of inorganic cations contained in natural wastewater [15] and in the post-blast residues [16, 17]. However, compared to IC, the capillary-based method could not mainly detect MeNH₃⁺ when this cationic component is present in the actual samples, such as pyrotechnic samples.

Attention to detecting cationic components in explosives or potentially explosive samples using the IC method still needs to be improved, and only a few scientific articles discuss it. Several articles focus on quantifying anionic components in the pre- and post-blast residue of pyrotechnic samples [3, 18, 20] and post-blast of low explosive from soil samples of forensic interest [19].

This work aims to state a convenient and straightforward single-column IC method with conductivity detection for simultaneously quantifying cationic components, including MeNH₃⁺ cationic components in pre-blast and post-blast residue material of pyrotechnics such as firecracker and firework samples. The pre-blast and post-blast residue samples were collected to ensure that this method could provide good analytical results. Potassium-based, potassium-barium-based, and barium-based firecrackers and firework types were used in this work.

Based on the optimum separation conditions, this work will also compare the levels of cationic components in pre- and post-blast residue to evaluate how well they produce the reaction efficiency. The reaction efficiency can be measured by comparing the expected amount of cationic components with the actual amount produced during blasting. Moreover, understanding the changes in the composition of cationic components can help evaluate the risks and safety associated with using explosive materials.

2. EXPERIMENTAL

2.1. Ion chromatograph

An ion chromatograph Metrohm Eco IC (Metrohm, Switzerland) was used for the present work, which consists of a serial double piston IC pump, a 10-μL sample loop, and an IC detector with a non-suppressed module. A Metrosep C4-150/4.0 (Metrohm) separation column (150 × 4.0 mm I.D.) was used for all simultaneous quantifications. Metrohm chromatography software IC Microdata performed the data collection and all instrument control for Windows. The eluent flow rate was established at 1.0 mL min⁻¹, except when optimizing the flow rate.

2.2. Reagents and chemicals preparation

All the used chemicals were of analytical reagent or HPLC grade. Purified water was used to prepare standard solutions and eluents and filtered before use. For IC, standard solutions of cationic components were prepared independently from 1,000 ppm (mg L⁻¹) stock solutions from Merck (Germany), except for methylammonium chloride (MeNH₄Cl), a white crystalline solid. To prepare 1,000 mg L⁻¹ methylammonium ion (MeNH₃⁺) from MeNH₄Cl (Mr = 67.52 g mol⁻¹) concentrate, 2.11 g was poured into a 1.0 L volumetric flask containing purified water. The eluent used to determine monovalent and divalent cationic components was mixed with 4 mM HNO₃ and 0.015 mM Na₂EDTA.

2.3. Standard solution preparation

Serial dilutions containing a mixture of cationic components were prepared from the 1,000 mg L⁻¹ independent cationic standard solutions. The serial dilution for lithium was 1.25 to 6.25 mg L⁻¹, and sodium, ammonium, methylammonium, potassium, magnesium, and calcium were 5 to 25 mg L⁻¹, while strontium and barium were 7.5 to 37.5 mg L⁻¹. To reduce the pseudo peak that sometimes appears in the chromatograms, the standard solutions were prepared daily, sonicated, stored in polyethylene containers, kept

<table>
<thead>
<tr>
<th>Samples</th>
<th>Brand</th>
<th>Model</th>
<th>Types</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFT</td>
<td>Happy Flower Tor (G3013T)</td>
<td>Big Tube</td>
<td>Firecracker</td>
<td>China</td>
</tr>
<tr>
<td>DST</td>
<td>Dinosaur Tabung</td>
<td>Tube</td>
<td>Firecracker</td>
<td>China</td>
</tr>
<tr>
<td>RC</td>
<td>Roman Candle 8-shots (1.2 Inc)</td>
<td>Roman Candle</td>
<td>Firework</td>
<td>China</td>
</tr>
<tr>
<td>PJ</td>
<td>Pendekar Jumbo-120</td>
<td>Long Wire</td>
<td>Firework</td>
<td>Indonesia</td>
</tr>
</tbody>
</table>
Fig. 1. Ion chromatography profiles of the cationic component's retention time at different eluent concentrations. Eluent: (a) 3 mM HNO₃, (b) 4 mM HNO₃, and (c) 5 mM HNO₃. Eluent flow rate: 0.9 mL min⁻¹. Analytical column: Metrosep C4-150/4.0 (Metrohm, Switzerland). Sample injector loop volume: 10-μL. Column temperature: 35 °C. Detector type: non-suppressed conductivity.
under refrigeration at 4°C, and filtered by syringe filters (PES 0.22 μm) before injecting the standards into the IC device.

2.4. Sampling and pyrotechnics sample preparation

Every two types of firework and firecracker samples were purchased from local shops in Ternate, North Maluku, and the profile of samples is detailed in Table 1. The pre-blast samples were obtained by removing the fireworks and firecrackers powder from their packaging. In contrast, the post-blast residue samples were obtained by blasting them and then collecting them for quantification. The collected samples were then prepared according to the following steps. Each 1.0 g of the sample powder (pre-blast and post-blast) was added to 25 mL of purified water and then mixed, shaken, and centrifuged at 2,000 rpm for 15 min. In the final stage, all samples were filtered by syringe filters (PES 0.22 μm) before being injected into the IC instrument.

3. RESULTS AND DISCUSSION

3.1. Effects of HNO₃ eluent concentration on retention time

Various eluent concentrations were used to check the quantification of cationic components using a standard sample. The concentration of HNO₃ was in the range of 3–5 mM. As in the chromatogram in Fig. 1, the eluent concentration increased as the retention time of cationic components decreased.

Nine cationic components were eluted entirely in the range of 16–36 min, depending on the concentration of eluent used. All cationic components were retained shorter on the separation column at more than 4 mM HNO₃ (i.e., 5 mM) eluent concentration and a 0.9 mL min⁻¹ flow rate. Whereas, if the eluent concentration was less than 4 mM HNO₃ (i.e., 3 mM), all cationic were retained longer in the separation column, so it took a more extended quantification time.

The linear relationships between the retention factor (log k) logarithm and the various HNO₃ eluents logarithm were observed, as shown in Fig. 2. Theoretically, the predicted slope values are the ratio of the analyte ionic charge to the eluent ionic charge. The value for analyte cationic components should be −1 or −2. However, the obtained values for the analyte monovalent cations were −0.41, −0.44, −0.45, −0.48, and −0.49 for lithium, sodium, ammonium, methylammonium, and potassium, respectively, whereas those for the analyte divalent cations were −1.52, −1.53, −1.57, and −1.61 for magnesium, calcium, strontium, and barium, respectively. The deviations above predicted values may be due to the imperfect dissociation of the HNO₃ eluent.

3.2. Effects of different eluent flow rates on retention time

Simultaneous quantification of a cationic standard sample using 4 mM HNO₃ as the eluent and different eluent flow rates of 0.6, 0.8, and 1.0 mL min⁻¹ indicated that the obtained most efficient cationic component’s separation at the eluent flow rate of 1.0 mL min⁻¹. As in Fig. 3, the cationic component’s retention times were reduced when using a 1.0 mL min⁻¹ flow rate compared to either 0.6 or 0.8 mL min⁻¹. Although these eluent flow rate variations did not drastically change in retention time, Fig. 3c showed the optimum conditions when using 4 mM HNO₃ as the

![Fig. 2. The retention factor (log k) logarithm versus the eluent concentration of HNO₃ logarithm for cationic components. Eluent: 3–5 mM HNO₃](image-url)
eluent at a flow rate of 1.0 mL min$^{-1}$. It also should be noted that all peaks were obtained without overlapping, except the baseline separation between cationic sodium and ammonium, which could not be achieved perfectly under the obtained optimum flow rate.

### 3.3. Effects of adding Na$_2$EDTA on HNO$_3$ eluent

Disodium ethylenediaminetetraacetate (Na$_2$EDTA) competes more powerfully with solute ions of doubly charged ions and is easier to dissolve in HNO$_3$. Adding Na$_2$EDTA

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**Fig. 3.** Effects of the eluent flow rate on the quantification of cationic components with a standard sample. Eluents: 4 mM HNO$_3$. Eluent flow rate (in mL min$^{-1}$): (a) 0.6, (b) 0.8, and (c) 1.0. Other chromatographic conditions, as in Fig. 1.
Fig. 4. Ion chromatograms of nine cationic components with a standard sample using different mix concentrations of eluents. Mixed eluents: (a) 4 mM HNO$_3$ and 0.1 mM Na$_2$EDTA, (b) 4 mM HNO$_3$ and 0.075 mM Na$_2$EDTA (c) 4 mM HNO$_3$ and 0.015 mM Na$_2$EDTA, and (d) 4 mM HNO$_3$. Separation column: Metrosep C4-150/4.0. Eluent flow rate: 1.0 mL min$^{-1}$. Other chromatographic conditions, as in Fig. 1.
affected cationic peak responses (height and area) and decreased peak resolution. The sodium ion peak height drastically reduced, and conversely, the ammonium ion peak height slightly increased, especially when 0.05 and 0.1 mM Na$_2$EDTA were added to 4 mM HNO$_3$ (Fig. 4a and b). However, the other cationic components did not change their peak heights during the quantifications. It was important to note that adding Na$_2$EDTA to the HNO$_3$ eluent potentially reduced the elution time, compared to Fig. 4d, the quantification of cationic components without containing Na$_2$EDTA. Moreover, a baseline separation between cationic sodium and ammonium was not achieved under the eluent condition, as in Fig. 4d. On the other hand, adding Na$_2$EDTA could only affect cationic sodium and ammonium peaks and yielded a good baseline separation when the HNO$_3$ eluent was added a small quantity of Na$_2$EDTA (i.e., 0.015 mM), as in Fig. 4c. In fact, Fig. 4c and d shows chromatograms with good resolution for all cationic peaks. However, the chromatogram in Fig. 4c can decrease the total quantification time.

The eluent background conductivity decreased with increasing the adding Na$_2$EDTA concentration on the 4 mM eluent.

<table>
<thead>
<tr>
<th>Table 2. Range of standards concentration by injecting 10-μL of aliquots</th>
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</thead>
<tbody>
<tr>
<td><strong>Cationic components</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Lithium</td>
</tr>
<tr>
<td>Sodium</td>
</tr>
<tr>
<td>Ammonium</td>
</tr>
<tr>
<td>Methylammonium</td>
</tr>
<tr>
<td>Potassium</td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td>Barium</td>
</tr>
</tbody>
</table>

Fig. 5. Ion chromatogram of cationic components with a standard sample. Mixed eluents: 4 mM HNO$_3$ and 0.015 mM Na$_2$EDTA. Concentration of mixed standard sample (in mg L$^{-1}$): lithium (5), sodium (20), ammonium (20), methylammonium (20), potassium (20), magnesium (20), calcium (20), strontium (30), and barium (30). Other chromatographic conditions, as in Fig. 1

Fig. 6. Sensitivity diagram of cationic components. Other chromatographic conditions, as in Fig. 5
HNO₃ eluent (e.g., 1,190 mS cm⁻¹ at 0.015 mM, 1,157 mS cm⁻¹ at 0.05 mM, and 1,148 mS cm⁻¹ at 0.1 mM). The total quantification time is normally longer when the eluent background conductivity decreases. However, in this study, the presence of Na₂EDTA in the HNO₃ eluent observed did not cause changes in the quantification time. As noted above, 4 mM HNO₃ and 0.015 mM Na₂EDTA as the mixed eluent were used in the subsequent quantifications.

3.4. Simultaneous quantification of nine cationic components using a standard sample

A solution containing a mixture of nine cationic components was successfully simultaneously quantified using the Metrosep C4-150/4.0 column. The cationic constituent’s retention by IC in the presence of eluent containing HNO₃ and Na₂EDTA followed the order lithium > sodium > ammonium > methylammonium > potassium > magnesium > calcium > strontium > barium, and all peaks were found to be eluted within 18 min (Fig. 5).

3.5. Validation methods

The linear range of the present method was investigated by quantifying a standard solution containing a mixture of nine cationic components with a known concentration range, as shown in Fig. 6 and Table 2. Their linear range, correlation coefficient, and regression equation are given in Fig. 7 and Table 3.

The present method’s limit of detection (LOD) was determined by injecting a 10-μL aliquot standard volume and calculated at S/N = 3. The results are summarized in Table 3. The detection limits obtained by the described method were 0.034–0.098 ppm (mg L⁻¹). Using this method, a sub-ppm detection level will be possible to simultaneously quantify nine cationic components in actual

![Graph](image)

**Fig. 7. Calibration graph of cationic components**

<table>
<thead>
<tr>
<th>Cationic components</th>
<th>LOD (mg L⁻¹)</th>
<th>Regression equation</th>
<th>Retention time, tᵣ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.034</td>
<td>y = 4.912x + 1.152</td>
<td>2.81</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.058</td>
<td>y = 1.002x + 2.325</td>
<td>3.42</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.067</td>
<td>y = 1.170x + 2.809</td>
<td>3.74</td>
</tr>
<tr>
<td>Methylammonium</td>
<td>0.091</td>
<td>y = 0.740x + 2.427</td>
<td>4.34</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.092</td>
<td>y = 0.472x + 0.510</td>
<td>4.70</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.063</td>
<td>y = 0.631x + 0.506</td>
<td>7.17</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.082</td>
<td>y = 0.373x + 1.211</td>
<td>8.87</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.094</td>
<td>y = 0.142x + 0.808</td>
<td>10.65</td>
</tr>
<tr>
<td>Barium</td>
<td>0.098</td>
<td>y = 0.065x + 0.256</td>
<td>15.49</td>
</tr>
</tbody>
</table>
samples, such as firecrackers and fireworks. Table 3 compares the LOD values obtained in this work with those from other works. It showed to be better than other LODs. This suggests that the method used in this work could be more accurate and effective in detecting low levels of cationic components than those used in previous works.

Precision was tested by performing 5 analytes of a standard mixture containing (in mg L\(^{-1}\)) 5, 20, 20, 20, 20, 20, 30, and 30 (Tables 2-IV) for lithium, sodium, ammonium, methylammonium, potassium, magnesium, calcium, strontium, and barium, respectively. In replicate chromatographic quantifications \((n = 5)\), the relative standard deviation (RSD) of response conductivity under the optimum chromatographic conditions was 0.93–3.98%, as shown in Table 4.

### 3.6. Application to firecracker and firework samples

The present IC method was satisfactorily applied to simultaneously quantify the nine cationic components contained in 2 types of firecrackers (HFT and DST) and 2 types of fireworks (RC and PJ) as pyrotechnic samples, as detailed in Table 1 above. These samples are commercially available in the local shops in Ternate City and are mainly sold during the New Year’s session.

The observed pre-blast and post-blast residue of 4 pyrotechnic samples were then dissolved in purified water. The concentration was determined according to the analytical chromatographic conditions, as shown in Fig. 5. Each sample was filtered through a 0.22 μm syringe filter before injection into the IC device to avoid accidental contamination of the sample. The quantification of the cationic components contained in all samples is summarized in Table 5.

Figure 8a and b shows that both HFT and DST samples were potassium-based firecrackers, which contained higher potassium ions than other cationic components (Table 5). In pre-blast, HFT and DST samples had 4,011 and 6,138 mg kg\(^{-1}\) of potassium, respectively. A large amount of potassium cationic was reduced during the blasting and remained in post-blast residue samples at 867 and 1,358 mg kg\(^{-1}\) for HFT and DST, respectively, while the other cationic components were observed almost unchanged in their concentrations.

As shown in Fig. 9a and b, the chromatograms were the result of simultaneously quantifying the concentration of cationic components in the pre-blast and post-blast residues of RC and PJ fireworks. Both samples were pyrotechnics of potassium-barium-based and barium-based materials for RC and PJ, respectively. However, barium was the primary cationic component in these firework types. In pre-blast, RC contains 5,586 mg kg\(^{-1}\) of barium, a drastic reduction in post-blast residue samples, and a small amount of 78 mg kg\(^{-1}\). In contrast, the barium concentration for the PJ sample was 6,190 mg kg\(^{-1}\) and the remaining 286 mg kg\(^{-1}\) in post-blast residues.

Lithium and methylammonium cationic components were not detected in all studied samples. It may be below the detection limit. Therefore, no peaks were seen in all chromatograms. Moreover, it is expected that both ions were not cationic components used to manufacture chemicals of the firecrackers and fireworks used in this study.

A peak shift in retention time occurred as barium cationic was quantified when it contained too much in both RC and PJ samples. It may be caused by the peak asymmetric and barium as the divalent ionic charge. It has been confirmed in Fig. 6 that the divalent cation’s peak shift...
Fig. 8. Chromatograms of cationic components in firecracker (a) HFT and (b) DST samples. Other chromatographic conditions, as in Fig. 5.
Fig. 9. Chromatograms of cationic components in a firework (a) RC and (b) PJ samples. Other chromatographic conditions, as in Fig. 5.
occurs as the concentration increases in the sample standards, while there is no change for the monovalent cations. However, when the samples were diluted to approximately the same as the sample standard, it was found that the cationic barium peak had the same retention time.

In the production of pyrotechnics (fireworks and firecrackers), the most common cationic components, such as ammonium (NH$_4^+$), potassium (K$^+$), and barium (Ba$^{2+}$), are often involved in their chemical composition. The compounds used may include ammonium perchlorate (NH$_4$ClO$_4$), potassium nitrate (KNO$_3$), or barium nitrate (Ba(NO$_3$)$_2$). In pre-blast, the chemicals in pyrotechnics are typically stable, and these cationic components are usually bound in relatively safe and non-reactive compounds. However, when pyrotechnics are being blasted, a rapid chemical reaction occurs, and these cations can transform into gas ions and other particles as products of the blasting reaction. Therefore, the residue samples in post-blast tend to contain deficient cationic component concentrations compared to pre-blast samples.

As the obtained quantification results from the above, which provide below 5% RSD and a low detection limit, can be promising for potential explosives applications such as pyrotechnics samples and valuable in identifying other common explosives, allowing the same separation conditions for all cases. Moreover, this proposed method is still quite effective, especially for application to post-blast samples.

4. CONCLUSIONS

IC is a powerful method for simultaneously quantifying nine cationic components in potential explosives, such as firecrackers and fireworks samples. The described method exhibited good quantitative performances regarding LOD, repeatability, and correlation coefficient.

Potassium is the cationic component with the highest concentration in firecrackers, while barium is in fireworks. During the blasting, potassium and barium ions were significantly reduced in their concentration in the post-blast residue samples. At the same time, sodium, ammonium, magnesium, calcium, and strontium did not change in concentration as in the post-blast residue samples, except for a slight reduction. Lithium and methylammonium were not found in both types of studied samples.

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