Analysis of nitramine and nitroaromatic explosives by capillary electrophoresis

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Abstract

Analysis of nitramine and nitroaromatic explosives is of interest for both environmental and forensic applications. Analysis of 14 nitramine and nitroaromatic explosives was accomplished by micellar electrokinetic capillary chromatography, MECC. Analysis times under 11 min were possible employing a phosphate–SDS electrolyte. Detection limits for each explosive at different wavelengths (185 nm, 214 nm, 229 nm and 254 nm) were calculated. Analysis of various extracts of high explosives such as composition C-4, tetrytol and detonating cord was performed. Detection limits less than 1 mg/L were possible using a hydrostatic injection and direct UV detection at 214 nm.

Keywords: Nitramine; Nitroaromatics; Explosives; Nitroglycerin; Pentaerythritol

1. Introduction

Recent work in this laboratory [1–3] and by others [4–6] has demonstrated the utility of capillary electrophoresis (CE) for the analysis of nitramine and nitroaromatic explosives. Applications for this technology include forensic and environmental analysis for explosives as well as for the evaluation of novel or new explosives [2,3]. Environmental concerns over the fate of various explosives has grown significantly with the closures of military bases throughout the world. The current analytical method for the analysis of explosives is described in an EPA draft method (SW-846 Method 8330). This method requires a salting-out liquid–liquid extraction (LLE) to preconcentrate the samples followed by reversed-phase HPLC analysis. One disadvantage of this HPLC method is that it does not fully resolve all the explosives. The EPA method requires the use of two different HPLC runs to fully separate and identify the explosives. Recently an improved method for explosives analysis using a single C_8 column or dual

C_8 and cyano columns has separated all explosives in under 25 min [7]. However, an alternative and complimentary technique for the analysis of explosives is desirable. This is especially true in the case of forensic work where verification of the presence of explosives and other illicit materials is important. Capillary electrophoresis (CE) is an attractive alternative technique for the analysis of explosives. Analysis of 12 common nitramine and nitroaromatic explosives discussed in EPA Method 8330 as well as two additional explosives of forensic interest, nitroglycerin (NG) and pentaerythritol tetranitrate (PETN), can be separated using CE in less than 12 min. Table 1 gives the names and common abbreviations for the nitramine and nitroaromatic explosives investigated in this paper.

The CE technique used for analyzing these explosives was micellar electrokinetic capillary chromatography (MECC). Several books have recently been published describing this and other CE techniques [8–11]. MECC employs a surfactant, typically sodium dodecylsulfate (SDS), at a concentration above

Table 1
Names and abbreviations of explosives analyzed by MECC

Name	Abbreviation
1,3,5,7-tetranitro-N-methylaniline	HMX
1,3,5-trinitro-1,3,5-triazacyclohexane	RDX
1,3,5-trinitrobenzene	TNB
trinitrotoluene	TNT
2,4-dinitrotoluene	2,4-DNT
2,6-dinitrotoluene	2,6-DNT
1,2,3-propanetriol trinitrate (nitroglycerin)	NG
pentaerythritol tetranitrate	PETN
2,4,6-N-tetranitro-N-methylaniline	Tetryl
2-nitrotoluene	2-NT
3-nitrotoluene	3-NT
4-nitrotoluene	4-NT
nitrobenzene	NB
1,3-dinitrobenzene	DNB

its critical micelle concentration (CMC), forming charged micelles. Selective partitioning of the analytes into the micellar phase causes them to migrate at different rates from that of the bulk electroosmotic flow. MECC has been used for a wide variety of applications including explosives [1–6], illicit drugs [12–14] and chiral separations [15]. Previous papers on explosives analysis have used a borate-boric acid buffer with detection at 254 nm and have separated some but not all of the 12 common explosives as well as NG and PETN [1–6]. This paper investigates the use of a UV transparent buffer, phosphate, at several different detection wavelengths and separation conditions. Detection limits at each wavelength as well as the effect on the separation of the addition of an organic modifier to the buffer are investigated. This phosphate–SDS electrolyte is used for the analysis of several extracts of various commercial and military explosives.

2. Experimental

2.1. Instrumentation

The capillary electrophoresis (CE) system employed was the Quanta 4000E CIA (Waters, Milford, MA, USA). Detection at 185 nm, 214 nm, 229 nm and 254 nm were carried out. AccuSep polyimide fused-silica capillaries (Waters, Milford, MA, USA) of dimension 60 cm×50 μm I.D. were used throughout. Computer control and data acquisition was

carried out with a Waters Millennium 2010 Chromatography Manager.

2.2. Preparation of electrolytes

High purity water (Milli-Q) was used to prepare all solutions (Millipore, Bedford, MA, USA). The phosphate electrolyte was prepared from a packet (Waters) containing a preweighed amount of mono- and dibasic phosphate such that diluting the contents to 200 ml gave a 25 mM solution with a natural pH of approximately 7.0. High purity sodium dodecyl sulfate (SDS) (electrophoresis grade, Millipore) was added to the electrolyte resulting in a final concentration of 50 mM SDS.

2.3. Sample information

Samples of various explosives were received as acetonitrile extract and were a gift from Mr. James Crippin (Colorado Bureau of Investigation, Pueblo, CO, USA). The extractions were done by taking a small piece of explosive (typically less than 5 mm^3) and extracting it in 3–4 ml of acetonitrile. These extracts were then diluted into the running buffer (dilution factor 1:5) and analyzed by CE.

2.4. Standard information

Standards were prepared from certified concentrates in acetonitrile (Accustandard, New Haven, CT, USA). Calibration curves were calculated from duplicate injections of four different levels of standards with a straight line forced through zero drawn. Correlation coefficients (r^2) of 0.99x with x being a value of 7 or better were achieved.

3. Results

Fig. 1 is an electropherogram of a 14 component explosives mix at a concentration of 5.0 mg/L each. Detection at various wavelengths using a twenty second hydrostatic injection was performed with detection limits ($S/N=3$) calculated and shown in Table 2. As can be seen the optimal wavelength for each compound varies. Typically 254 nm has been adequately used for the analysis of most explosives,
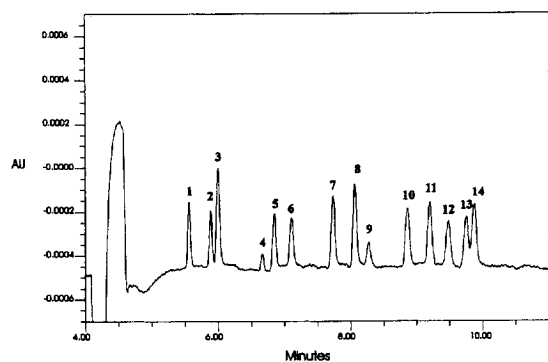
Fig. 1. Electropherogram of a 5 mg/L explosives standard. CE Conditions: fused-silica 60 cm×50 μm I.D. capillary, voltage: 20 kV (positive); electrolyte: 25 mM Phosphate–50 mM SDS; Direct UV detection at 214 nm; hydrostatic injecton (10 cm for 20 s). Solutes: 1=HMX; 2=RDX; 3=TNB; 4=NG; 5=DNB; 6=NB; 7=TNT; 8=Tetryl; 9=PETN; 10=2,4-DNT; 11=2,6-DNT; 12= 2-NT; 13=3-NT; 14=4-NT. Refer to Table 1 for full names of solutes.

with NG and PETN being the only two exceptions since they do not absorb above 214 nm. Detection at 185 nm is slightly more sensitive for some explosives but has the potential limitation of interferences, especially in environmental samples. Detection at 214 nm provides a reasonable detection limit for most of the explosives investigated, including NG and PETN. An increase in sensitivity can be achieved by increasing the sampling time as shown

Table 2
Detection limit for explosives analyzed by MECC*

Analyte	185 nm	214 nm	229 nm	254 nm
HMX	0.50	0.62	0.57	0.78
RDX	0.45	0.78	0.97	0.66
TNB	0.58	0.42	0.34	0.31
DNB	0.38	0.78	0.51	0.23
NB	0.26	1.19	2.53	0.42
TNT	0.40	0.61	0.54	0.34
Tetryl	0.39	0.55	0.51	0.41
2,4-DNT	0.33	0.55	0.51	0.41
2,6-DNT	0.17	0.74	0.87	0.45
2-NT	0.11	1.18	2.16	0.60
4-NT	0.16	1.08	2.23	0.72
3-NT	0.15	0.84	2.41	0.54
NG	0.50	1.56	ND	ND
PETN	0.59	1.82	ND	ND

ND=none detected.
* Hydrostatic injection for 20 s, conditions as stated in text. Amounts are in mg/L.

Table 3
Comparison of injection times*

Analyte	30 s	20 s
HMX	0.45	0.62
RDX	0.57	0.78
TNB	0.31	0.42
DNB	0.58	0.78
NB	0.88	1.19
TNT	0.46	0.61
Tetryl	0.42	0.55
2,4-DNT	0.65	0.85
2,6-DNT	0.60	0.74
2-NT	0.91	1.18
4-NT	0.83	1.08
3-NT	0.70	0.84
NG	1.21	1.56
PETN	1.42	1.80

* Amounts are in mg/L.

in Table 3. However, increasing the sample load will eventually result in a loss of resolution. Reproducibility of migration times and peak areas for five replicate injections of a 10 mg/L standard was done and the average migration time and peak area as well as %R.S.D. for each are summarized in Table 4.

Analysis of several explosive extracts was performed using this method and are shown in Figs. 2–4. Fig. 2 is an electropherogram of a sample extract of composition C-4, a common plastic explosive consisting of RDX. HMX was found in this sample and is commonly found in C-4 since it is a

Table 4
Migration time and peak area reproducibility*

Analyte	Migration Time (min)	Peak Area (uV*sec)
HMX	5.61 (0.03)	1947 (1.14)
RDX	5.94 (0.03)	1566 (1.42)
TNB	6.05 (0.03)	3256 (1.01)
DNB	6.92 (0.02)	2042 (1.32)
NB	7.18 (0.05)	1195 (0.62)
TNT	7.82 (0.04)	2849 (1.30)
Tetryl	8.16 (0.03)	3239 (1.23)
2,4-DNT	8.97 (0.05)	2331 (1.14)
2,6-DNT	9.32 (0.04)	2608 (0.87)
2-NT	9.60 (0.06)	1532 (1.37)
4-NT	9.88 (0.07)	1846 (1.24)
3-NT	10.02 (0.04)	2332 (1.50)
NG	6.67 (0.05)	435 (1.52)
PETN	8.28 (0.04)	825 (1.43)

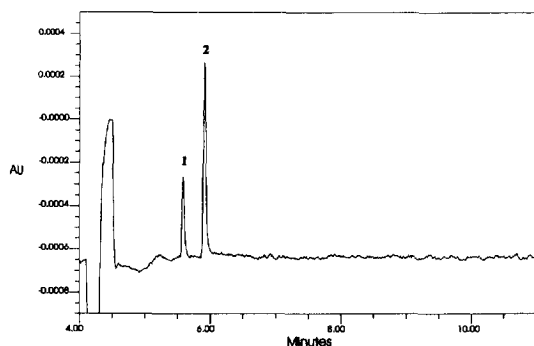* Five replicate injections, %R.S.D.'s are in parentheses. Conditions as stated in Fig. 1.

Fig. 2. Electropherogram of composition C-4 extract. Conditions as stated in Fig. 1. Solutes: 1=HMX; 2=RDX. Refer to Table 1 for full names of solutes.
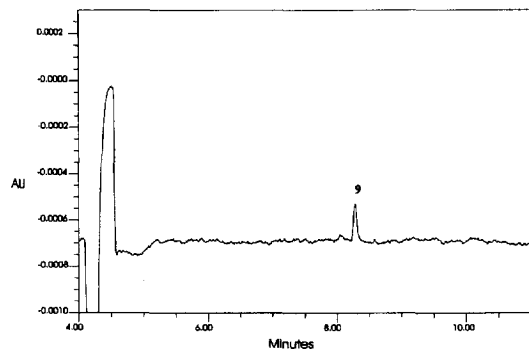

Fig. 3. Electropherogram of detonating cord extract. Conditions as stated in Fig. 1. Solutes: 9=PETN. Refer to Table 1 for full names of solutes.
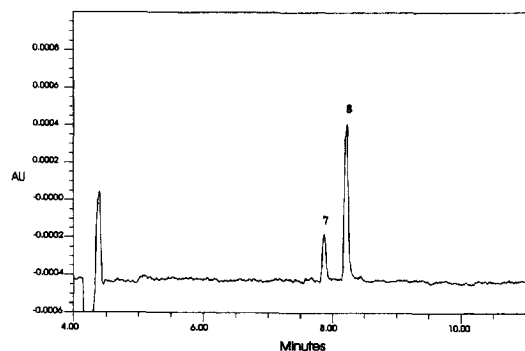

Fig. 4. Electropherogram of Tetrytol extract. Conditions as stated in Fig. 1. Solutes: 7=TNT; 8=Tetryl. Refer to Table 1 for full names of solutes.

by-product of the synthesis of RDX and is explosive as well. [16,17]. Fig. 3 is an electropherogram of an extract from detonating cord which is a PETN based explosive typically used as an initiator. Fig. 4 is an electropherogram of tetrytol extract which consist of a mix of tetryl and TNT and is used as a shape charge for general demolition. Typical mixes of tetrytol contain either 75:25 tetryl and TNT or 70:30 tetryl and TNT depending on the manufacturer and grade. In this case the sample contained approximately 23% TNT which is similar to the mix found in most "military" grades of shape charges which this extract came from.

Further work investigating the effect of organic modifiers on the separation was performed. Fig. 5 shows the effect of adding acetonitrile to the electrolyte. The addition of acetonitrile was found to improve the resolution of the later migrating nitrotoluenes (2-NT, 3-NT, etc.), however, a loss of resolution and changes in the migration order for the first three peaks (HMX, TNB and RDX) occurs. The optimal separation condition for all of the explosives was found to be without the addition of acetonitrile to the running buffer. Optimization of the SDS concentration has been discussed previously and an SDS concentration of 25–50 mM SDS was found to provide adequate separation [4].

4. Conclusions

This work demonstrates the feasibility of using CE for the analysis of explosives. Good linearity and detection limits for the common explosives can be accomplished in under 11 min. Further work will investigate the analysis of environmental pink water samples as well as explosive blast residues.
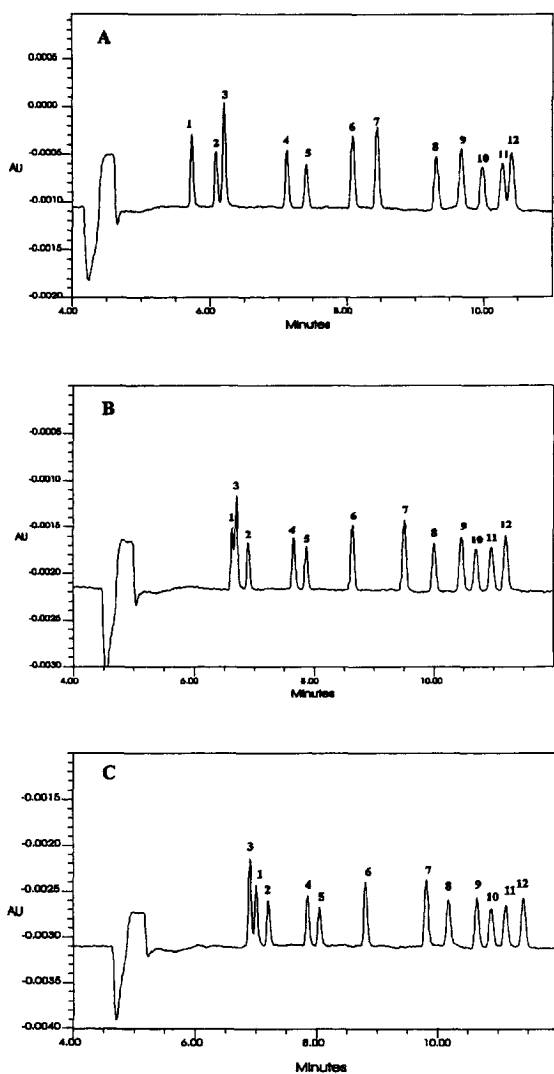
Acknowledgments

Fig. 5. Electropherogram showing the affects of the addition of acetonitrile to the running buffer. Conditions as stated in Fig. 1 except that acetonitrile was added in the following amount: 0% (A); 5% (B); and 10% (C). Solutes: 1=HMX; 2=RDX; 3=TNB; 4=DNB; 5=NB; 6=TNT; 7=Tetryl; 8=2,4-DNT; 9=2,6-DNT; 10=2-NT; 11=3-NT; 12=4-NT. Refer to Table 1 for full names of solutes.

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