



Micellar electrokinetic chromatography of organic and peroxide-based explosives



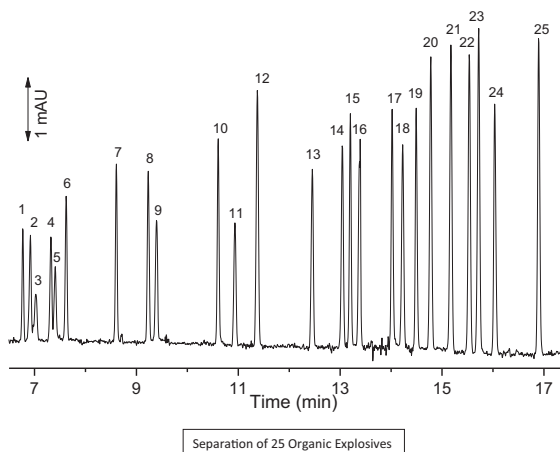
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HIGHLIGHTS

- MEKC method developed to separate 25 analytes relevant to organic explosives.
- For the first time, a CE method has been developed for the analysis of peroxide based explosives.
- Methods were applied to the post-blast analysis of residues from organic and peroxide based explosives.

GRAPHICAL ABSTRACT



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ABSTRACT

CE methods have been developed for the analysis of organic and peroxide-based explosives. These methods have been developed for deployment on portable, in-field instrumentation for rapid screening. Both classes of compounds are neutral and were separated using micellar electrokinetic chromatography (MEKC). The effects of sample composition, separation temperature, and background electrolyte composition were investigated. The optimised separation conditions (25 mM sodium tetraborate, 75 mM sodium dodecyl sulfate at 25 °C, detection at 200 nm) were applied to the separation of 25 organic explosives in 17 min, with very high efficiency (typically greater than 300,000 plates m⁻¹) and high sensitivity (LOD typically less than 0.5 mg L⁻¹; around 1–1.5 μM). A MEKC method was also developed for peroxide-based explosives (10 mM sodium tetraborate, 100 mM sodium dodecyl sulfate at 25 °C, detection at 200 nm). UV detection provided LODs between 5.5 and 45.0 mg L⁻¹ (or 31.2–304 μM), which is comparable to results achieved using liquid chromatography. Importantly, no sample pre-treatment or post-column reaction was necessary and the peroxide-based explosives were not decomposed to hydrogen peroxide. Both MEKC methods have been applied to pre-blast analysis and for the detection of

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post-blast residues recovered from controlled, small scale detonations of organic and peroxide-based explosive devices.

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1. Introduction

Explosives can be divided into two broad categories, namely high and low explosives. High explosives can be further subdivided into primary explosives which burn very rapidly or detonate when ignited, and are extremely sensitive to heat, shock, or friction (e.g. nitroglycerin, triacetone triperoxide) and secondary explosives (e.g. RDX, HMX, TNT) which are much less sensitive and are typically detonated via a primary explosive. Low explosives, also called homemade explosives or HMEs, tend to be based on inorganic and organic compounds. Peroxide based explosives can be formed from both inorganic and organic compounds and can be both primary and secondary explosives. Because of the different chemical properties of these explosives, no one analytical technology is capable of detecting all, and thus for the purposes of this paper, we classify the explosives on their chemical properties because this is insightful when considering how they may be determined. As such, we have referred to the explosives analysed in this study as being organic, inorganic and peroxide based explosives.

HPLC and GC–MS have been the most commonly used separation technique for organic explosives, with several comprehensive reviews available on this topic [1–8]. However neither HPLC nor GC–MS are capable of analysing the entire suite of explosives, and are particularly unsuited to the inorganic residues. Ion chromatography can be used to separate the inorganic species [9,10], but this has different instrumental requirements than HPLC and analysis times are in excess of 30 min to separate the entire compliment of relevant target, degradation and background ions.

Recent work in our group has concentrated on the development capillary electrophoretic (CE) [11–14] methods for the detection of these in post-blast residues. These methods have been implemented in portable instrumentation designed for rapid analysis of samples collected near the crime scene. This platform is also suitable for the separation of organic explosives have by micellar electrokinetic capillary chromatography (MEKC) [15–20] and capillary electrochromatography (CEC) [15,21–24], the latter of which has the additional advantage of being easily interfaced to a mass spectrometer to improve the reliability of accurate identification. However, CEC uses a packed or monolithic column which is slow to flush and not ideally suited for rapid screening. MEKC is the preferred approach due to the ease with which the capillary solutions can be replaced and changed. The first use of MEKC for organic explosive analysis was reported in 1991, when Northrop et al. [20] investigated 26 gunpowder and organic explosive constituents. The analytes included 9 of the EPA Method 8330 analytes, and notably also trinitroglycerin, EGDN and PETN. Gunshot residues were examined from spent ammunition casings, and extracts from plastic explosives were also analysed. Sodium tetraborate/boric acid (buffer) with sodium dodecyl sulfate formed the background electrolyte, with β - and γ -cyclodextrins also being investigated as additives to enhance the separation selectivity. Detection limits of 5×10^{-6} to 1×10^{-5} mol L⁻¹ were reported and 19 analytes were baseline-resolved (7 others were co-eluted as 4 peaks) in under 10 min. The most comprehensive separation thus far is by Mussenbrock and Kleiböhmer [19] who separated 24 analytes (including all 12 EPA Method 8330 analytes specified at that time plus 1,4-dinitrobenzene, 2,4-dinitro-6-methylphenol, 1,2-dinitrobenzene, 3-methyl-4-nitrophenol,

2-methyl-3-nitroaniline, 2-methyl-5-nitroaniline, 3,4-dinitrotoluene, 2,3-dinitrotoluene, 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 1,5-dintronaphthalene and diphenylamine). All 24 analytes were separated in under 10 min using 2.5 mM disodium tetraborate, 12.5 mM boric acid (pH 8.12), 1% (v/v) methanol and 50 mM SDS. UV detection was at 230 nm and no detection limits were recorded. Notably, several analytes which are now of interest (including nitroglycerins, R-salt, ETN, PETN, EGDN) were not studied. Indirect fluorescence has also been applied [15,18] although detection limits achieved were inferior to UV detection (1–10 mg L⁻¹), due to low frequency oscillations in the fluorescence background (suspected to be the result of Joule heating effects) so only low electric field strengths (~ 100 V cm⁻¹) could be utilised, resulting in 30 min separation times.

Organic peroxide explosives are a relatively newer threat and the body of research in this area is considerably less. Both HPLC and gas chromatography (GC) have been used successfully [25–30]. Armitt et al. [25] investigated the use of GC–MS for the analysis of TATP and its degradation products after exposure to various acids. Head-space solid phase microextraction (SPME) with GC–MS was used for separation and detection. The technique was able to separate 9 analytes, including TATP in 10 min, however detection limits were not reported. Sigman et al. [29] demonstrated GC–MS and GC–MS/MS to detect sub-ng amounts of TATP using single quadrupole and ion trap mass spectrometry. These workers employed ammonia positive ion chemical ionisation (PCI), electron impact ionisation (EI), and methane negative ion chemical ionisation (NICI) for these analyses, and were able to show LODS with quadrupole MS and ion trap PCI or NICI of 0.05 ng and 0.5 ng, respectively. When separated by HPLC, UV detection can be used for applications in which sensitivity is not a major issue, for example, to study the influence of reaction conditions on the formation of TATP and by-products [31] and the spontaneous transformation of TATP to DADP [32]. Whilst the TATP concentrations were significantly higher at ~ 3000 – 8000 mg L⁻¹ compared to other studies, it does demonstrate that TATP has absorbance in the low UV region. A similar approach was used for analysis of a standard reference material developed by the National Institute of Standards and Technology, consisting of TATP coated onto polystyrene–divinylbenzene beads [33]. Two peaks reported as TATP conformers could be observed in extracts which were approximately 60 mg L⁻¹. The LC–UV method agreed with an independent LC–MS analysis. There are reports in the literature of the use of LC–MS for the analysis of TATP and its associated conformers and side-products, including DADP, such as that published by Widmer et al. [34]. These researchers employed LC with a quadrupole MS operated in atmospheric pressure chemical ionisation (APCI) positive ion mode for the trace determination and quantitation of TATP. These authors indicate that the use of LC–MS overcomes the problem of stationary phase activation observed with GC–MS as a result of the lower temperature employed with this technique. The method produced detection limits for TATP of 100 mg L⁻¹ (100 pg μ L⁻¹), which are not particularly low compared to GC. Despite this research relating to the use of HPLC and GC for these analyses, there are no previous reports of the use of CE for this purpose.

In this paper we present a MEKC method for the separation of 25 organic explosive analytes and a second method for the separation of peroxide based explosives; the first CE method for this analyte set. Whilst the total number of organic explosives

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