



Ion Chromatographic Method for the Simultaneous Determination of Anions and Cations in Firecrackers and Matches Samples as Known Potential Explosives

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ABSTRACT

A reference ion chromatography method based on column switching has been presented for the simultaneous determining anions (Cl^- , ClO_3^- , NO_2^- , SO_4^{2-} , and NO_3^-) and/or cations (NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) using one pump, one type of mobile phase, and one detector. The reference method performed anion-exchange column and cation-exchange column and arranged serially via one 10-port valve. The determination of either anions or cations in one determination system could be made by switching the valve. When the use of 1.25 mM trimellitic acid as a mobile phase and the instrument was operated at a flow rate of 0.6 mL/min, five anions and five cations were determined on the anion-exchange column and the cation-exchange column, respectively. All anions target could be determined completely within 55 minutes, whereas the cations target could be determined within 35 minutes. The calculation of limit of detection using $S/N=3$ was 3.85 – 14.10 μM for anions and 2.95 – 10.58 μM for cations. The relative standard deviations of all ions were less than 3.82%, 3.29%, and 3.21% for retention time, peak area, and peak height, respectively. The reference method was then applied for the simultaneous determining anions and/or cations contained in firecrackers and matches samples as known potentially explosives.

Keywords: anions and cations, column switching, firecrackers, ion chromatography, matches

INTRODUCTION

Since ion chromatography (IC) method was first introduced by Small *et al.* in 1975, (Weiss, 1995), now become an excellent analytical tool for determining inorganic ions in forensic sciences (Doyle and McCord, 1998; Hopper *et al.*, 2005; Feng *et al.*, 2008; Johns *et al.*, 2008; Meng *et al.*, 2008), counter-terrorism (Amin, 2014; Mishra and Jaiswal, 2017), and the most application is in the environmental water monitoring (Ohta, *et al.*, 1996; Jackson *et al.*, 2003). A conventional, anions and cations are determined separately

using different determination optimum conditions. And a number of published papers have been discussed for determining simultaneously both anions and cations in a one determination system due to a potential to increase the efficiency of ion chromatographic determination in a laboratory work (Jones and Tarter, 1984; Saari-Nordhaus and Anderson, 1991; Amin, *et al.*, 2007; 2008).

Fast identification of inorganic ions in explosives materials is an important factor for counterterrorism procedures. The main analytical techniques have been used for the determination of ionic components related to explosive samples such as capillary electrophoresis (CE) (Doyle and Mccord, 1998), capillary zone electrophoresis (CZE) (Hopper *et al.*, 2005; Feng *et al.*, 2008), and IC (Johns *et al.*, 2008). CE promises faster separation and low cost of operation. However, it offered poorer detection sensitivity in their analysis. IC is currently used in many wide ranges of application including the detection of cations and anions presented in explosives and potentially explosives samples such as firecrackers and fireworks (Amin, 2014).

Referring to the recent development, there are at least two approaches known for determining simultaneously anions and cations in one arrangement determination system, namely (1) using one column which allows partially determining simultaneously anions and cations (Iskandarani and Miller, 1985; Jones and Tarter, 1984; Saari-Nordhaus and Anderson, 1991), and (2) using two analytical separators parallelly- and seriesly-connected with or without column switching (Amin, *et al.*, 2007; 2008). For the latter, in which there is no column switching, an appropriate mobile phase should be considered for the simultaneous determining both cations and anions. However, the obtained anions and cations peaks often overlapped; therefore, it is not a promising method anymore. In 2008, Meng *et al.* suggested an alternative method for the simultaneously determining cations and anions normally found in explosive residues samples which can be achieved by connecting directly cation-exchange/anion-exchange analytical columns with the series arrangement. However, it gave the poor selectivity of anions and not satisfactory baseline separation for anion peaks under the chosen mobile phase (Meng *et al.*, 2008).

The most advantage of the column switching method is the ability for simultaneous determining cations and anions in one determination arrangement system in terms of providing better peaks shape and selectivity without peaks overlapping. An IC method based on column switching is intended to use two columns arranged in series in a single determination system. In this case, the cation-exchange column was prepared to determine the cations concentration in the samples, while the anion-exchange column was prepared to

determine the anions concentration. However, a switching device is surely needed to ensure the ions targets.

Inorganic compounds commonly found in explosives such as ammonium nitrate (NH_4NO_3), potassium chlorate (KClO_3), sodium nitrate (NaNO_3), potassium perchlorate (KClO_4), and potassium nitrate (KNO_3). Potassium chlorate (KClO_3) is one of the most widely used and as dangerous oxidizers in firecracker and matches samples. The application of ion chromatography technique can be used for analyzing the ion content in explosives of both of pre- and post-blast residues. The inorganic ions such as Cl^- , ClO_3^- , NO_2^- , SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are the ions that are very crucial and important to be detected in order to determine the type of explosives used by criminalists.

Therefore, this present study discusses the improvement of ion chromatographic method for the simultaneous determining inorganic anions particularly ClO_3^- and inorganic cations in one determination system, and its application for potentially explosive materials such as firecrackers and matches. The improved method was performed with a 10-port valve that as a key part of the method to easily switch and control the target ions and determinations.

EXPERIMENTAL METHOD

Ion Chromatograph

The ion chromatograph and the column switching performances were almost the same as the previous study (Amin *et al.*, 2008) except for both analytical columns. The experimental setup consisted of PU-2080i HPLC pump (Jasco, Japan), 5095 loop injector model with 20- μL of sample volume (Rheodyne, USA), CM 8020 detector (Tosoh, Japan), 10-port valve (Rheodyne), and computer-aided chromatography (Filcon, Japan). TSKgel IC Anion PWxl PEEK (7.5 cm x 0.46 cm i.d.) (Tosoh, Japan) and TSKgel IC Cation/P (15 cm x 0.46 cm i.d.) (Tosoh, Japan) analytical columns were used for anions and cations determinations, respectively.

Reagents and Solutions

The ionic liquid employed was analytical grade chemicals and were available from Nacalai Tesque in Kyoto, Japan. All standards were prepared using deionized water. First, each 50 mM of stock standard solutions for 5 anions (chloride, chlorate, nitrite, nitrate, and sulfate) and 5 cations (sodium, ammonium, potassium, magnesium, and calcium) were prepared as individual ions standards. The calibration curves were prepared from a mixed cations standard (0.1, 0.2, 0.3, 0.4, 0.5) mM and mixed anions standard series (0.1, 0.2, 0.3,

0.4, 0.5) mM of the stock standard solutions. The trimellitic acid mobile phase was available from Wako (Osaka, Japan). Since the mobile phase could critically become an unstable solution, it was freshly prepared before the experiment.

The collection, Preparation, and Treatment Samples

The samples were collected from the firecrackers and matches powders. Firecrackers powder was obtained by removing from its packaging, while matches powder was obtained by scraping the top-end of the match, as shown in Figure 1. The samples were prepared by the following approach. Each 1.0 g powder sample was added to 50 mL of deionized water and then mixed the samples with a shake followed by centrifuging at 2000 rpm for 15 minutes. Finally, the samples were filtered through a 0.45 μm of pore size filter membrane before injection into the instrument.

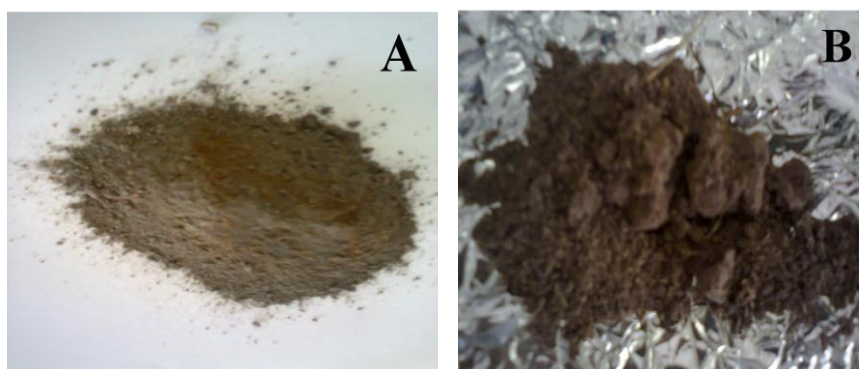


Figure 1. Powder of the real samples: firecrackers sample (A) and matches sample (B)

Mobile Phase and Operating Conditions

The mobile phase concentration used in this work was 1.25 mM trimellitic acid. The determination conditions were under isocratic mode. Each column has a pressure limit, 8 MPa for the anion-exchange column and 10 MPa for the cation-exchange columns. Since the developed method used two columns connected in a series arrangement, the inlet pressure should be kept at maximum 8 MPa by operating the flow-rate pump at 0.6 mL/min.

Column Switching Performances

Figure 2 shows the setup of the method including both ion-exchange columns positions and the 10-port valve. The improved method was performed following the procedure as follow.

In setup A, the eluent passed both ion-exchange columns until obtaining a straight baseline. A 20 μL of anions standard volume was then injected into the instrument. The analytes containing anions and cations would arrive at the anion-exchange column, and the

system determined the analyte anions only. While the anion-exchange column was being operated to determine anions, the other column was remained conditioned with the mobile phase. Therefore, when the valve switched to the determination of cations, a straight baseline could be quickly obtained.

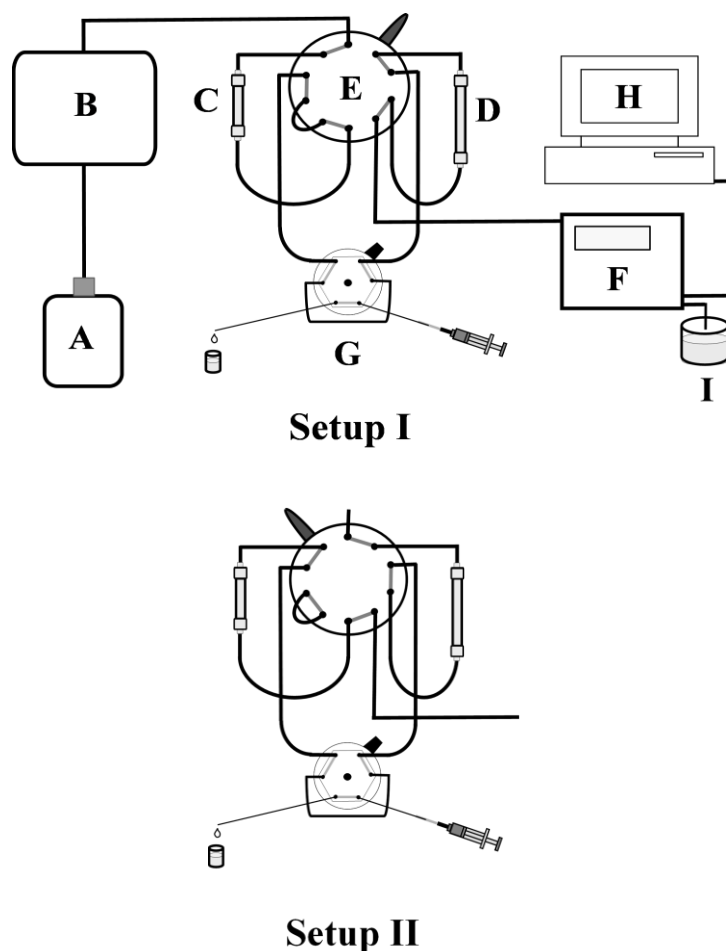


Figure 2. The setup of the reference method with anion- and cation-exchanger connected in series arrangement via a 10-port valve. Determination of anions (setup I) and determination of cations (setup II). Remarks: A. Mobile phase, B. Pump, C. Anion-exchanger, D. Cation-exchanger, E. 10-port valve, F. Conductivity, G. Sample injection, H. Data processor, I. Waste.

In setup B, after the valve was switched for the determination of cations, and then a 20 μL of cations standard volume was injected into the instrument. The analytes containing anions and cations would arrive at the cation-exchange column, and the system determined the analyte cations only. While the cation-exchange column was being operated to determine cations, the other column was also remained conditioned with the mobile phase, so that a straight baseline could be quickly re-obtained when the valve re-switched to the determination of anions.

RESULTS AND DISCUSSION

The Effects of Trimellitic Acid Mobile Phase Concentrations

In order to investigate the optimum of mobile phase concentration, various concentrations containing trimellitic acid was used to check the effects of the determination of anions and cations on retention time. The samples of standard for anions and cations were injected on anion-exchange and cation-exchange columns, respectively, where the concentration of trimellitic acid was in the range 1.0 - 2.0 mM.

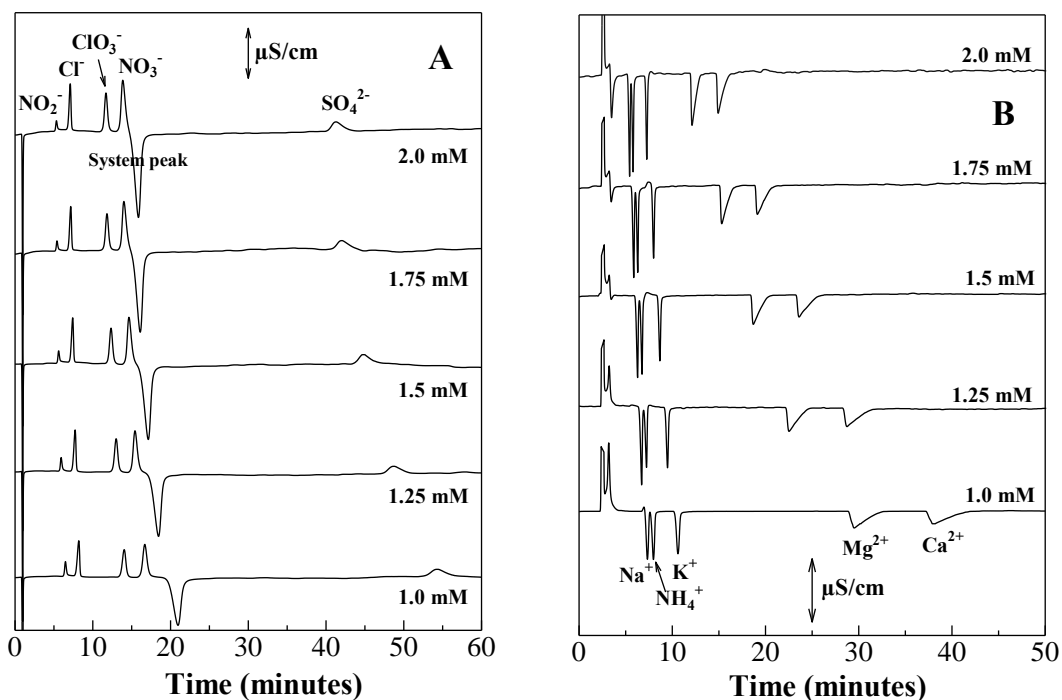


Figure 3. The differences of chromatographic profiles on the retention time, (A) for anions and (B) for cations by changing the mobile phase concentration. Mobile phase: 1.0 - 2.0 mM trimellitic acid. Columns: TSKgel IC Anion PWxl PEEK (7.5 cm x 0.46 cm i.d.) and TSKgel IC Cation/P (15 cm x 0.46 cm i.d.). Flow-rate: 0.6 mL/min. Injection: 20 μL .

Figure 3 displays the chromatograms of five anions and five cations at different mobile phase concentrations. The mobile phase concentration increased as retention time values of both anions (Cl^- , ClO_3^- , NO_2^- , SO_4^{2-} , and NO_3^-) and cations (NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) decreased. When the concentration of the mobile phase was less than 1.25 mM, the divalent ions (Mg^{2+} , Ca^{2+} , and SO_4^{2-}) were retained longer. When the concentration of the mobile phase was higher than 1.25 mM, the baseline determination between Na^+ and NH_4^+ was not achieved, and NO_3^- tends to overlap with the system peak. The system peak generally appears in the chromatogram when the analyte or solute is injected into the chromatographic system. The elution time of system peak and its size depends on the sample matrix and pH of the mobile phase (Okada and Kuwamoto, 1984). However, their capacity ratio is independent of solute injected.

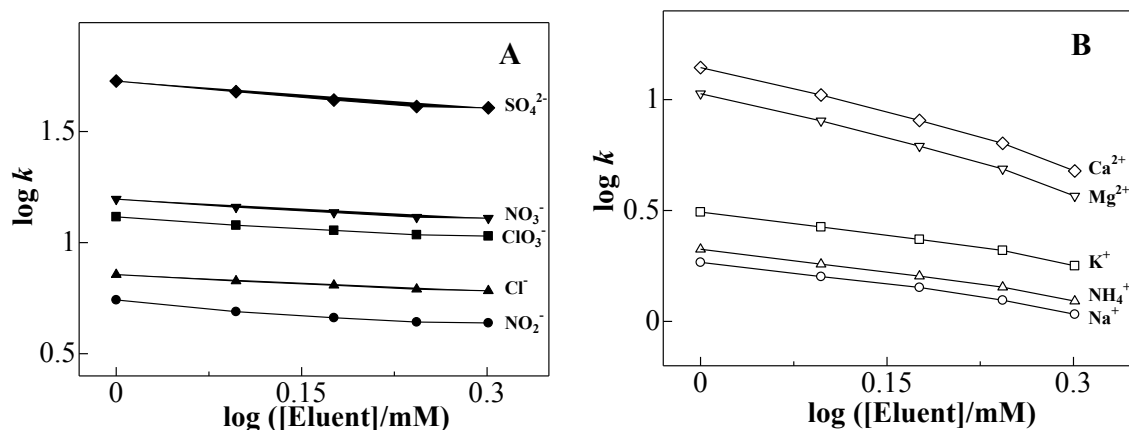


Figure 4. Effect of mobile phase concentrations on retention factors of anions and cations. Mobile phase: trimellitic acid. Plot lines: A. anions, and B. cations. Other analytical conditions, as in Figure 3.

A linear relationship between the logarithm of the mobile phase concentration (Log [Eluent]) and the logarithm of the factor of retention ($\log k$) of anions and cations and were observed, as plotted in Figure 4. In other words, the slope values are the eluent ionic valency (\log [Eluent]) and the ratio of the analyte ionic valency ($\log k$) (Grushka and Grinberg, 2007). As illustrated in Figure 4A, the obtained slope for analyte anions were -0.35 , -0.24 , -0.29 , -0.29 , and -0.42 for NO_2^- , Cl^- , ClO_3^- , NO_3^- , and SO_4^{2-} , respectively. Therefore, it is expected that the slope values for monovalent anions should be -0.5 and the divalent anions should be -1 . Figure 4B illustrates the slopes value for cations were -0.76 , -0.76 , -0.78 , -1.51 , and -1.52 for Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} , respectively. The expected slope values for mono- and divalent cations should be -1 and -2 , respectively. As the above results, it was found that the trimellitic acid mobile phase average valence was about 1.5.

The Effects of Anion- and Cation-exchange Columns Connected via 10-port Valve

As shown in Figure 5, the anion- and cation-exchange columns are connected serially arrangement via a 10-port valve. The desired determinations could be controlled by switching the valve. It also means that the determination of anions and/or cations can be done in one chromatographic system. However, the obtained anions and cations chromatograms are independent. The five anions target (Cl^- , ClO_3^- , NO_2^- , SO_4^{2-} , and NO_3^-) could be determined completely within 55 minutes, whereas, the five cations target (NH_4^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) could be determined within 35 min, as displayed in Figure 5. Attention to Figure 5A, system peak appeared between NO_3^- and SO_4^{2-} ions. At lower concentration of eluent (<1.25 mM), the monovalent and divalent anions could be

separated further from the system peak. However, the divalent anions and cations took longer analysis time.

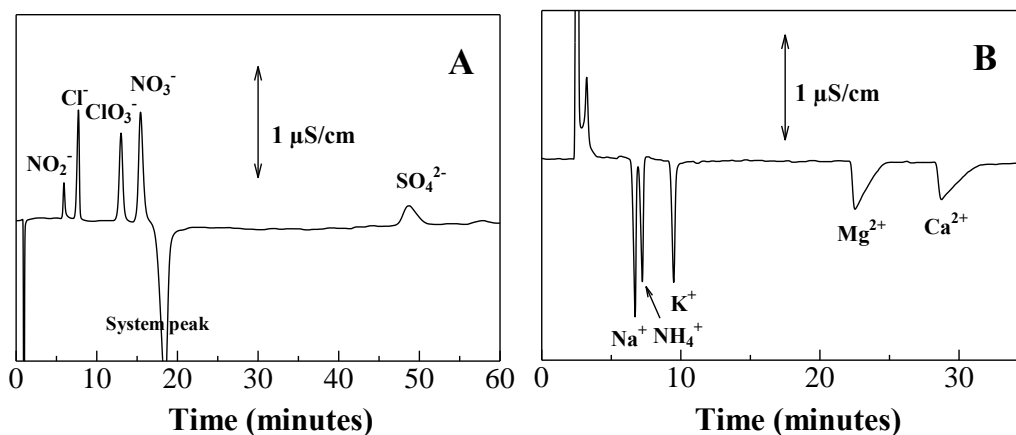


Figure 5. Determination of anions and/or cations using the column-switching method. Mobile phase: 1.25 mM trimellitic acid. Analytes are containing 0.5 mM of each ion. Other analytical conditions, as in Figure 3.

Method Validation

The coefficient of correlation (r^2) for the cations and anions are listed in Table 1. Peak heights showed a good linear correlation on the range of ion concentration from 0.1 to 0.5 mM. The limit of detection (LOD) of all ions was calculated at a signal-to-noise (S/N) ratio is 3, and the results are summarized in Table 1. The LOD obtained by the developed method was 3.85 – 14.10 μM for the anions and 2.95 – 10.58 μM for the cations.

Table 1. Summarized data for LOD, r^2 , and t_R of anions and cations obtained under the optimum analytical conditions, as in Figure 5.

Analytes	LOD		Coefficient correlation ^a (r^2)	t_R (minutes)
	μM	ppm		
Anions:				
NO_2^-	9.31	0.43	0.9954	5.59
Cl^-	3.85	0.14	0.9963	7.52
ClO_3^-	4.28	0.36	0.9994	13.01
NO_3^-	3.54	0.22	0.9998	15.44
SO_4^{2-}	14.10	1.34	0.9928	48.59
Cations:				
Na^+	2.95	0.07	0.9971	6.59
NH_4^+	3.08	0.06	0.9956	7.24
K^+	3.55	0.14	0.9921	9.52
Mg^{2+}	8.08	0.19	0.9935	22.53
Ca^{2+}	10.58	0.42	0.9918	28.58

^aThe concentration range of standard samples: 0.1 to 0.5 mM for all ions

Table 2 shows the repeatabilities of the signals (retention time, peak area, and peak height) of analytes (anions and cations) for seven measurements under the optimum analytical conditions described in Figure 5. The relative standard deviation (RSD) of all ions were less than 3.82%, 3.29%, and 3.21% for retention time, peak area, and peak height, respectively. It means that these values are significantly lower than the limit of imposed.

Table 2. RSD of anions and cations under the optimum analytical conditions in Figure 5.

Analytes	RSD (%), n = 7		
	Retention time	Peak area	Peak height
Anions:			
NO ₂ ⁻	1.96	1.93	1.82
Cl ⁻	2.78	2.15	1.94
ClO ₃ ⁻	2.83	1.98	2.80
NO ₃ ⁻	3.05	2.84	3.22
SO ₄ ²⁻	3.82	3.21	3.29
Cations:			
Na ⁺	1.59	2.16	1.34
NH ₄ ⁺	1.82	1.89	1.78
K ⁺	1.92	2.72	2.92
Mg ²⁺	2.74	2.98	3.16
Ca ²⁺	3.09	3.06	2.39

n = number of measurements

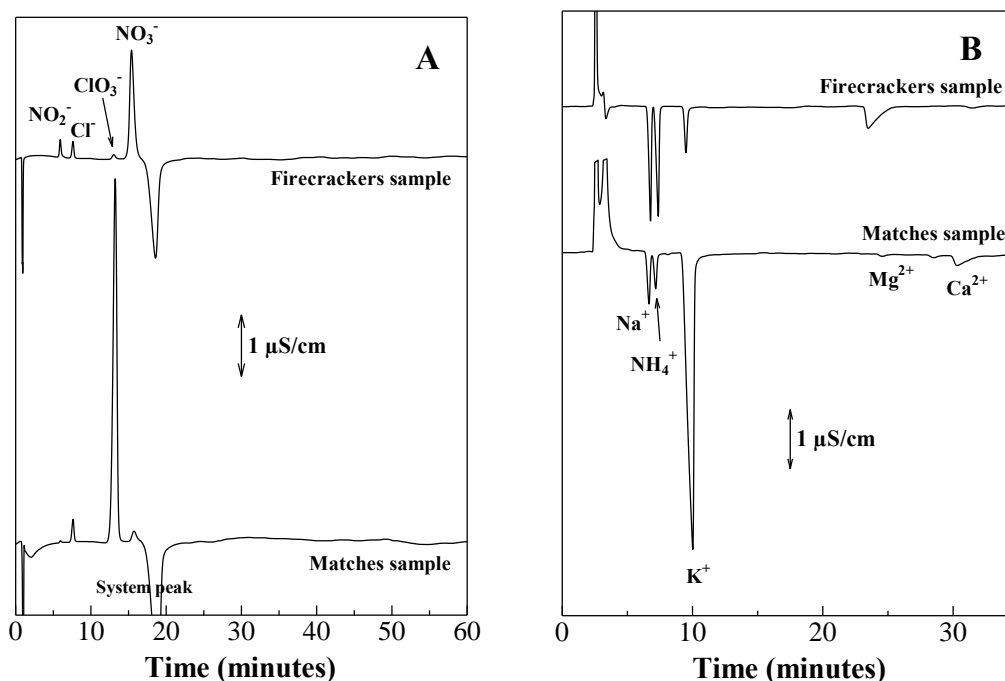


Figure 6. Chromatograms of anions (A) and cations (B) determined in firecrackers and matches samples

Application to Potentially Explosive Samples

The present method was successfully applied for simultaneously determining anions and cations in firecrackers and matches samples as known potentially explosive. These samples are available commercially in the market. The samples taken were firecrackers and matches unfired samples have dissolved into deionized water and determined according to the analytical conditions described in Figure 5. To avoid accidental contamination of the samples, each sample was filtered through a 0.45 μm of pore size filter membrane before injection into the instrument.

Figure 6 shows the typical chromatograms for both potentially explosive samples. In the firecrackers sample, all ions were detected except Ca^{2+} and SO_4^{2-} ions. It is expected that Ca^{2+} and SO_4^{2-} ions are not contained in the raw material used in the manufacture of firecrackers. Therefore, both ions were not found in the detection results. In matches sample, Mg^{2+} and SO_4^{2-} ions were not detected under this condition. It is also expected that Mg^{2+} and SO_4^{2-} ions are not contained in the raw material used in matches samples. It is observable that the K^+ and ClO_3^- ions levels were the highest concentration. Therefore, it should be noted that potassium chlorate is the main compound in matches.

Table 3. Determination results of anions and cations in firecrackers and matches samples (n=7) using the developed method

Analytes	Firecrackers		Matches	
	Mean value mM ($\mu\text{g/mL}$)	RSD (%)	Mean value mM ($\mu\text{g/mL}$)	RSD (%)
Cations				
Na^+	0.585 (13.5)	2.37	0.251 (5.8)	1.93
NH_4^+	0.659 (11.9)	1.92	0.206 (3.7)	2.75
K^+	0.315 (12.3)	2.46	2.038 (79.5)	3.22
Mg^{2+}	0.289 (6.9)	3.89	0.034 (0.8)	2.73
Ca^{2+}	0.044 (1.8)	2.93	0.206 (8.2)	2.81
Anions				
NO_2^-	0.499 (22.9)	2.45	0.055 (2.5)	2.46
Cl^-	0.142 (5.0)	2.01	0.187 (6.6)	2.43
ClO_3^-	0.043 (3.6)	3.28	3.857 (322.1)	3.52
NO_3^-	0.923 (57.2)	3.05	0.078 (4.8)	2.09
SO_4^{2-}	ND		ND	

ND = not detected

Moreover, Table 3 consists of the reproducibility data (n = 7) and the determination results for the anions and cations presented in the firecrackers and the matches samples with lower RSD. Therefore, it is suggestable that the present method can be applied as a practical and reference method.

CONCLUSIONS

One prominent aspect of the developed method is that the anion- and cation-exchange columns are arranged serially via a 10-port valve, performing one pump and one detector for the simultaneous determining of five anions (NO_2^- , Cl^- , ClO_3^- , NO_3^- , and SO_4^{2-}) and five cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) in firecrackers and matches samples which are usually found as potential explosives. The 1.25 mM trimellitic acid mobile phase concentration exhibited good performance in term of the selectivity and sensitivity of anions, particularly ClO_3^- and cations in both samples. The presented method offered as simple operation and as a reference method, in which it could be applied for routine purposes, especially in the potential explosive samples.

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