Journal of Chromatography A, 1218 (2011) 3007–3012

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

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

Éadaoin Tyrrell[a], Greg W. Dicinoski[a], Emily F. Hilder[a], Robert A. Shellie[a], Michael C. Breadmore[a], Christopher A. Pohl[b], Paul R. Haddad[a,*]

[a] Australian Centre for Research on Separation Science (ACROSS), School of Chemistry, University of Tasmania, Private Bag 75, Hobart, TAS 7001, Australia
[b] Dionex Corporation, PO Box 3603, Sunnyvale, CA 94088, USA

ARTICLE INFO

Article history:
Received 16 January 2011
Accepted 17 March 2011
Available online 7 April 2011

Keywords:
Ion chromatography
High performance liquid chromatography
Coupled chromatography
Inorganic explosives
Organic explosives
Forensic science
Improvised explosive devices (IEDs)

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].

---

[*] Corresponding author. Tel.: +61 3 6226 2179; fax: +61 3 6226 2858.
E-mail address: Paul.Haddad@utas.edu.au (P.R. Haddad).

0021-9673/$ – see front matter Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2011.03.046

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.