

Simultaneous Determination of Organic and Cationic Species in Explosives Residues with Column-Switching Liquid Chromatography–Ion Chromatography System

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Abstract

A new column-switching method has been proposed for the determination of 14 organic explosives (1,3,5,7-tetranitro-N-methylaniline, 1,3,5-trinitro-1,3,5-triazacyclohexane, 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, nitrobenzene, 2,4,6-N-tetranitro-N-methylaniline, Trinitrotoluene, 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 2-nitrotoluene, 4-nitrotoluene, and 3-nitrotoluene) and/or five inorganic cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) using liquid chromatography linked to ion chromatography by a switching valve. The mobile phase was methanol–water (40/60, v/v) for a C18 reversed-phase column and 3 mM of methanesulfonic acid (pH 2.5) for a cation-exchange column, respectively. Under the optimal conditions, the 14 organic explosives and the five inorganic cations were separated and detected simultaneously within 45 min. The limits of detection ($S/N = 3$) of the 14 organic explosives and the five inorganic cations were in the range of 0.0048–0.0333 mg/L and 0.0116–0.1851 mg/L, respectively. The linear correlation coefficients were 0.9971–0.9999, and the relative standard deviation of the retention time and the peak area were 0.02–0.31% and 0.51–3.64%, respectively. The method was successfully applied to the determination of organic explosives and inorganic cations in dust samples.

Introduction

As explosives have been increasingly developed, they have been widely used in various industrial and commercial settings, and sometimes even find their way into the hands of terrorists and criminals, which has become a serious social problem. For explosives are abundant in variety and complex in components, determination of explosives is a challenging problem that requires the ability to identify and determine quantitatively a large number of inorganic and organic materials. At present, the main methods developed to detect explosives are high performance liquid chromatography (HPLC) (1–3), high-performance liquid chromatography-mass spectrometry (4,5), gas chro-

matography (6–8), electrospray ionization ion mobility spectrometer (5,9), fluorescence (10), spectrophotometry (11), and biosensor (12) for organic explosives, while ion chromatography (IC) (7,13,14) and capillary electrophoresis (15) are used for detecting inorganic explosives. However, all of these methods can not determine organic explosives and inorganic cations simultaneously, which need more time and more samples for determination. Therefore, the HPLC–IC method for the simultaneous determination of both organic explosives and inorganic cations were developed by connecting two columns via a 6-port switching valve.

The types of explosives that the public are most aware of are the organic explosives, which commonly include 1,3,5,7-tetranitro-N-methylaniline (HMX), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3-dinitrobenzene (1,3-DNB), nitrobenzene (NB), 2,4,6-N-tetranitro-N-methylaniline (Tetryl), Trinitrotoluene (2,4,6-TNT), 4-amino-2,6-dinitrotoluene (4-Am-2,6-NDT), 2-amino-4,6-dinitrotoluene (2-Am-4,6-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT), and 3-nitrotoluene (3-NT) listed in the EPA SW-846 Method 8330 Nitroaromatics and Nitramines by HPLC. Because Dionex (Sunnyvale, CA) has developed a one of a kind of special column named the Acclaim Explosives E1, all of these organic explosives can be resolved under an isocratic mode.

On the other hand, the most widely used inorganic explosives in the world are ammonium nitrate explosives, chlorate explosives, and black powder (7,13,14). After a blast of these inorganic explosives, the residue ions are mostly NH_4^+ for ammonium nitrate explosives; Na^+ , K^+ , Mg^{2+} , and Ca^{2+} for chlorate explosives; and K^+ and Na^+ for black powder. Because the cations are important evidences used to identify explosives, it is necessary to determine them. IC is widely considered to be the premier technique for the analysis of inorganic ions; with the IonPac SCS1 column, the five cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) can be determined expediently.

In this study, simultaneous determination of organic explosives and inorganic cations by the Acclaim Explosives E1 column and the IonPac SCS1 column connected with a column-switching method was established. This method was successfully applied to determine the organic explosives and inorganic

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cations in real samples, which was very important for evaluating the type of explosives. This method was simple, sensitive, and cost-effective, and it could be applied to simultaneous determination of organic and inorganic species in other areas.

Experimental

Chromatography system

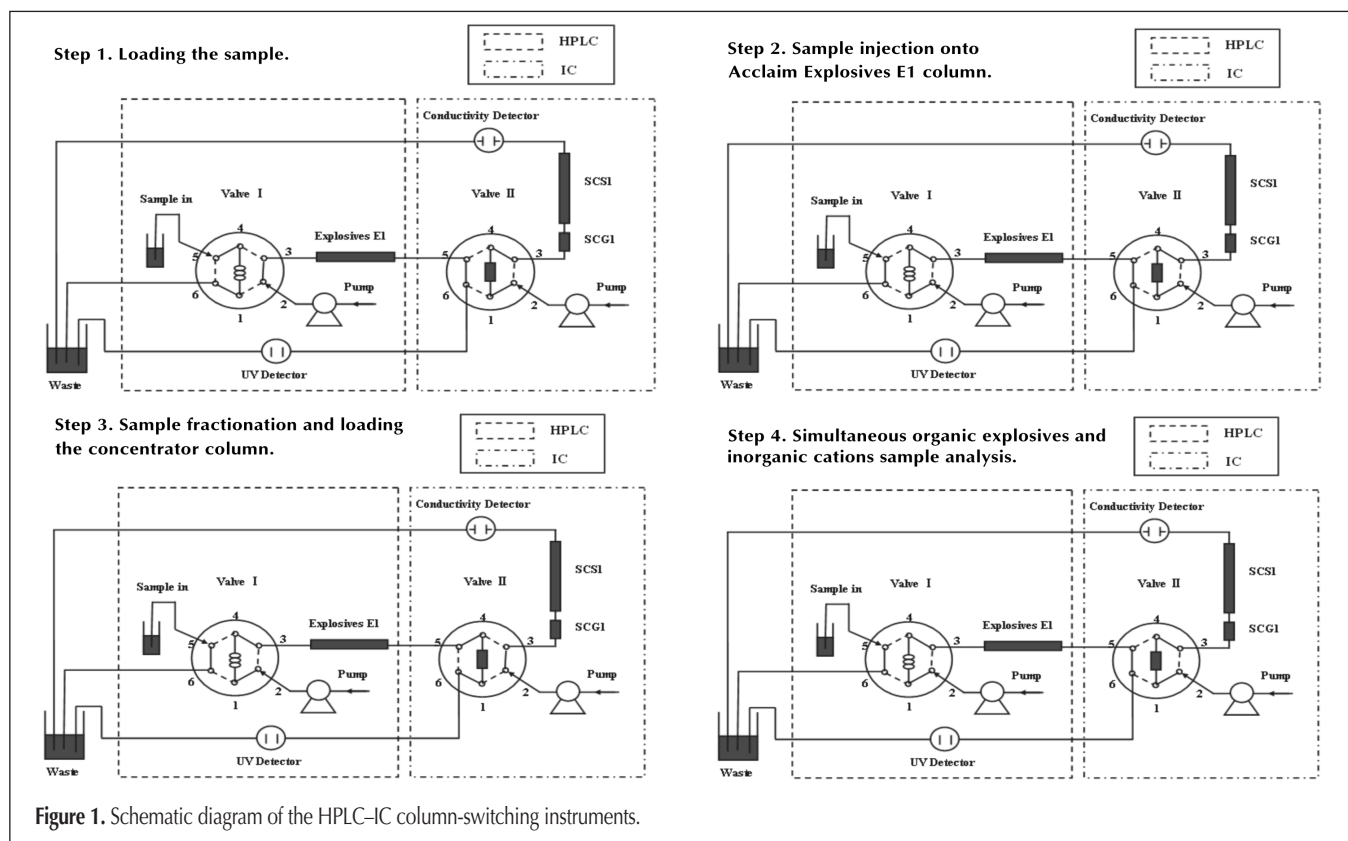
The diagram for the instruments employed in this study is illustrated in Figure 1. The column-switching HPLC–IC system consisted of two parts: HPLC and IC, which were connected by a 6-port switching valve directly. The Dionex Summit HPLC instrument was equipped with a HPLC pump (P680), an automated sample injector (ASI-100), a column oven (TCC-100), and an UV detection (UVD340U). The column employed was an Acclaim Explosives E1 column (250 mm × 4.6 mm, i.d.) that was obtained from Dionex. The Dionex ICS-2000 instrument was equipped with a pump, an injection valve, a column heater, and a conductivity cell (DS6). The columns employed were an IonPac SCS1 column (250 mm × 4 mm, i.d.) and two IonPac SCG1 columns (50 mm × 4 mm, i.d.). All of these columns were obtained from Dionex. Chromeleon 6.8 chromatography data management software (Dionex) was used for system control and data processing. All data acquisition and data evaluation were performed automatically. Polyether ether ketone (PEEK) tubes were used to connect all of the hardware. The lengths of the connecting tubing were kept as short as possible to minimize system void volume.

Chemicals

All chemicals used for the preparation of the standard solutions of the desired organics and cations were of analytical grade or higher. The methanol used was of an HPLC grade (Tedia Co., Fairfield, OH), while the methanesulfonic acid (MSA) used was better than 98.0% pure (Sigma-Aldrich, St. Louis, MO). The deionized water (18.2 MΩ/cm) used throughout this study was prepared in the laboratory using a Millipore Milli-Q Plus system (Millipore Co., Milford, MA). The inorganic standards were initially prepared at a concentration of 1000 mg/L and diluted to the desired concentration. The standards were prepared from an analytical reagent grade comprised of NaCl, NH₄Cl, KCl, MgCl₂, and CaCl₂, which were purchased from Xinguang Chemical Reagent Factory (Beijing, China). For the organic explosives analysis, a standard mixture of HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, Tetryl, 2,4,6-TNT, 4-Am-2,6-NDT, 2-Am-4,6-DNT, 2,6-DNT, 2,4-DNT, 2-NT, 4-NT, and 3-NT was purchased from Sigma-Aldrich, with a concentration of 1000 mg/L per each component in acetonitrile. Working standards covering the range of 0.1–0.5 mg/L were obtained by serial dilution of the original mixture in deionized water.

Sample preparation and storage

The real sample analyzed was provided by a public security bureau in Jiangshu Province, China. The sample was first heated overnight at a temperature of 100°C in a drying oven, and stored in the oven at that temperature until use. The sample (5 g) was weighed into 250 mL conical vials before extracting it with 100 mL deionized water, followed by sonicate for 30 min, then centrifuging it for 20 min at 5000 rpm. Then the extract was filtered by 0.45 μm filters prior to injection without dilution.



Operating conditions

In a non-suppressed IC, 3 mM MSA was selected as the eluent for separation of the five inorganic cations. When the column temperature was 30°C and the eluent flow rate was 1.00 mL/min, the pressure of the instrument was about 2400 psi for connecting with the concentrator column as shown in Figure 1 (Step 1, Step 2, and Step 4), and about 2200 psi for not connecting with the concentrator column as shown in Figure 1 (Step 3). For the determination of the 14 organic explosives, the eluent used was methanol–water (40/60, v/v). The column temperature was controlled at 32°C strictly, for the Acclaim Explosives E1 column was very sensitive toward the changes of temperature. The eluent flow rate was 1.00 mL/min. When the Acclaim Explosives E1 column was not connected with the concentrator column such as in Figure 1 (Step 1, Step 2, and Step 4), the pressure of the instrument was about 2700 psi; when they were connected as in Figure 1 (Step 3), the pressure was about 3500 psi. For the UVD detection, a detection wavelength range of 200 nm–595 nm was selected, and the peak spectra could be acquired automatically. This provided an individual library to be compiled for each compound.

Column-switching

The method was accomplished in four steps: (i) filling the sample loop; (ii) separating the inorganic cations from the organic explosives; (iii) loading the concentrator; (iv) analyzing the organic explosives and the inorganic cations simultaneously. Figure 1 illustrates how the system performed these tasks. First, the samples were loaded into the 20- μ L sample loop (Figure 1, Step 1). To ensure that the loop contained a representative sample, at least four loop volumes (80- μ L) were passed through the sample loop that was finished by an automated sample

injector. After the sample loop had been filled, the workstation program activated Valve I, and then the eluent (40:60, v/v) pushed the sample out of the loop and onto the Acclaim Explosives E1 column (Figure 1, Step 2). The organic explosives were retained on the Acclaim Explosives E1 column, when the inorganic cations were flowing by washing the column with the eluent at 1.00 mL/min. After 1.5 min, the inorganic ions started to be washed out, and the workstation program activated Valve II, (Figure 1, Step 3). The cations were then retained on the concentrator column, and most of the eluent (40:60, v/v) was washed out at the limited volume of the concentrator column. This step required at least 1 min for all cations to be collected. All cations were collected by the concentrator column; by activating Valve II again, the concentrator column was switched in-line with the 3 mM MSA as eluent and the IonPac SCS1 column (Figure 1, Step 4). After that, the five inorganic cations were eluted from the concentrator column and separated on the IonPac SCS1 column. At the same time, the 14 organic explosives were separated on the Acclaim Explosives E1 column simultaneously. All of these steps were finished within 45 min.

Results and Discussion

Selection of the switching time

In this experiment, a conductivity detector and a UVD detector were directly fixed after the Acclaim Explosives E1 column without any other sets. The signals of the inorganic and organic ions were recorded by the conductivity detector and the UVD detector, respectively. Figure 2 illustrates the signals from the unsuppressed conductivity detector for the inorganic ions with methanol–water (40:60, v/v) as eluent. Because inorganic ions could not be reserved on the reversed-phase column, all of the ions were washed out without reserve and eluted before the organics. Hence, there is an inorganic ions peak between 1.5–2.7 min on the conductivity chromatogram (Figure 2) before the organic peaks on the UVD chromatogram, whose earliest peak was at approximately 5.0 min.

The standard samples of the organic explosives and the inorganic cations were injected into the column-switching HPLC–IC system (Figure 1). Because the inorganic ions that were washed out started from 1.6 min, 1.5 min was selected for the first switching time of Valve II to make sure none of inorganic ions were lost. Due to the second switching time of Valve II, consideration of the retention capacity for the concentrator column, and collection completeness for the inorganic cations, the relationships between the different switching time and the peak area of each ion are plotted in Figure 3, and various switching times of 2.1 min, 2.2 min, 2.3 min, 2.4 min, 2.5 min, 2.6 min, 2.7 min, 2.8 min, 2.9 min, and 3.0 min were selected. As shown in Figure 3, the peak area increased with increasing switching time between 2.1–2.4 min. Then, the peak areas of each cations were kept on the same level between 2.5 min and 2.9 min. After that, some cations were washed out from the concentrator, so the peak areas of the cations decreased. From the previously mentioned, 1.5–2.7 min was selected as the switching time in the following experiments.

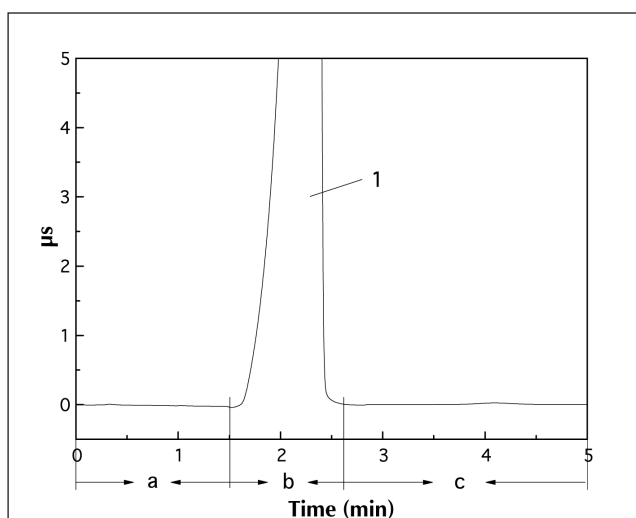


Figure 2. Unsuppressed conductivity chromatogram of inorganic ions. Peaks: 1 = inorganic ions (comprised of 10 mg/L cations and corresponding anions). Sample volume: 20 μ L; RP column: Acclaim Explosives E1 column (250 mm \times 4.6 mm i.d.); detection: UV, 254 nm; eluent: methanol–water (40:60, v/v); eluent flow rate: 1.00 mL/min; column temperature: 32°C. (a) (0–1.5 min): the rudimental resolution in the instrument was washed out; (b) (1.5–2.7 min): the inorganic ions which could not be reserved by RP column was washed out; (c) (2.7 min >): the eluent of methanol–water (40:60, v/v).

Organic explosives separation

The 14 organic explosives (HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, Tetryl, 2,4,6-TNT, 4-Am-2,6-NDT, 2-Am-4,6-DNT, 2,6-DNT, 2,4-DNT, 2-NT, 4-NT, and 3-NT) were determined by HPLC. To comply with U.S. EPA Method 8330, the separation of the organic explosives on the Acclaim Explosives E1 column was optimized by the methanol–water system. However, this column was less sensitive toward the changes in methanol content in the mobile phase. To achieve good separation in a reasonable run-time, 40% methanol (v/v) was selected. For the column temperature, which influenced the separation capacity of the Acclaim Explosives E1 column, sensitivity was selected at 32°C. Separation between 2-Am-4,6-DNT and 2,6-DNT deteriorates gradually when decreasing the temperature below 32°C. At 25°C, these two molecules completely coelute. As depicted in Figure 4B, a baseline separation between 2-Am-4,6-DNT and 2,6-DNT was not achieved under the eluent condition, but both organics could be determined. This drawback can be solved by the Acclaim Explosives E2 column, which is good at the separation of 2-Am-4,6-DNT and 2,6-DNT, behaving as a complementary column for the Acclaim Explosives E1 column.

Inorganic cations separation

In the chromatograms as shown in Figure 4A, the complete separation of the five inorganic cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) was achieved within 30 min with 3 mM MSA as the eluent. Since the IC instrument used three columns (two IonPac SCG1 columns and one IonPac SCS1 column), more attention should be paid to the pressure limit of these three columns. The practical backpressure limit for the IonPac SCS1 column is 4000 psi. When connecting one IonPac SCS1 column and two IonPac SCG1 columns together with 1.00 mL/min flow rate, the backpressure is about 2400 psi, so the method is feasible to determine organic explosives and inorganic cations simultaneously in the selected conditions.

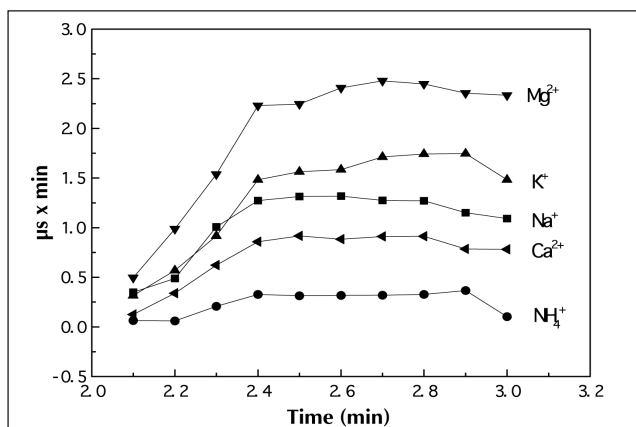


Figure 3. The peak area versus the second switching time of Valve II for inorganic cations (5 mg/L). HPLC conditions: Dionex Acclaim Explosive E1 column (250 mm × 4.6 mm, i.d.) with methanol–water (40:60, v/v) as eluent; eluent flow-rate: 1.00 mL/min; column temperature: 32°C; injection volume: 20 μL; detection: UV, 254 nm. IC conditions: Dionex IonPac SCG1 column (50 mm × 4 mm, i.d.) and the IonPac SCS1 column (250 mm × 4 mm, i.d.) with 3 mM MSA as eluent; eluent flow rate: 1.00 mL/min; column temperature: 30°C; concentrator: Dionex IonPac SCG1 column (50 mm × 4 mm, i.d.); detection: non-suppressed conductivity.

System blank

A system blank was determined by performing all the steps of the analysis with deionized water as the sample. The solution from the outlet of the concentrator column was injected into the IC system via switching the 6-port valve. The results showed that the inorganic cations (NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) were not detected, with the exception for Na^+ (1.26 mg/L). The blank value consisted of the impurities from the sample pretreatment and the chromatographic system. This result was then applied as a correction to all subsequent sample determination.

Analytical performance parameters

The limits of detection (LOD) for this method were determined by injecting a 20 μL sample solution and was calculated based on signal-to-noise ratio of 3 ($S/N = 3$). The results are shown in Table I. The LOD obtained by this method was 0.0048–0.0333 mg/L for the organic explosives and

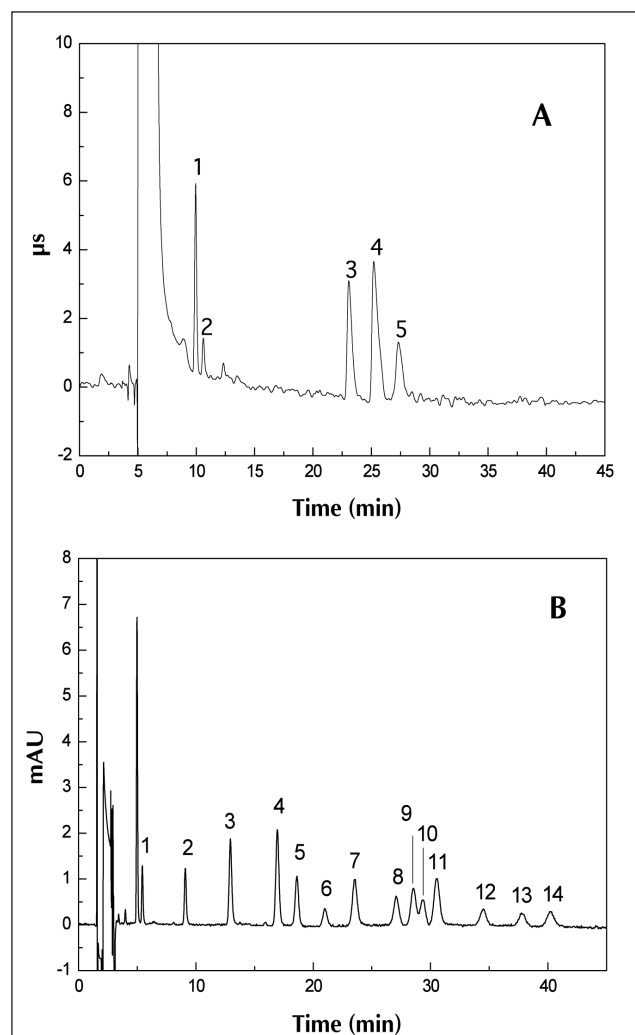


Figure 4. (A) Chromatograms of extract from the dust sample spiked at 3.0 mg/L inorganic cations; (B) 0.2 mg/L organic explosives via column switching. Switching time: 1.5–2.7 min. A: (1) Na^+ ; (2) NH_4^+ ; (3), K^+ ; (4) Mg^{2+} ; (5) Ca^{2+} . B: (1) HMX, (2) RDX, (3) 1,3,5-TNB, (4) 1,3-DNB, (5) NB, (6) Tetryl, (7) 2,4,6-TNT, (8) 4-Am-2,6-NDT, (9) 2-Am-4,6-DNT, (10) 2,6-DNT, (11) 2,4-DNT, (12) 2-NT, (13) 4-NT, (14) 3-NT. Other conditions are shown in Figure 3.

Table I. Summarized Data for the Calibration Graphs, LODs* and RSD* of Retention Times and Peak Area of Organic Explosives and Inorganic Cations†

Analyte	Linear range (mg/L)	Correlation coefficient	LOD (µg/L)	RSD (% , n = 8)	
				Retention time	Peak area
<i>Organic explosives</i>					
HMX	0.1–1	0.9999	0.0078	0.31%	1.00%
RDX	0.1–1	0.9999	0.0081	0.27%	0.92%
1,3,5-TNB	0.1–1	0.9999	0.0053	0.23%	1.82%
1,3-DNB	0.1–1	0.9994	0.0048	0.20%	0.82%
NB	0.1–1	0.9998	0.0083	0.22%	2.03%
Tetryl	0.1–1	0.9992	0.0247	0.21%	1.72%
2,4,6-TNT	0.1–1	0.9998	0.0095	0.25%	0.51%
4-Am-2,6-NDT	0.1–1	0.9996	0.0154	0.30%	3.26%
2-Am-4,6-DNT	0.1–1	0.9997	0.0130	0.29%	3.64%
2,6-DNT	0.1–1	0.9994	0.0173	0.28%	2.94%
2,4-DNT	0.1–1	0.9998	0.0095	0.27%	0.77%
2-NT	0.1–1	0.9993	0.0237	0.27%	1.39%
4-NT	0.1–1	0.9995	0.0333	0.28%	2.44%
3-NT	0.1–1	0.9999	0.0247	0.19%	1.47%
<i>Inorganic cations</i>					
Na ⁺	0.5–8	0.9971	0.0116	0.08%	1.85%
NH ₄ ⁺	0.2–8	0.9993	0.1851	0.08%	3.36%
K ⁺	0.2–8	0.9992	0.0440	0.02%	2.94%
Mg ²⁺	0.2–8	0.9998	0.0148	0.07%	1.80%
Ca ²⁺	0.5–8	0.9988	0.0342	0.10%	2.48%

* LOD = limit of detection and RSD = relative standard deviation.
† Obtained under the optimum operating condition as in Figure 6.

Table II. Determination Results for Organic Explosives and Inorganic Cations in Dust Sample (n = 3)

Anions	Found* (mg/L)	Added (mg/L)	Total* (mg/L)	Recovery (%)
<i>Organic explosives</i>				
HMX	ND	0.2	0.20 ± 0.00	98.05 ± 1.23
RDX	ND	0.2	0.20 ± 0.00	99.03 ± 1.68
1,3,5-TNB	ND	0.2	0.20 ± 0.00	100.45 ± 1.26
1,3-DNB	ND	0.2	0.21 ± 0.00	103.15 ± 0.36
NB	ND	0.2	0.20 ± 0.00	98.15 ± 0.36
Tetryl	ND	0.2	0.20 ± 0.00	97.73 ± 1.44
2,4,6-TNT	ND	0.2	0.20 ± 0.00	101.88 ± 2.47
4-Am-2,6-NDT	ND	0.2	0.21 ± 0.01	104.55 ± 3.95
2-Am-4,6-DNT	ND	0.2	0.21 ± 0.01	104.93 ± 4.48
2,6-DNT	ND	0.2	0.20 ± 0.01	99.38 ± 2.99
2,4-DNT	ND	0.2	0.20 ± 0.00	99.62 ± 1.53
2-NT	ND	0.2	0.19 ± 0.01	96.23 ± 3.01
4-NT	ND	0.2	0.20 ± 0.00	98.08 ± 1.13
3-NT	ND	0.2	0.19 ± 0.01	96.83 ± 2.73
<i>Inorganic cations</i>				
Na ⁺	1.52 ± 0.04	3.0	4.36 ± 0.21	94.67 ± 7.01
NH ₄ ⁺	0.46 ± 0.02	3.0	3.47 ± 0.11	100.18 ± 3.67
K ⁺	4.45 ± 0.03	3.0	7.65 ± 0.05	106.59 ± 1.57
Mg ²⁺	2.49 ± 0.13	3.0	5.44 ± 0.02	98.41 ± 0.61
Ca ²⁺	3.03 ± 0.13	3.0	6.08 ± 0.07	101.72 ± 2.20

* Corrected for system blank.
† ND, not detectable.

0.0116–0.1851 mg/L for the inorganic cations, which was feasible detecting the organic explosives and inorganic cations in real samples. The calibration curves were obtained by preparing a series of standard solutions with the concentration range of 0.1–0.5 mg/L for 14 organic explosives, 0.2–8.0 mg/L for NH₄⁺, K⁺, and Mg²⁺, and 0.5–8.0 mg/L for Na⁺ and Ca²⁺. All the calibration curves of the organic explosives and the inorganic cations showed good linearity with a correlation coefficient of $r \geq 0.997$ in the studied range. The reproducibility of the peak area was studied by eight repetitive determinations of 0.5 mg/L standard for 14 organic explosives, and 5.0 mg/L for the five inorganic cations under the condition in Figure 4. The relative standard deviations were below 0.31% and 3.64% for retention time and peak area, respectively. Table I summarizes the analytical data.

Application

The method was applied to the determination of organic explosives and inorganic cations in the dust sample. The real sample was taken from a public security bureau in Jiangshu Province, China, and pretreated as described in the “Experimental: Sample preparation and storage” section. The chromatograms of the dust sample spiked at 3.0 mg/L for the inorganic cations and 0.2 mg/L for the organic explosives under the optimal experimental conditions are shown in Figure 4. Figure 4A and 4B demonstrate the separation of inorganic cations and organic explosives, respectively. The concentrations of common organic explosives and inorganic cations were determined by using the present HPLC–IC column-switching method, and the results are shown in Table II. The obtained results show that the organic explosives were not detected in the dust sample, while the five inorganic cations were detected higher than their detection limits. The results also demonstrated that the recoveries of spiked samples were between 94.67%–106.59%.

Conclusions

The present system offered simple and easy operation as well as better selectivity for determining the 14 organic explosives (HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, Tetryl, 2,4,6-TNT, 4-Am-2,6-NDT, 2-Am-4,6-DNT, 2,6-DNT, 2,4-DNT, 2-NT, 4-NT, and 3-NT) and the five inorganic cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺). Compared to the traditional method, the HPLC–IC column-switching instrument applies a relatively short analysis time and low cost for the sample. The recoveries obtained in the range of 94.67–106.59% were satisfactory. The results of this study indicate that the HPLC–IC column-switching instrument will be convenient and applicable to real samples.

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