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Determination of chlorine containing species in explosive residues using chip-based isotachophoresis

Jeff E. Prest[a,*], Matthew S. Beardah[b], Sara J. Baldock[a], Sean P. Doyle[b], Peter R. Fielden[a], Nicholas J. Goddard[a], Bernard J. Treves Brown[a]

[a] *School of Chemical Engineering and Analytical Science, The University of Manchester, Manchester, UK*
[b] *Forensics Explosives Laboratory, Dstl, Fort Halstead, Sevenoaks, Kent, UK*

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ABSTRACT

A new method has been developed to allow the determination of the chlorate, chloride and perchlorate anions in inorganic explosive residues to be made using isotachophoresis (ITP). To enable a good separation of these species to be achieved the method involves the use of two complexing agents. Indium(III) is used to allow the determination of chloride whilst using nitrate as the leading ion and α-cyclodextrin is used to allow the separation of chlorate and perchlorate. Separations were carried out using a miniaturised poly(methyl methacrylate) (PMMA) separation device. The method was applied to analysing both model samples and actual inorganic explosive containing residue samples. Successful determinations of these samples were achieved with no interference from other anions typically found in inorganic explosive residues. Limits of detection (LOD) for the species of interest were calculated to be 0.80 mg l^{-1} for chloride, 1.75 mg l^{-1} for chlorate and 1.40 mg l^{-1} for perchlorate.

1. Introduction

The number of inorganic explosives related terrorist and criminal bombings in recent years, e.g. London (1999), Bali (2002) and Istanbul (2003), has heightened the importance of the rapid characterisation of ionic constituents present in explosive residues [1].

Many improvised explosive devices (IEDs) contain home-made inorganic explosive mixtures as the explosive charge. Such explosives typically comprise a mixture of an inorganic oxidiser, a fuel and a range of other substances that are used to modify the performance of the composition for a given purpose. For devices that have been initiated, the post-explosion residues will often comprise a complex mixture of combustion products and possibly some unconsumed low explosive composition.

Expeditious reporting of results to investigators is an essential part of any criminal investigation. Often, in the initial stage of an investigation, a purely qualitative appraisal of the composition of post-blast explosion residues may be required. In terms of forensics analysis, it is the identification of unconsumed materials which is of most value. The capability to provide such 'live' results at a scene of crime, using portable detection equipment, could be extremely beneficial to the investigation [1].

Currently the most widely used laboratory-based technique for analysing inorganic explosive residues is ion chromatography (IC) [2–5]. However, capillary zone electrophoresis (CZE) has also been proven to be a useful technique for use in this application area. Methods have been developed for the capillary zone electrophoretic analysis of both inorganic anions [3,6–8] and cations [8,9] found in explosive residues. A method incorporating reversed electroosmotic flow and dual end injection has also been developed to enable the simultaneous determination of both of these types of ions in a range of inorganic explosives [10]. CZE has also been successfully applied to the analysis of dermal nitrate, a marker of firearm discharge [11] and for the determination of inorganic and organic cations found in gunshot residues [12].

CZE has shown itself to be a suitable technique for performing in a miniaturised format. There have been reported separations using miniaturised devices with contactless conductivity detectors of some inorganic anions [13–15] and inorganic cations [13–16] that are likely to be found in explosive residues. A device with dual-opposite injection which achieves detection by means of a contactless conductivity has also been demonstrated to allow the determination of both anions and cations found in a model inorganic explosive residue [14,17]. Capillary electrophoretic methods have also been found to be useful for analysing organic explosives. Thus, miniaturised separations of model mixtures of such materials have also been achieved using non-aqueous CZE [18] and micellar electrokinetic chromatography (MEKC) [19–21]. The simultaneous

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[*] Corresponding author. Tel.: +44 161 3068900; fax: +44 161 3064896.
E-mail address: j.prest@manchester.ac.uk (J.E. Prest).

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determination of ionic and nitroaromatic explosives has also been achieved. This was done using a chip device fitted with two types of detector; a contactless conductivity detector for ionic species and an amperometric detector for electroactive species [22].

Another type of electroseparation technique is isotachophoresis (ITP). This method offers a number of useful features compared to CZE such as the ability to preconcentrate dilute samples and the ability to limit the species which can be detected by careful selection of the electrolytes employed. However, whilst the technique is eminently suitable for the analysis of small anions, and has been widely used for this purpose [23,24], it has not been previously employed for the testing of post-explosion residues. Like many of the other forms of electrophoresis, ITP has also previously shown itself to be adaptable to performing in a miniaturised format. Thus, miniaturised ITP has been used for a number of applications such as the determination of anions in wine [25] and metal cations in industrial process streams [26].

This paper presents the first known application of miniaturised isotachophoresis for the analysis of inorganic explosive residues. A number of species, such as chlorates, nitrates, perchlorates and sulphur, are used in the production of different kinds of inorganic explosives. Of these, the determination of the chlorate and perchlorate species in post-explosion residues is of particular interest. This is because these species are rarely encountered in significant amounts in the natural environment [27]. The determination of chloride in association with chlorate and perchlorate is also of some importance. This is because chloride is found in post-explosion residues associated with perchlorate/chlorate-based explosives.

To achieve the analysis of inorganic explosive residues using ITP, a new electrolyte system was developed to enable the determination of the chlorine containing anions chloride, chlorate and perchlorate. The new electrolyte system was successfully used on a poly(methyl methacrylate) (PMMA) separation device to analyse both model mixtures and actual explosives residues.

2. Materials and methods

2.1. Instrumentation

Separations were performed using a directly milled, miniaturised PMMA chip device. Full details of the fabrication procedure have been described previously [28]. The device essentially comprised a 78 mm long, 78 mm wide, 6 mm thick PMMA block, incorporating two separation channels with an integrated on-column conductivity detector. Sealing was achieved using a sheet of 400 μm thick self-adhesive polyester laminate (Ritrama, Monza, Italy). A schematic of the layout of the device is shown in Fig. 1. In this work, the two perpendicular, connected channels were used as effectively a single, long, separation column. The first channel, from the cross to the junction point was 57 mm long, 300 μm wide and 300 μm deep, whereas the second, from the junction point to well B was 200 μm wide and 300 μm deep. The conductivity detector was incorporated into this latter channel at a distance of 44 mm from the junction point. The detector consisted of a pair of 75 μm diameter platinum wire (Aldrich, Gillingham, Dorset, UK) electrodes arranged in opposed configuration. All of the channels intersecting at the cross were 300 μm wide by 300 μm deep. Fluid connections to and from the separation device were made using 062 Minstac fittings (Lee, Westbrook, CT, USA).

Sample injection and movement of solutions around the separation device was achieved using a hydrodynamic sample transport system based on a series of gravity feed reservoirs and solenoid actuated valves, as previously reported by the authors [28]. The constant currents used to drive the separations were provided by a PS350 5000 V–25 W high-voltage power supply (Stanford Research Systems, Sunnyvale, CA, USA). Detection was achieved using an in-house built single channel conductivity detector that is isolated from the electric field applied to drive the separations using capacitive coupling.

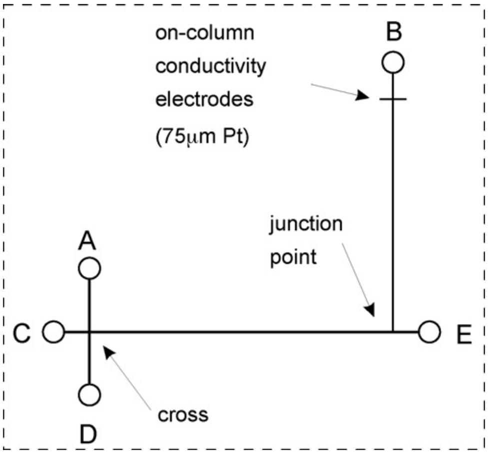

Fig. 1. Schematic diagram of the miniaturised separation device. Letters A, B, C, D and E refer to the wells through which fluid connections into and out of the device are made. All the channels are 300 μm wide by 300 μm deep with the exception of that from the junction point to well B that is 200 μm wide by 300 μm deep. The distance from the cross to the junction point is 57 mm and from the junction point to the detector is 44 mm.

Control of the sample transport system, high-voltage power supply and conductivity detector was achieved using LabVIEW software (version 7.1) (National Instruments, Austin, TX, USA), running under the Windows XP operating system (Microsoft, Redmond, WA, USA) on a standard personal computer. The hardware interface is achieved using three National Instruments cards controlled using the NIDAQ driver (National Instruments) and programmed using LabVIEW code. The cards used were a PCI-GPIB board for the power supply, a PCI-6601 timing and digital input/output board for the detector and a PCI-6503 digital input/output card for the sample transport system. Data analysis was also performed using a LabVIEW program, which determines relative step heights (RSHs) and lengths. In this work RSH was calculated using the following expression:

$$\mathrm{RSH} = \frac{f_{\mathrm{S}} - f_{\mathrm{LE}}}{f_{\mathrm{TE}} - f_{\mathrm{LE}}}$$

where f_{LE} is the frequency of the response produced by the leading electrolyte (Hz); f_{S} the frequency of the response produced by the sample (Hz); and f_{TE} is the frequency of the response produced by the terminating electrolyte (Hz).

Frequency was used for the calculation of RSHs rather than more commonly encountered resistance or voltage as this is the form of the output from the conductivity detector. This occurs because the design is based on an astable oscillator coupled to the detection electrodes and thus uses capacitive coupling as a low cost method to isolate the low voltage detection circuitry from the high separation voltages. Over the range of conductivities encountered during isotachophoretic separations, the conductivity increases and the frequency decreases with a near linear relationship.

2.2. Separation conditions

The miniaturised separations performed in this investigation were achieved using the control program shown in Table 1. The first two steps flushed the device and filled the separation channels with leading electrolyte. The timing of these steps was set sufficiently