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Coupled reversed-phase and ion chromatographic system for the simultaneous identification of inorganic and organic explosives

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ABSTRACT

There are many methods available to detect and positively identify either organic or inorganic explosives separately, however no one method has been developed which can detect both types of explosive species simultaneously from a single sample. In this work, a unique coupled-chromatographic system is reported for the simultaneous determination of both organic and inorganic explosive species and is used for pre-blast analysis/identification purposes. This novel approach is based on the combination of reversed-phase high performance liquid chromatography and ion chromatography which allows trace levels of organic and inorganic explosives to be determined simultaneously from a single sample. Using this procedure, a 20 min reversed-phase separation of organic explosives is coupled to a 16 min ion-exchange separation of anions present in inorganic explosives, providing a complete pre-blast analysis/identification system for the separation and detection of a complex mixture containing organic and/or inorganic explosive species. The total analysis time, including sufficient column re-equilibration between runs, was <25 min using the coupled system. By this method, the minimum resolution for the organic separation was 1.16 between nitroglycerin and tetryl and the detection limits ranged from 0.31 mg L^{-1} for cyclotetramethylene tetranitramine (HMX) and 1.54 mg L^{-1} for pentaerythrite tetranitrate (PETN), while the minimum resolution for the inorganic separation was 0.99 between azide and nitrate, and the detection limits ranged from 7.70 μg L^{-1} for fluoride and 159.50 μg L^{-1} for benzoate.

1. Introduction

In recent years, due to an increase in world-wide terrorist events, the need for an improvement in the identification and detection of homemade explosive devices (HMEs) has gained considerable interest, both in terms of identifying unknown components prior to detonation (pre-blast analysis) and analysing debris and residues after an explosion (post-blast analysis). An increase in the number of incidents perpetrated using HMEs, fabricated from a variety of different chemical compositions, has resulted in an increasing demand for security checks of explosives. The relative ease of attainment and ready availability of some HME components, along with the fact that chemicals or materials are often less restricted or uncontrolled, has made HMEs relatively easy to fabricate and difficult to detect and control. As a result, more sophisticated and improved technologies and methods are essential for the identification and detection of both organic and inorganic based explosive devices.

Some of the earlier detection methods for explosive components have been based upon various chemical colour spot tests [1–3] but more sensitive and selective techniques have since been developed. Many high explosives based on organic compounds are quite successfully detected using technology such as ion mobility spectrometry (IMS) [4], which while lacking the ability to provide quantitative results, offers rapid and reliable on-site detection. For more sensitive analysis and identification of organic and inorganic components of explosives, a number of spectroscopic methods [5,6] have been successfully employed for explosive residue analysis including electrothermal atomic absorption spectroscopy (ET-AAS) and mass spectrometry (MS). Further alternatives based upon X-ray powder diffraction (XRD), Fourier transform infra-red spectroscopy (FT-IR), capillary electrophoresis (CE) [7,8], or chromatographic methods [9,10] such as ion chromatography (IC), liquid chromatography (LC) or gas chromatography (GC) can also be employed as less expensive and often more suitable analytical techniques. The use of CE, IC or LC is typically preferable due to their sensitivity and selectivity, along with their field deployability. These methods also minimise potential issues associated with thermal stability of some explosives, such as tetryl or some nitrate esters which can decompose or hydrolyse, as they are carried out at room temperature [9].

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Methods based upon HPLC have been applied routinely to the analysis of organic explosives [11]. The application of reversed phase HPLC is more often used than normal phase, due to system stability, low toxicity and transparency of the mobile phase to ultraviolet (UV) light [9]. When combined with UV detection, HPLC provides a powerful tool for the analysis of explosives in aqueous extracts. For example, this technique is used by the Environmental Protection Agency (EPA) as the specified method for the quantitative analysis of high explosives (nitroaromatics, nitramines and nitrate esters) in environmental samples [12].

In terms of inorganic explosives, IC can be used to provide an extremely sensitive and selective method for the analysis of explosive residues [13]. Since its development in the early 1970s [14], this technique has been used to determine low levels of both inorganic anions and cations, and as early as 1983 the US Federal Bureau of Investigation (FBI) reported the use of IC for the analysis of explosive residues [15]. IC has since proven to be an extremely efficient technique for the analysis of inorganic explosives due to its high sensitivity and accuracy [13,16]. Previous work in our laboratory has led to a fast IC method, based on short ion-exchange columns, for the rapid determination of a range of inorganic anions present in inorganic explosives [17]. Johns et al. developed an IC system for the identification of inorganic-based improvised explosive devices [18]. This system was successfully employed to detect 18 target anions and 12 target cations from post-blast residues of a number of common inorganic explosives, including ammonium nitrate/fuel oil mixtures, black powder, chlorate/sulfur/aluminium and chlorate/perchlorate/sugar mixtures. CE has also been successfully employed for the positive chemical identification of explosive residues. Hutchinson et al. developed a portable CE system, with indirect photometric and conductivity detection, for the determination of 15 target anions and 12 target cations in homemade inorganic explosives [19,20]. Hargadon and McCord also used IC and CE in tandem for the analysis of explosive residues [21]. Due to the almost orthogonal separation mechanisms of CE and IC, this determination resulted in a sensitive and highly efficient separation of both the anionic and cationic components from various pipe bomb residues.

The comprehensive separation and determination of complex mixtures of explosives, including both organic and inorganic analytes, is a difficult task due to the range of components which may potentially be present in the sample. As a result, there are only a limited number of conventional separation techniques available for the simultaneous determination of both organic and inorganic components. Warren et al. [22] developed a procedure for the simultaneous extraction and recovery of organic and inorganic explosives from a single sample swab. However, two separate techniques were required for sample analysis, namely GC for the organic samples and IC/CE for the inorganic analysis. In more recent advances, Morales and Vázquez developed a method to simultaneously determine inorganic cations and organic gunshot residues using capillary electrophoresis [23]. Using this method, 11 organic and 10 inorganic cation components were successfully detected from residues such as unburned powder, primer and cartridge particles and metals from the gun barrel. To date, no single system has been developed for the simultaneous determination of organic and inorganic anionic components of explosive devices. It has been reasoned by the authors and the forensic user community that anion determination provides far more diagnostic information towards the chemical identification of the explosive than the cationic components for the detection and identification of these inorganic improvised explosive devices [19], hence the focus of this paper.

In the work presented here, a coupled chromatographic method based on HPLC and IC was developed for the pre-blast analysis/identification of organic and inorganic explosive components from a single sample. Individually, a single, conventional HPLC or IC system cannot provide the separation power required for the simultaneous detection of both organic and inorganic explosives, but when combined as a coupled chromatographic system, the techniques can offer an excellent solution for the separation and detection of these explosives.

2. Experimental

2.1. Instrumentation

A Dionex ICS-3000 ion chromatography system controlled using Chromeleon® software (version 6.80) was used for all analyses during this work and all the instrumental components were obtained from Dionex (Sunnyvale, CA, USA). The dual system and modular design of the ICS-3000 instrument allows a variety of configurations to be employed, including two completely independently controlled chromatographic systems, or a coupled chromatography system combining both IC and HPLC. Both modes were used during this work, with independent organic and inorganic analyses being carried out in the initial stages of the study, and subsequent combination of both systems to form a coupled manifold in later studies. A schematic of the coupled chromatography system combining both HPLC and IC is shown in Fig. 1.

The HPLC separations were carried out on a commercially available Dionex Acclaim® Explosives E2 column (150 mm × 3 mm), containing a silica-based reversed-phase substrate (3-μm particle diameter) designed specifically for the separation of nitroaromatics, nitramines and nitrate esters. The gradient pump enabled the aqueous-methanol eluent to be prepared on-line by the system. A packed-bed gradient mixer (48 mm × 4 mm, GM-3 mixer column packed with Teflon rods) was installed to improve the mixing of the eluent components. The HPLC system was fitted with a 5 μL sample loop that was used to introduce the sample via a Dionex AS autosampler. All of the sample vials for use with the autosampler were rinsed thoroughly with deionised water prior to use. UV detection was carried out at 210 nm to monitor the eluted organic analytes. This low wavelength was chosen as nitrated esters, such as nitroglycerin and PETN only absorb at wavelengths less than 215 nm. An IonPac® ultra trace anion concentrator column (UTAC) was incorporated after the UV detector to collect the inorganic anions from the sample, which were unretained by the reversed phase column. These inorganic anions were then transferred via a switching valve to the coupled IC system for separation. The UTAC is an ultra clean (low sulfate), low pressure anion-exchange concentrator column (50 mm × 4 mm, 145 μL void volume) designed specifically for stripping ions from an aqueous sample and concentrating the analytes of interest.

The IC separations were carried out using a commercially available polymeric Dionex AS20 column (250 mm × 4.6 mm). This stationary phase is a hyperbranched anion-exchange polymer electrostatically attached to a surface-sulfonated polymeric substrate (7.5-μm diameter). The IC system used a reagent-free eluent generator (RF-IC) with an EluGen Cartridge (EGC II KOH cartridge) to generate potassium hydroxide eluent of the required composition for the gradient separations. A continuously regenerated anion trap column (CR-ATC, <100 μL void volume) was employed to remove trace contaminants from the eluent. Post-column eluent suppression was carried out using an anion self-regenerating suppressor (ASRS-ULTRA II 4 mm, <50 μL void volume), and suppressed conductivity detection was used to monitor the eluted inorganic analytes.

Both of the chromatographic systems used 0.030" ID polyetheretherketone (PEEK) tubing throughout the system. Chromatographic data were collected from both systems at 5 Hz and chromatograms were processed using the Chromeleon® software.

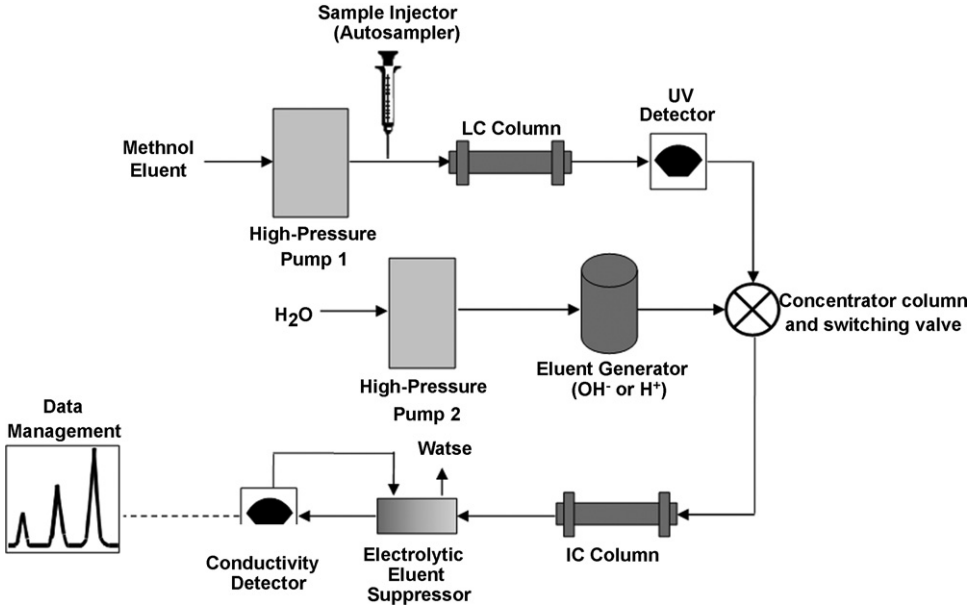

Fig. 1. Schematic of coupled chromatography system based on HPLC using a silica-based reversed phase Acclaim® Explosives E2 column and IC using a polymeric IonPac® AS20 column.

2.2. Methods

The Acclaim® E2 column used for the separation of the organic explosives was operated using a flow-rate of 0.7 mL/min. The aqueous-methanol eluent gradient programme was as follows: 0–10 min at 38.5% methanol (v/v) isocratic eluent followed by 10–20 min at a linear gradient ramp of 38.5–70.0% methanol (corresponding to an increase in eluent strength of 3.15% methanol per minute). As gradient elution was used, a column re-equilibration period of approximately 3 min was required after each gradient analysis. The column was housed in the lower chromatography compartment in the ICS-3000 instrument which was thermostatically controlled at 32 °C.

The AS20 column was operated at a flow-rate of 1.4 mL/min and a temperature of 30 °C. This column was housed in the upper chromatography compartment of the ICS-3000 instrument. The potassium hydroxide multistep eluent profile consisted of 0.0–9.5 min at 10 mM, 9.5–16.0 min at 55 mM and 16.0–20.0 min at 10 mM eluent. The final 4 min step allowed for re-equilibration of the column back to the starting potassium hydroxide concentration.

2.3. Reagents

All solvents were HPLC grade unless stated otherwise. All chemicals used were of analytical reagent grade and were used as supplied by Sigma–Aldrich (Sydney, Australia) unless otherwise stated. The eluents and standard solutions were prepared using ultra-pure, deionised, 18.2 MΩ water from a Millipore Milli-Q water purification system (Bedford, MA, USA). HPLC grade methanol was obtained from Chromasolv® (Sigma–Aldrich, Sydney, Australia). Working inorganic anion standards were prepared from 1000 mg L^{-1} stock standard solutions. The chloride, chlorate, nitrate, perchlorate, and thiocyanate standard solutions were all prepared from their respective sodium salts, while the standard solutions of sulfate, benzoate, azide, fluoride and phosphate were prepared from their potassium salts. All of the standard solutions were filtered using 0.45-μm nylon membrane filters (Millipore) and degassed by ultrasonication. Individual organic explosive standards (1000 mg L^{-1} in acetonitrile) were obtained from AccuStandard (New Haven, CT, USA) and were used to prepare working standard solutions by dilution with acetonitrile (Chromasolv®, Sigma–Aldrich, Sydney, Australia).

2.4. Sample preparation

A range of sample swabs of the inorganic anion analytes were collected from a variety of surfaces including glass, plastic, cloth and skin using sterile sample swabs (Mediprep Inc.), after applying standard solutions of these analytes to the surfaces and allowing them to air dry at room temperature. These sample swabs are individually pre-packaged and pre-saturated with 70% isopropanol. Following sampling, the swabs were allowed to dry and then placed in a vial containing 2.0 mL of Milli-Q water. The swabs were then extracted in an ultrasonication bath for 5 min. The resulting extract was filtered through 0.45 μm nylon membrane filters to remove any particulate material prior to sample analysis. Sample blanks were also collected of the sterile sample swab employing a similar extraction procedure.

In order to assess the capability of the coupled system a series of organic samples, containing known concentrations of organic explosive species, were prepared 'in-house' by depositing varying amounts of the target organic explosive standards onto a glass surface. These samples were then allowed to air dry at room temperature before sampling was carried out. When the samples had completely dried, the surface of the glass was swabbed using sterile MWE102 rayon sample swabs (Imbros, Tasmania, Australia) which had previously been moistened with an extraction solution. Three extraction solutions (Milli-Q water, pure acetonitrile and a mixture of 50/50 v/v acetonitrile/Milli-Q water) were investigated for comparative purposes during the course of this study. The sample swabs were then placed in individual glass sample vials containing 1.0 mL of extraction solution and extracted by ultrasonication for 5 min. The resulting extracts were then filtered through 0.45-μm nylon membrane filters to remove any particulate material prior to sample analysis. Sample blanks were collected from the glass surface, prior to sample deposition, using a similar swabbing and extraction procedure. A swab blank was also collected from an unused sterile sample swab using 1.0 mL of extraction solution using the method described previously.

Table 1
Figures of merit associated with the IC system for the separation and detection of the target inorganic anionic based species using the IonPac® AS20 column for separation purposes.

Target	Retention time Mean ($n = 3$)	Retention time % RSD	Resolution ($n = 3$)	Peak area % RSD	Detection Limit (mg L^{-1})
Fluoride	3.53	0.5	–	0.2	0.01
Chloride	5.29	0.4	7.90	4.2	0.01
Chlorate	7.27	0.4	7.39	2.4	0.04
Benzoate	8.20	0.5	2.57	2.0	0.16
Nitrate	8.91	0.3	1.83	3.1	0.04
Azide	9.31	0.2	0.99	1.1	0.04
Sulfate	11.05	0.3	3.77	1.5	0.03
Phosphate	13.09	0.2	10.24	1.3	0.07
Thiocyanate	14.94	0.3	13.01	2.6	0.03
Perchlorate	15.90	0.2	2.42	2.6	0.08

3. Results and discussion

3.1. Inorganic analysis

In this study, a set of inorganic target analytes was identified after consultation with various Australian protective service agencies. This analyte set consisted of anions potentially present in inorganic explosives (prior to detonation), together with some common background anions. In total, ten inorganic anions (fluoride, chloride, sulfate, nitrate, benzoate, phosphate, chlorate, azide, thiocyanate and perchlorate) were selected. It was deemed necessary to identify and separate the background anions from the explosive anions in order to minimise the likelihood of both false positive and false negative results arising from common background or environmental interferences.

Preliminary investigations were carried out in order to identify and evaluate suitable stationary phases and eluents for the separation of the inorganic target analytes. Using the Virtual Column® Separation Simulator software [Dionex, Sunnyvale, CA, USA], a systematic search of a wide range of commercial columns and eluents for the separation of the targets was carried out. This software is a useful modelling tool for assessing the retention characteristics and separation selectivities of various stationary phases and eluents. From these simulations, the Dionex AS20 stationary phase with a potassium hydroxide multi-step gradient eluent was chosen on the basis of separation selectivity and overall analysis time. Highly polarisable ions, such as thiocyanate and perchlorate, can be strongly retained on anion-exchange stationary phases which can result in longer analysis times. The use of an AS20 column is therefore particularly suited to this work as it is designed specifically for the rapid elution of perchlorate. The 7.5 μm particle size is also advantageous in reducing column back-pressures, allowing elevated flow-rates for even faster analyses. It is envisaged this system could be used for the pre-blast screening and detection of explosive species where analysis times should ideally be kept as short as possible allowing higher sample throughput.

The IonPac® AS20 analytical column (4.6 mm × 250 mm) was optimised for the separation of the target anions using the Virtual Column® simulation software and Table 1 shows the analytical figures of merit for the optimised separation using a multi-step hydroxide gradient elution profile. Triplicate injections were carried out under the optimised conditions with the average percentage relative standard deviation (%RSD) values for retention time and peak area being 0.3% and 2.1%, respectively. The minimum resolution was 0.99 between azide and nitrate and the detection limits ranged from 0.01 mg L^{-1} for fluoride to 0.16 mg L^{-1} for benzoate, based on a signal-to-noise (S/N) ratio of 3. A maximum flow-rate of 1.4 mL/min was achieved when using optimal conditions. It was found that further elevation of flow-rates was not possible due to the maximum back-pressure limitation of 3000 psi applicable with this IC system.

3.2. Organic analysis

The Dionex Acclaim® Explosives series of columns (E1 and E2) have been designed for the separation of the 14 organic explosives listed in USEPA method 8330, which is the specified method for the quantitative analysis of explosives in groundwater samples. The Acclaim® Explosives E1 column provides high separation efficiency, symmetrical peaks and good linearity for all the compounds listed in this EPA method. The Acclaim® Explosives E2 column on the other hand provides complementary selectivity to the E1 column with comparable efficiency and linearity. It also has the added advantage of allowing separation of the nitrate ester species along with the nitroaromatics and nitramines. Fig. 2 shows the optimised isocratic separation on the Acclaim® Explosives E2 column with UV detection at 210 nm of 2,4,6-trinitrotoluene (TNT), cyclotetramethylene-tetranitramine (HMX), cyclotrimethylene-trinitramine (RDX), tetryl, 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), nitrobenzene (NB), 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT), 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), plus the nitrate esters pentaerythrite tetranitrate (PETN) and ethylene glycol dinitrate (EGDN). The average %RSD for retention time was 0.4% and for peak area was 1.9% ($n = 3$). The minimum resolution was 0.92 for the 3-NT and 4-NT peak pair and the detection limits ranged from 1.38 mg L^{-1} for PETN and 0.12 mg L^{-1} for 1,3-DNB (S/N = 3).

In view of the length of the analysis for the separation of the 16 explosive species in Fig. 2, it was decided to reduce the range of

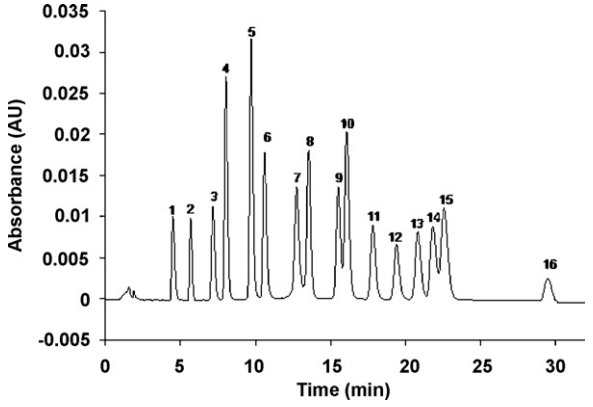

Fig. 2. Optimised separation of the 16 target organic based explosive species carried out on an Acclaim® Explosives E2 column 3.0 mm × 150 mm commercial analytical column. Peak: 1 = HMX, 2 = EGDN, 3 = RDX, 4 = 1,3,5-TNB, 5 = 1,3-DNB, 6 = NB, 7 = TNT, 8 = tetryl, 9 = 4-A-2,6-DNT, 10 = 2-A-4,6-DNT, 11 = 2,6-DNT, 12 = 2,4-DNT, 13 = 2-NT, 14 = 4-NT, 15 = 3-NT, 16 = PETN. Chromatographic conditions: injection = 5 μL, 5 mg L^{-1}; flow-rate = 0.42 mL/min; temperature = 30 °C; detection = ultra violet detection at 210 nm; mobile phase = 48/52 v/v methanol/Milli-Q.

Table 2
Figures of merit associated with the LC system for the separation and detection of the target organic based explosive species using the Acclaim® Explosives E2 column.

Target	Retention time Mean ($n=3$)	Retention time % RSD	Resolution ($n=3$)	Peak area % RSD	Detection Limit (mg L^{-1})
HMX	3.51	0.2	–	0.4	0.31
EGDN	4.57	0.1	3.80	2.0	0.56
RDX	5.70	0.3	3.90	2.7	0.39
Tetryl	11.44	0.1	15.15	2.7	0.45
NG	12.19	0.1	1.16	1.8	1.07
TNT	13.02	0.2	1.23	1.7	0.47
DNT[a]	14.43	0.1	2.89	2.6	0.84
PETN	19.67	0.3	14.31	2.0	1.54

[a] 2,4-DNT and 2,6-DNT.

analytes to the more common organic-based explosives, consisting of a selection of nitroaromatics, nitramines and nitrate esters. Nine target organic explosives were selected, consisting of HMX, RDX, tetryl, TNT, 2,4-DNT and 2,6-DNT, PETN, EGDN and nitroglycerin (NG). The Acclaim® Explosives E2 column was best suited for this group of analytes. Methanol was chosen over acetonitrile for the eluent as precipitation of salts can occur when employing acetonitrile. Table 2 shows the analytical figures of merit obtained under optimised gradient conditions. The average %RSD for retention time was 0.1%, while that for the peak area was 2.0% ($n=3$). The minimum resolution was 1.16 for NG and tetryl and the detection limits ranged from 0.31 mg L^{-1} for HMX and 1.54 mg L^{-1} for PETN (S/N = 3). It should be noted that this method was optimised such that both of the dinitrotoluene species (2,4-DNT and 2,6-DNT) co-eluted as a single peak.

3.3. Coupled chromatography

In order to permit the simultaneous determination of both the inorganic and organic analytes, a coupled chromatographic system was implemented (Fig. 1). Using this configuration, the two independent separation techniques developed earlier can be combined so that all analytes can be separated from a single sample injection. The sample (5 μL) is introduced via the autosampler into the LC system where the organic explosive species are separated on the Acclaim® Explosives E2 column, whereas the inorganic species are unretained (or weakly retained in the case of benzoate) and pass rapidly through this column before being transferred into the IC system for separation on the IonPac® AS20 analytical column.

There are several techniques which could be employed to transfer the unretained inorganic anions to the IC system, including the use of a stopped-flow system or a trap/concentrator column. The stopped-flow system has the drawback of extending the total analysis time, so the use of a concentrator column was investigated. An ultra clean, low pressure UTAC column (Dionex, Sunnyvale, CA, USA) was incorporated in-line to collect and concentrate the inorganic anions from the LC system and transfer these to the IC system via a switching valve. A loading/trapping time of 5 min was deemed to be sufficient for collection of the unretained inorganic species on the UTAC column.

Using this coupled chromatographic system, a sample comprising 10 inorganic anions and 9 organic explosives could be separated and identified in 20 min, as shown in Fig. 3(a) illustrates the separation of the organic explosive species; while Fig. 3(b) shows the separation of the inorganic anions, with both separations running simultaneously. It should be noted that in Fig. 3(b) the first 5 min prior to the start of the analysis (shown as $t=0$) was the allocated collection period for the trapping of the inorganic anions on the UTAC column. At $t=0$, the switching valve was actuated, transferring the inorganic ions from the trap column to the IC system. The analytical figures of merit for the coupled system were similar to those reported in the previous sections for the individual chromatographic systems. The total analysis time using the coupled system, including allowance for column re-equilibration was <25 min.

3.4. Sample analysis

Field sample swabs containing inorganic anion analytes were obtained from a variety of surfaces, including skin, fabric, metal, plastic, glass and granite. The loaded swabs (and blanks) were then extracted with water and the extract filtered through a syringe filter, followed by analysis using the optimised coupled chromatographic system. The samples were analysed in triplicate using the optimised coupled chromatographic system. In addition, extracts from blank swabs were also analysed and measurable amounts of chloride and sulfate were found, which was taken into account

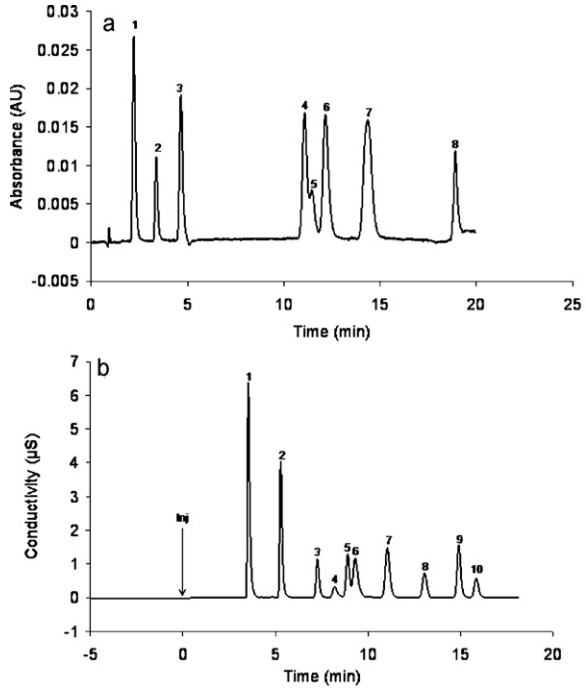

Fig. 3. Simultaneous separation of (a) organic and (b) inorganic anionic based explosives on coupled chromatographic system (blank signal subtraction carried out in both cases). (a) Peak: 1 = HMX, 2 = EGDN, 3 = RDX, 4 = tetryl, 5 = NG, 6 = TNT, 7 = DNT (2,4-DNT and 2,6-DNT), 8 = PETN. Chromatographic conditions: Acclaim® Explosives E2 column 3.0 mm × 150 mm analytical column; injection = 5 μL, 5 mg L^{-1}; flow-rate = 0.70 mL/min; mobile phase = methanol gradient: 38.5% from 0 to 10 min, 38.5% to 70.0% from 10 to 20 min; detection = ultra violet detection at 210 nm; temperature = 32 °C. (b) Peak: 1 = fluoride, 2 = chloride, 3 = chlorate, 4 = benzoate, 5 = nitrate, 6 = azide, 7 = sulfate, 8 = phosphate, 9 = thiocyanate, 10 = perchlorate. Chromatographic conditions: IonPac® AS20 4.6 mm × 250 mm analytical column; injection = 5 μL, 5 mg L^{-1}; flow-rate = 1.4 mL/min; temperature = 30 °C; detection = suppressed conductivity (ASRS-ULTRA II 4 mm, current 168 mA); eluent = potassium hydroxide gradient: 10 mM from 0.0 to 9.5 min, 55 mM from 9.5 to 16.0 min, 10 mM from 16.0 to 20.0 min.

Table 3
Percentage recoveries of simulated samples.

Target	Milli-Q	50/50 v/v Acetonitrile/Milli-Q	Acetonitrile
HMX	38 ± 2%	83 ± 2%	82 ± 3%
EGDN	64 ± 3%	81 ± 1%	85 ± 6%
RDX	47 ± 3%	62 ± 1%	78 ± 5%
Tetryl	53 ± 2%	77 ± 2%	95 ± 7%
NG	43 ± 1%	76 ± 3%	75 ± 5%
TNT	41 ± 6%	82 ± 4%	102 ± 6%
DNT	39 ± 5%	73 ± 2%	89 ± 2%
PETN	25 ± 5%	82 ± 6%	91 ± 5%
Fluoride	98 ± 6%	84 ± 3%	23 ± 5%
Chloride	92 ± 3%	75 ± 5%	43 ± 2%
Chlorate	101 ± 4%	72 ± 6%	30 ± 3%
Nitrate	97 ± 2%	91 ± 5%	32 ± 3%
Sulfate	99 ± 3%	83 ± 4%	22 ± 2%
Phosphate	93 ± 5%	79 ± 1%	16 ± 6%
Thiocyanate	92 ± 4%	76 ± 3%	33 ± 3%
Perchlorate	87 ± 3%	71 ± 3%	12 ± 5%

when analysing the sample swabs. A blank subtraction was carried out by the Chromeleon® software by simply subtracting the blank signal from the actual sample during data processing to give a corrected result. Quantitative recoveries were found for all inorganic analytes. All of the analysed sample swabs were found to contain low levels of fluoride (0.2–1.4 mg L^{-1}), chloride (2.5–7.8 mg L^{-1}), nitrate (0.2–1.5 mg L^{-1}) and sulfate (0.4–1.8 mg L^{-1}) however no traces of organic explosives were found in any of these field samples.

A series of samples were prepared by applying known quantities of the target organic analytes to a glass substrate, followed by extraction as described in the experimental section. Milli-Q water can be used for organic extraction purposes [24] however the solubility of some organic explosives, such as nitramines, is lower in water than organic solvents. For comparative purposes, three extraction systems were investigated in this work, namely Milli-Q water, pure acetonitrile and a mixture of 50/50 v/v acetonitrile/Milli-Q water. Table 3 summarises the results of this study and recoveries of >62% were obtained for 50/50 v/v acetonitrile/Milli-Q water, while recoveries of >75% were obtained when pure acetonitrile was used. Although Milli-Q water could be used for extraction purposes, the recoveries were found to be considerably lower than with pure acetonitrile or a mixture of acetonitrile/Milli-Q water due to the earlier mentioned solubility issues. A series of inorganic samples were also analysed in a similar manner using the three extraction systems to investigate the effect of acetonitrile on recoveries. Recoveries of >87% were obtained when Milli-Q water was used for extraction purposes, while recoveries of >71% and <43% were obtained when 50/50 v/v acetonitrile/Milli-Q and pure acetonitrile were used respectively. As a result a 50/50 v/v mix of acetonitrile/Milli-Q was deemed most suitable in this case for the extraction of both organic and inorganic targets in this study.

4. Conclusions

The current investigation shows the potential of a coupled chromatography system for the simultaneous separation and detection of both organic and inorganic anionic explosive components, by combining the use of HPLC and IC for pre-blast analysis/identification purposes. The coupled system requires a total analysis time of less than 25 min, including system re-equilibration, and accomplishes the separation and detection of both organic and inorganic anionic based explosive species at low levels from a single pre-blast sample. The system was found to be reproducible and reliable, with typical %RSD of under 0.4% being achieved for retention times and under 2.0% for peak areas. To the best of our knowledge, this system is the first total analysis system for the separation and detection of both pre-blast organic and/or inorganic anionic explosive species from a single sample.

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