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Novel CE–MS technique for detection of high explosives using perfluorooctanoic acid as a MEKC and mass spectrometric complexation reagent

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ABSTRACT

To address the need for the forensic analysis of high explosives, a novel capillary electrophoresis mass spectrometry (CE–MS) technique has been developed for high resolution, sensitivity, and mass accuracy detection of these compounds. The technique uses perfluorooctanoic acid (PFOA) as both a micellar electrokinetic chromatography (MEKC) reagent for separation of neutral explosives and as the complexation reagent for mass spectrometric detection of PFOA-explosive complexes in the negative ion mode. High explosives that formed complexes with PFOA included RDX, HMX, tetryl, and PETN. Some nitroaromatics were detected as molecular ions. Detection limits in the high parts per billion range and linear calibration responses over two orders of magnitude were obtained. For proof of concept, the technique was applied to the quantitative analysis of high explosives in sand samples.

1. Introduction

High explosives constitute the majority of modern military and industrial explosive applications [1]. Moreover, high explosives such as TNT, RDX and PETN are commonly used in terrorist activities including the cargo bomb plot and attempts to blow up airplanes by explosives hidden in underwear [2,3]. In addition, because of their wide use, the environmental footprint of these compounds is an issue [4,5]. Therefore, identification of high explosives and their post-blast degradation products is important both forensically due to their wide military use and by their potential acute and chronic effects on the environment and population [6]. Currently, GC–MS [7], HPLC–UV [8,9], and HPLC–MS [10] are the preferred techniques for the analysis of explosives yet these techniques have some drawbacks.

Conventional GC–MS is the preferred technique for forensic analysis of explosives due to its availability, ease of use and low detection limits; however, it has some shortcomings for the analysis of high explosives such as RDX, HMX and tetryl. In the case of tetryl, one of its thermal degradation products, n-methylpicramide, is often detected [10]. GC–MS with a programmable temperature vaporizing (PTV) injector has been successfully used for the detection of high explosives including thermally labile compounds [7,11–14]. High explosives are introduced into the injector at low temperature, minimizing their decomposition; subsequently the injector temperature is increased to introduce higher boiling point explosives into the column. On-column injection is yet another technique used for minimizing the decomposition of high explosives in GC–MS [7]. Additionally, to reduce the residence time of thermally labile high explosives in the GC oven, shorter columns can be utilized [15]. The PTV and on-column injection programs are part of a specialized inlet made to decrease thermal degradation of labile compounds. Most laboratories are not equipped with these types of injectors and are instead equipped with split/splitless inlets, as they are useful for most other GC–MS analyses. Therefore, thermally labile compounds such as HMX and RDX are difficult to detect using GC–MS systems present in most laboratories. Further, with the shorter

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column, HMX was still not detectable, and RDX produced a much lower signal by GC when compared to HPLC [15]. Moreover, GC–MS analysis of high explosive under electron impact ionization produces very weak molecular ions [12,13].

HPLC–MS is another analytical technique that has also been used for the analysis of explosives; however, because of the neutral nature of high explosives and thereby their low ionization efficiency under electrospray ionization (ESI), they are difficult to detect in both positive and negative ionization modes. To enhance the ionization of high explosives under HPLC–ESI/MS, a variety of additives have been incorporated into the mobile phase. Both pre-column and post-column addition of cationization and anionization reagents has been studied [16,17]; however, cationization usually forms multiple components, which can complicate complex mixture analysis and reduce sensitivity [18]. Additives including ammonium formate or sodium nitrite have been used to promote complex formation to enable detection of the mono-nitrotoluenes (MNTs) and nitrobenzene [19].

Capillary electrophoresis (CE) has also been utilized for the detection of explosives [20] but most explosives are neutral and are not separated by CE without the presence of a pseudo-stationary phase in the background electrolyte (BGE). To this end micellar electrokinetic chromatography (MEKC) is often employed [21–23]. Separation by MEKC is based on varied interaction of analytes with the micelles which result in separation if there are sufficient differences in hydrophobicity and electrophoretic mobility of analytes [24]. One commonly used MEKC reagent is sodium dodecyl sulfate (SDS); however, it causes ion suppression under electrospray ionization [25]. SDS was found to have poor affinity for HMX and RDX causing their elution to be close to the electroosmotic front [26]. Cyclodextrins (CDs) have also been used as pseudo-stationary phases in CE to separate explosives. For example, nitroaromatic and cyclic nitramine compounds were analyzed by CE–MS using sulfobutylether-β-CD [27]. However, the authors reported complex CE–MS background spectra which made the identification of the explosive peaks very difficult [27]. To avoid the electrospray incompatibility and background issues of SDS and CDs, respectively, perfluorohexanoic to perfluorodecanoic have been introduced as volatile MEKC reagents [24]. It was found that perfluorooctanoic acid (PFOA) produced the best results for the analysis of pharmaceutical drugs and synthetic cannabinoids without impairing the MS signal over extended use [24,28].

In this manuscript we introduce an alternative method for the analysis of high explosives with high mass accuracy and minimal fragmentation which complements GC–MS analysis. The technique uses PFOA as an MEKC–MS reagent for the separation of and as a complexation reagent for high sensitivity electrospray ionization MS detection of high explosives and other organic explosives. The purpose of this manuscript is to introduce a novel technology useful for the analysis of high explosives which would be applicable to a whole host of matrices of forensic interest including soil and water. The analysis in sand given as a real life example represents both a forensic and environmental application.

2. Materials and methods

Analytical explosive standards EPA 8330 Mix A and Mix B (see Table 1 for list of compounds) and PFOA ammonium salt were purchased from Sigma–Aldrich (St. Louis, MO, USA). A standard of pentaerythritol tetranitrate (PETN) was purchased from Cerilliant Corporation (Round Rock, TX, USA). Contaminated sand (505989 and 506139) samples were provided by the US Army CBRNE Analytical & Remediation Activity Mobile Expeditionary Laboratory (CARA-MEL) (Edgewood, MD, USA). HPLC-grade acetonitrile (ACN) and methanol were purchased from Fisher Scientific (Pittsburgh, PA, USA), as well as ammonia and formic acid. Stock solutions of PFOA were made using deionized water. Nylon syringe filters with a 0.45 μm pore size were used to prepare the sample extracts for instrumental analysis.

2.1. Optimal BGE selection

Optimization of the BGE was achieved using Beckman Coulter PA800 Plus (Fullerton, CA, USA) with UV/Vis diode array detection. A 90 cm (50 μm inner diameter) underivatized fused silica capillary (Polymicro Technologies, Phoenix, AZ, USA) was conditioned with 1 M sodium hydroxide, deionized water, and BGE prior to each injection. Injections were performed at 0.5 psi for 10 s and separations were carried out using an applied voltage of +25 kV at 25 °C. PFOA was selected as the surfactant for MEKC separation based on previous studies [28]. All aqueous solutions were prepared using deionized water. A stock solution of 200 mM PFOA was diluted to the desired PFOA concentration and buffered to a pH of 9.4 using 3 M ammonia. BGE solutions containing 15 mM, 25 mM, 30 mM, 40 mM, 50 mM, 60 mM, 70 mM, 80 mM, 90 mM, and 100 mM PFOA were studied. Organic modifier addition to the BGE was also studied; however, no added benefit on the resolution or detection of the analytes was observed.

2.2. Sample preparation

Individual explosive standards and EPA Method 8330 Mix A and Mix B were prepared at varying concentrations in BGE for MEKC analysis. Sand samples labeled 506139 and 505989 were measured in ~5 g portions and extracted with ACN according to EPA Method 8330 except no calcium chloride was added and they were sonicated for only 1 h. The supernatant was removed from each sample and passed through a 0.45 μm nylon syringe filter into a clean glass vial. The solvent was then evaporated completely and the residue was reconstituted in 50 μL of ACN. After reconstitution, each extract was diluted with BGE for analysis.

2.3. Instrumentation MEKC–MS

MEKC–MS analyses were performed on a Beckman Coulter Proteomelab PA800 Capillary Electrophoresis System (Beckman Coulter, Fullerton, CA, USA) interfaced with a high resolution Orbitrap Elite mass spectrometer (Thermo Scientific, Waltham, MA, USA) using a porous tip [29]. A 15 or 20 μm inner diameter underivatized fused silica capillary (Polymicro Technologies, Phoenix, AZ, USA) with a total length of ~90 cm was used at 25 °C. The capillary was conditioned for 6 min at a time using 1 M sodium hydroxide, followed by water, then methanol and finally BGE. Injections were made at 1 psi for 4 s and separations were performed using forward polarity mode (+25 kV to inlet) and 5 psi of inlet pressure. Electrical connection was established by using 0.1% formic acid as the conductive liquid [29]. ESI-MS detection was performed in negative ion mode with a −1.1 kV ESI voltage and the mass spectrometer heated capillary was held at 150 °C to minimize PFOA-explosive complex fragmentation while maintaining efficient desolvation. Discussion of sensitivity refers to the *S*/*N*. Scan ranges included a low mass range of 100–350 *m*/*z*, intermediate mass range of 500–750 *m*/*z*, and high mass range 1000–2000 *m*/*z*, with a resolving power of 120,000.

2.4. Safety precautions

When using EPA Method 8330, samples are meant to be homogenized however if explosive levels greater than 100 ppm are suspected, this should not be done due to possible explosion hazard. Further, some of the explosive compounds are sensitive