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Research Article

Determination of nitroaromatic explosives residue at military shooting ranges using a sweeping-MEKC method

We report on the application of sweeping-MEKC, for the first time, using the Environmental Protection Agency Method 8330 stock standard (a mixture of 14 explosives). The use of a traditional MEKC mode provided the LODs (at $S/N = 3$) ranging from 1.5 to 2.9 $\mu\text{g/mL}$ for the 14 explosives standards, which were improved by as low as 3.1–6.5 ng/mL when a sweeping-MEKC technique was used. A set of 21 soil samples were collected from surface soil at military shooting ranges located at Kinmen County in Taiwan, and the findings showed that hexahydro-1,3,5-trini-tro-1,3,5-triazine and 2,4,6-trinitrotoluene made up the explosives residue present at the highest concentrations. This study is very useful for determining current levels of explosives residue and as a reference for making appropriate recommendations concerning future site characterization techniques.

Keywords:

Environmental Protection Agency Method 8330 / Explosive / Nitroaromatic / Soil / Sweeping-MEKC
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1 Introduction

Currently, GC-based methods are frequently used for the analysis of explosives and analogs [1–8], although several commercially available machines, based on ion mobility spectrometer or FTIR, are made for routine analysis and are being steadily adopted for applications such as airports, prisons and nuclear power plants. EPA (Environmental Protection Agency) Method 8095 utilizes GC/electron capture detector and reports quantitation limits from 0.03 to 5 ng/mL for common nitroaromatic and nitramine explosives by 1 μL injection. These methods can be used not only for warning of potential dangers from explosive materials but also for forensic investigations, hazardous waste site characterization and land mine detection. However, nitroaromatic explosives are easily decomposed by heat. Therefore, based on current GC methods, the detection limits of these nitroaromatic standards are not satisfactory, and thus improved methods of high sensitivity, such as HPLC and CE, are needed. EPA Method 8330 utilizes the HPLC/UV absorption method for

separation and detection; LOD ranges are 0.26–7.3 ng/mL by 20–100 μL injections [9–11]. Meanwhile, several studies have reported on the use of capillary-based techniques [12–18]. Douse *et al.* [15] reported on the determination of high explosives using MEKC/indirect fluorescence detection. Bailey and Yan reported [16] on the use of a CEC technique, wherein the separation of a series of EPA 8330 compounds was achieved in 7 min. Recently, various types of rapid screening methods were developed for this including the use of a single-channel microchip [17], a mass spectrometric method [13] and secondary electrospray ionization-ion mobility spectrometry [19]. Collins *et al.* [12] achieved a detection limit of 1 mg/L by using high-salt stacking. Each of the above methods has unique advantages and disadvantages with respect to sensitivity, precision and simplicity of use. In the study, the sweeping-MEKC [20] was applied, for the first time, to the EPA method 8330 stock standard. Under optimized separation conditions, 21 soil samples obtained from military shooting ranges were investigated using the sweeping-MEKC method. Several electrophoretic parameters were optimized, and the results are reported here.

2 Materials and methods

2.1 Reagents

The EPA Method 8330 stock standard (a mixture of 14 explosives), including RDX (hexahydro-1,3,5-trini-tro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), TNT (2,4,6-trinitrotoluene), tetryl (trinitrophenyl-methyl-nitramine), 2,4-DNT (2,4-dinitrotoluene), 2,6-DNT,

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Abbreviations: DNT, dinitrotoluene; EPA, Environmental Protection Agency; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; NT, nitrotoluene; RDX, hexahydro-1,3,5-trini-tro-1,3,5-triazine; Tetryl, trinitrophenyl-methyl-nitramine; TNT, 2,4,6-trinitrotoluene

2-NT (2-nitrotoluene), 3-NT, 4-NT, nitrobenzene, 2-amino-4,6-DNT, 4-amino-2,6-DNT, 1,3,5-trinitrobenzene and 1,3-dinitrobenzene, was purchased from Cerilliant (TX, USA); concentration level was 200 $\mu\text{g}/\text{mL}$ each. In order to identify each explosive *via* spiking, individual explosives were obtained either by laboratory synthesis (including RDX, HMX, TNT, tetryl, 2,4-DNT and 2,6-DNT) or by purchase. Twenty-one surface soil samples were collected from different military shooting ranges located at Kinmen County (Taiwan). All other chemicals were of analytical grade and were obtained from commercial sources.

2.2 Apparatus

The CE setup was identical to that used in our previous study [21]. Briefly, a high-voltage power supply (Model RR30-2R, Gamma, FL, USA) was used to drive the electrophoresis, and a 50 μm id fused-silica capillary column (J&W Scientific, CA, USA) was used for the separation (total/effective length: 100/85 cm in the case of MEKC and sweeping-MEKC modes, respectively). A UV-detector (CE-971 UV, Jasco, Japan) was used for the determination of the analytes, and the wavelength used for the detection was 210 nm. A gas chromatograph (GC 5890 Hewlett-Packard, Avondale, PA, USA) equipped with a mass spectrometer (Hewlett-Packard 5972 mass selective detector) was also used for comparison.

2.3 Preparation of real samples

Preparation procedures of soil samples were followed the EPA Method 8330 [11]. A 3.5 g soil sample (mainly sandy, light brown to gray color) was added to 3.5 g of acetonitrile. The mixture then was shaken for 15 h in the dark. After this, the mixture underwent further ultrasonic treatment for 15 min at room temperature. Following these, the muddy mixture was filtered using 0.9 mm filter paper followed by a 0.45 μm filter. The filtrate was collected and transferred to a clean tube for the subsequent CE separation. This procedure provided 70% ($\pm 5.9\%$) recovery for the nitroaromatic explosives.

3 Results and discussion

3.1 CE separation for nitroaromatic standards

In this study, EPA Method 8330 stock standards were first examined by GC/MS. Figure 1A shows a typical GC chromatogram of the EPA Method 8330 stock standard (concentration level, each 10 $\mu\text{g}/\text{mL}$). As can be seen, the peaks of RDX, tetryl and HMX could not be found. The retention times at 12.8 and 15.1 min (marked as broken arrows) should correspond to RDX and tetryl, respectively, which were recognized *via* a spiking test with higher concentrations (up to 150 $\mu\text{g}/\text{mL}$); HMX is very easily decomposed by heat and could not be found even when

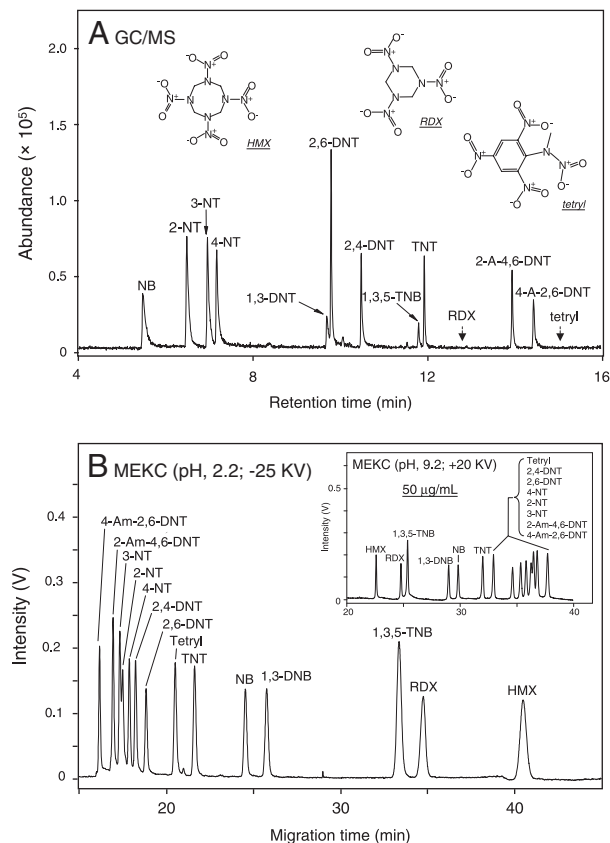


Figure 1. (A) Typical GC/MS chromatogram of the EPA 8330 method stock standard (a mixture of 14 common explosives; concentration level, each 10 $\mu\text{g}/\text{mL}$). (B) Typical MEKC electropherogram of the stock standard obtained by the MEKC method, buffer pH 2.2. The total and effective lengths of the capillary were 100 and 85 cm, respectively; id, 50 μm . Inset: MEKC electropherogram of these standards; buffer pH 9.2.

spiked with a higher concentration. Thus far, several online sample concentration methods have been developed based on CE separation [20, 22]. However, nitroaromatic compounds cannot be analyzed using the CZE-based techniques, including stacking and pH-junction, which are prohibitively difficult. For this reason, the MEKC and sweeping-MEKC methods were used exclusively in all subsequent experiments. Figure 1B shows a typical MEKC electropherogram of the EPA Method 8330 stock standard (concentration level, each 50 $\mu\text{g}/\text{mL}$), obtained by the MEKC method (applied voltage, -25 kV; pH 2). The total and effective capillary lengths were 100 and 85 cm, respectively. A complete optimal separation of the analytes was achieved using phosphoric buffer (10 mM NaH_2PO_4 and 10 mM H_3PO_4) containing SDS (50 mM) in an aqueous solution (pH 2.2); the applied voltage was -25 kV. In this case, the EOF was suppressed, and the major driving force for the separation was derived from the SDS-micelles (negative charge), carrying the nitroaromatic standards and moving toward the outlet. For this reason, an analyte, for which either the size is smaller or the interaction force with the

SDS-micelles is stronger, should move toward the outlet, leading to a shorter migration time. We found that 2-amino-4,6-DNT and 4-amino-2,6-DNT moved faster than the others because their amino-groups provided stronger interaction forces with the SDS micelles. HMX and RDX move slower than the others, since such interaction forces are weak, which leads to a longer migration time. To examine the order of migration when different separation conditions are used, basic solutions were applied. The inset in Fig. 1B shows an MEKC electropherogram of the stock standard using a basic buffer (+20 kV, pH 9.2). In this case, the EOF was the major driving force carrying the analytes to the detector and moved quickly toward the outlet (detection window), while the SDS-micelles (negative charge), carrying the analytes, moved toward the inlet. We found that the order of migration was almost reversed, except for 2,6-DNT and 2,4-DNT groups. Figure 2A shows the typical sweeping-MEKC electropherogram of the stock standard. Herein, the stock standards were dissolved in a phosphoric buffer without SDS, which resulted in a non-micelle sample solution. The sample solution of the stock standard was hydrodynamically injected by raising the reservoir 30 cm relative to the exit reservoir (at this height, the flow rate for the sample injection was 0.25 mm/s) to provide the injection length (depending on the specific situations). When the injection was completed, -25 kV was applied to power the CE separation; the optimized injection length was 23 cm.

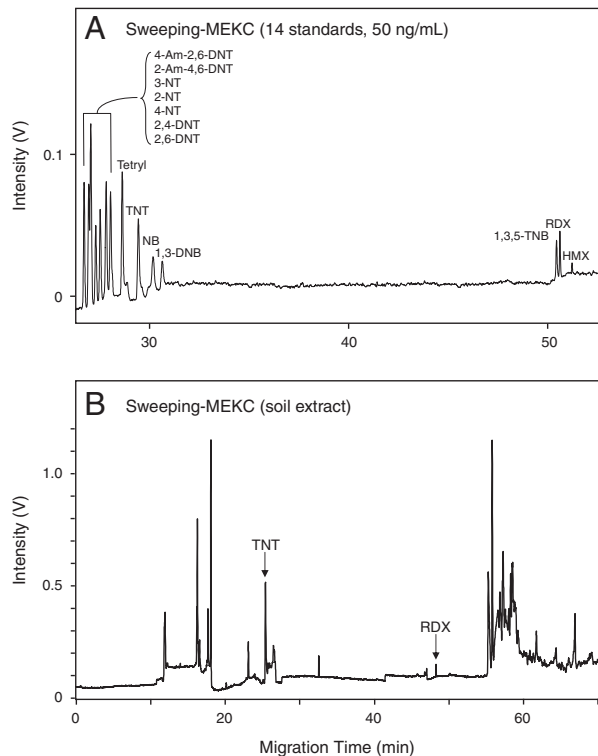


Figure 2. (A) Sweeping MEKC electropherogram of the EPA 8330 method stock standard. Conditions are described in the text. (B) Electropherogram of an extract of a soil sample from military shooting ranges applying the sweeping-MEKC technique.

Table 1. LOD values (at $S/N = 3$), RSD values and plate numbers for 14 standards of nitroaromatic and nitramine explosives based on MEKC and sweeping-MEKC methods, respectively ($n = 3$).

	MEKC	Sweeping-MEKC
<i>Detection of 14 standards of EPA 8330 method</i>		
LOD	1.5–2.9 $\mu\text{g/mL}$	3.1–6.5 ng/mL
Plate number	2.5×10^5 – 3.2×10^5	8.1×10^5 – 4.3×10^6
RSD%		
Migration time (%)		
Intra-day	1.43	0.43
Inter-day	1.11	0.75
Peak area (%)		
Intra-day	3.27	1.11
Inter-day	0.61	0.18

A complete optimal separation of these compounds (concentration level, each 50 ng/mL) was achieved using a phosphoric buffer (7.5 mM NaH_2PO_4 and 7.5 mM H_3PO_4) containing SDS (150 mM) in a mixed water–acetonitrile–methanol solution (W:A:M = 7:2:1 v/v). In order to investigate the effects of organic solvents, various W:A:M solutions (such as W:A:M = 6:2:2; 8:2:0; 8:0:0) were examined, but in all cases the separation was poorer. Based on optimized conditions, an ~ 1000 -fold improvement was achieved when the sweeping-MEKC method was applied. Table 1 summarizes the LODs, RSD values and plate numbers obtained under optimized conditions by the MEKC and sweeping-MEKC methods. It is clear that the sweeping-MEKC method makes possible the determination of nitroaromatic and nitramine explosives even at ppb levels.

3.2 Analysis of nitroaromatic explosives residue at military shooting ranges

Thus far, HMX and RDX are present in most currently used high explosives in military and industrial applications; these high explosives are frequently used mixed with TNT. Figure 2B shows a typical MEKC electropherogram of an extract of a soil sample from a military shooting range by applying the sweeping-MEKC technique. Numerous unknown peaks are shown. After the standard spiking method was used, we found that TNT and RDX were the major residues found at military shooting ranges, and their concentrations were determined to be 3.4 and 1.0 mg/kg, respectively, which were below the values permitted by EPA (TNT < 17.2 mg/kg, RDX < 5.8 mg/kg, respectively). Using the same procedure, 21 soil samples were examined and the results show that the concentration levels of RDX and TNT estimated to 4.00–0.07 and 8.14–0.0 mg/kg, respectively. These data reveal that RDX and TNT, traditional explosives since World War II, are the major explosives residue at these military shooting ranges. HMX could be used by mixing with plastic binders as shaped charges, but it was not found in these soil samples. Table 2 summarizes the RSD

Table 2. RSD values and accuracy and precision of migration time and peak area obtained from the soil samples, which contained TNT and RDX based on the sweeping-MEKC method.

	TNT		RDX	
	Intra-day	Inter-day	Intra-day	Inter-day
Migration time (min)	25.81 ± 0.57	24.9 ± 1.28	45.8 ± 0.28	45.75 ± 1.06
RSD%	2.2	5.1	0.6	2.3
Peak area (× 10 ⁵)	2.56 ± 0.07	2.53 ± 0.03	0.77 ± 0.01	0.67 ± 0.00
RSD%	2.84	1.31	1.70	0.40

values, as well as the accuracy and precision of migration time and peak area, obtained from the 21 soil samples based on the sweeping-MEKC method. Thus, we conclude that the sweeping-MEKC method is a very useful and simple method for the determination of current levels of explosives residue in soil samples with only a small amount of sample needed.

4 Concluding remarks

This study shows that the sweeping-MEKC technique can be successfully used for online sample concentration and separation of 14 common nitroaromatic and nitramine explosives suggested by the EPA 8330 method. This method also was applied to complicated soil samples at a Taiwan military shooting range where TNT and RDX were the major explosives residue. Thus, the present method has the potential for use as a routine monitoring tool in related fields. In the near future, if the method of surface-enhanced Raman spectroscopy can be applied instead of UV absorption, that is, if a combination of sweeping-MEKC and surface-enhanced Raman spectroscopy can be achieved, further applications can be expected.

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The authors have declared no conflict of interest.

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