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Capillary and Microchip Electrophoretic Analyses of Explosives and their Residues

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For 20 years, the upsurge of terrorist threat on Western countries and the appearance of new environmental policies have been generating an important demand for the detection and identification of explosives. Sensitive, fast, and cheap analysis methods of explosives and their residues on the bombing site or in environmental samples (water, soil . . .) are necessary for the security of citizens or local residents. Within this context, electrophoresis, in capillary or in microchip format, displays attractive features. This article is an overview of the different applications of capillary and microchip electrophoresis for the analysis of organic- or inorganic-based explosives and their residues.

KEYWORDS *Explosives, capillary electrophoresis, microchip electrophoresis*

ABBREVIATIONS *BGE, background electrolyte; 18-C-6, 18-crown-6 ether; CCD, contactless conductivity detection; CD, cyclodextrin; CE, capillary electrophoresis; CEC, capillary electrochromatography; CMC, critical micellar concentration; CZE, capillary zone electrophoresis; EC, Electrochemical; EOF, electro-osmotic flow; HIBA, 2-hydroxyisobutyric acid; HPLC, high performance liquid*

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chromatography; IC, ion chromatography; IDLIF, indirect laser-induced fluorescence; LED, light emitting diode; LIF, laser-induced fluorescence; LOD, limit of detection; MEKC, micellar electrokinetic chromatography; MES, morpholinoethanesulfonic acid; MS, mass spectrometry; NTS, 1,3,6-naphthalenetrisulfonic acid; SDS, sodium dodecylsulfate; SPE, solid-phase extraction; SB-β-CD, sulfobutyl ether-β-cyclodextrin.

ABBREVIATION OF EXPLOSIVE COMPOUNDS CL-20, 2,4,6,8, 10,12-hexanitro-2,4,6,8,10,12-hexaaza-isowurtzitane; ADNT, 2-amino-4,6-dinitrotoluene; 4-ADNT, 4-amino-2,6-dinitrotoluene; DANT, diaminonitrotoluene; DBP, dibutylphtalate; DEDPU, N,N-diethyl-N,N-diphenylurea; DEGDN, diethylene glycol dinitrate; DNB, dinitrobenzene; DNN, dinitronaphthalene; 2,4-DNP, 2,4-dinitrophenol; DNT, dinitrotoluene; DPA, diphenylamine; EGDN, ethylene glycol dinitrate; 2-HADNT, 2-hydroxylamino-4,6-dinitrotoluene; 4-HADNT, 4-hydroxylamino-4,6-dinitrotoluene; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; MDNA, methylenedinitramine; MMA, monomethylammonium; MNX, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine; NB, nitrobenzene; 2-nDPA, 2-nitrodiphenylamine; N-nDPA, N-nitrosodiphenylamine; NG, nitroglycerine; NGU, nitroguanidine; 2-NN, 2-nitronaphthalene; NT, nitrotoluene; PA, picric acid; PETN, pentaerythritol tetranitrate; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; Tetryl, methyl-2,4,6-trinitrophenylnitramine; TAT, 2,4,6-triaminotoluene; TNB, trinitrobenzene; TNT, 2,4,6-trinitrotoluene.

INTRODUCTION

The bombing that occurred in Bali in October 2002, in Madrid in March 2004, and in London in July 2005, as well as the closure and remediation of former ammunition plants and military facilities, generated an important demand for the determination of explosives and their residues in various matrices (tissues, plastics, metallic pieces, soils, waters . . .). However, many types of explosives exist, comprised of inorganic and organic components.

Explosives are classified as low- or high-explosives, according to their rates of burn: low-explosives burn rapidly (or deflagrate), while high-explosives detonate. High-explosives normally are employed in mining, demolition, and military warheads. They are usually based on nitrated organic compounds, such as trinitrotoluene (TNT), 1,3-dinitrobenzene (DNB), and more recently hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), or methyl-2,4,6-trinitrophenylnitramine (tetryl).

Figure 1 presents the structures of the main nitroaromatic, nitramine, and nitrate ester explosives. Raman spectroscopy (1) or electrochemical sensing (2)

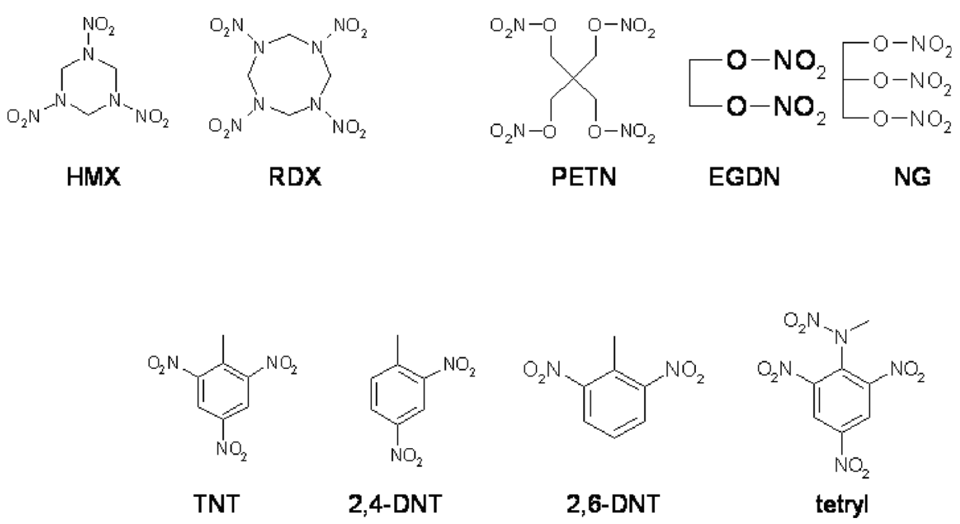

FIGURE 1 Structure of the most often used nitrated explosives classified in 3 families: nitramines, nitrate esters, and nitroaromatics.

allow detection of explosives. As forensic samples are complex, a separation step is often involved prior to identification of explosive compounds. Due to chemical instability of explosives, even if gas chromatography can be used (3), high-performance liquid chromatography (HPLC) is often the technique of choice with UV or mass spectrometry (MS) detection (4), after various extraction methods such as solid-phase extraction (SPE), ultrasonic, Soxhlet extraction, liquid-liquid extraction, or solid phase microextraction (5).

The only official method for analysis of explosives was specified by the US EPA under EPA method 8330 for monitoring nitroaromatic compounds in environmental samples (6). The method recommended using a C18 phase as a primary column and a CN phase as a confirmation column. The separation offered by these two phases can be somewhat problematic, with many co-elutions on both phases, and required 60 min. Therefore, there was a need for a complementary technique, involving an orthogonal mechanism, and, possibly, also being fast and cheap.

A low-explosive is usually a mixture of a combustible substance and an oxidant that decomposes rapidly, such as black powder (potassium nitrate, charcoal, and sulfur), flash powder (aluminum or magnesium powder with a strong oxidizer, e.g., potassium chlorate or perchlorate), ANFO mixture (ammonium nitrate and fuel oil), and pyrotechnics. These kinds of bombs leave a significant amount of inorganic residues upon deflagration, which are characteristic of the initial mixture used. The determination of specific cations, such as ammonium, monomethylammonium (MMA), and potassium, and anions, such as chloride, nitrate, and perchlorate, is critical for the identification of the nature of the explosive mixture used. Different techniques were used for this task, but the most classical one was ion chromatography (IC) (7). Nevertheless, IC suffered from the lack of a complementary technique for confirmation purposes.

For the last 20 years, capillary electrophoresis (CE) has become a valuable alternative to chromatography for the analysis of all low- or high-explosives (8–10), except peroxide-based ones as far as we know (this latter class has not been analyzed by CE yet and the interested readers are invited to consult references [11–14] for more details on others methods). Thanks to their unique properties of efficiency, speed, versatility, and miniaturization, CE is now essential for analyzing or monitoring explosives. Portable systems were developed for on-site measurements (15), which were highly necessary after terrorist attacks (16) or for use in the environmental field.

The introduction of the concept of the micro total analytical system, 20 years ago, brought additional advantages such as sample size and savings (17–19). Thus, lots of effort was paid to develop analytical microsystems, also called "chips", for explosive analysis. This paper is intended to provide a comprehensive review on the use of electrophoretic analytical methods in the explosive field, involving different modes of separation and detection, with capillary or chip format. It may supplement and update the previous published reviews on this subject (8,9,20).

ANALYSIS OF EXPLOSIVES BY CE

Analysis of Inorganic Explosives by CE

For the past 20 years, CE has known a real development for ion analysis and appears now as a valuable complementary technique to IC, as the separation mechanisms are completely different. Numerous commercial or homemade explosive mixtures contain inorganic species in large amounts. This is the case, among others, of ANFO mixture or black powder. The most frequently encountered ions are chloride, nitrate, nitrite, thiosulfate, sulfate, chlorate, perchlorate, thiocyanate, carbonate, phosphate, cyanate, fluorure, acetate, and benzoate anions, and MMA, ammonium, potassium, sodium, barium, strontium, magnesium, calcium, manganese, zinc, lead, aluminum, and iron cations.

Detection modes

Since low-molecular-mass ions commonly lack suitable absorbance properties, which is the detection mode available for all commercial CE instruments, indirect UV detection has to be performed. A visualizing agent, also called a chromophore, with adequate spectroscopic and electrophoretic properties is thus introduced into the background electrolyte (BGE) (21,22). For explosive-related anion analysis, the chromophore must be an anion, and most often chromate ion was selected for its proper spectroscopic properties and electrophoretic mobility in the range of the analytes (15,23–27). 1,3,6-naphthalenetrisulfonic acid (NTS) was also used (28).

For explosive-related cation analysis, imidazole (25,28,29), 4-methylbenzylamine (UV-Cat 1^{TM}) (24), chrysoidine (15), histidine (30), and pyridine (26) were cited in literature. The electrophoretic mobilities of those chromophores belong to the mobility range of the targeted compounds, precluding for highly asymmetrical peaks. The obtained limits of detection (LODs) were between 1 ppm and several hundreds of ppb.

Conductivity detection mode became within the last years a frequently used detection technique in CE methods (31,32). This detection mode is the most universal for inorganic ions as the signal response is related to the equivalent conductivity of a solute. Analyte ions displace BGE co-ions during electrophoretic separations. Thus, the response arises from the difference in conductivity between analytes and BGE co-ions and, for optimum signal-to-noise ratio, a difference as large as possible between the conductance of analyte and electrolyte is required.

Conductivity detection in CE is performed in two modes, either with or without direct contact of the sensing electrodes with the BGE and the sample components. However, problems may arise from the direct contact of the separation electrolyte with the measuring electrode, such as electrode contamination by BGE additives or sample components. This is why the capacity-coupled contactless conductivity detection (CCD) is often preferred, especially as the recent improvements in the detector design and its electronic circuitry led to higher sensitivity and robustness, and also to its commercial release. CCD detection was thus performed for explosive-related ion analysis (30). Low conductivity BGEs were used, such as morpholinoethanesulfonic acid (MES) and Tris mixture in the case of anions. LODs between some tens and hundreds of ppt were obtained.

SEPARATION STRATEGIES

Whatever the detection mode, all explosive-related ion analyses involved capillary zone electrophoresis (CZE), with a separation mechanism based on differences in ion apparent mobilities, combining electrophoretic and electro-osmotic contributions. In 1992, Hargadon and McCord published the first analysis of anionic inorganic explosive residues by CZE, investigated as a complementary technique to IC (23).

The BGE was composed of 2 mM borate and 40 mM boric acid for buffering at pH 8.7, 1.8 mM sodium dichromate (chromophore) and 1 mM diethylene triamine. UV indirect detection mode at 280 nm was mainly involved, but it is worthwhile to notice that direct detection at 205 nm was also performed for confirmation of the identity of nitrate, nitrite, and thiocyanate anions, due to their UV absorbance properties at this low wavelength.

The separation of 7 inorganic anions was obtained in 6 min by CE instead of 20 min by IC, and the LODs were about 0.5 ppm in CE against 2 ppm in IC.

Both techniques were successfully applied for the analysis of real extracts, such as black powder. The orthogonal property of IC and CE was next clearly demonstrated and an example of its usefulness clearly appeared, as cyanate/thiocyanate and fluoride/phosphate anion pairs co-eluted in IC, whereas they were resolved by CE (33). Table 1 details the methods published in the literature allowing the analysis of explosive-related anions by CE, highlighting the ionic mixture and matrix natures, BGE, detection mode, and LODs. In all cases, the electro-osmotic flow (EOF) was reversed for reducing the analysis time, either by the presence of an EOF modifier in the separation electrolyte (23–25), such as diethylenetriamine, or by a pre-analysis modification of the capillary surface via the flush of a solution of hexadimethrine bromide (15,27,30). Hutchinson et al. recently succeeded in determining 15 anions in less than 9 min, with LODs close to 1 ppm (15).

The explosive-related cation separation of ammonium, potassium, and MMA was highly challenging, because of their close electrophoretic mobilities. Doyle and Mc Cord succeeded first in separating these three cations by additions of both 18-crown-6 ether (18-C-6) and acetonitrile in a BGE composed of 2-hydroxyisobutiric acid (HIBA, complexing agent for alkaline earth and transition metal cations to improve their separation) and imidazole as chromophore (29). 18-C-6 formed inclusion complexes with K^+, enabling it to be separated from NH_4^+, but next, the K^+ comigrated with MMA cation. The addition of 5% of acetonitrile in the BGE affected the equilibrium constant for the inclusion complex of K^+ and 18-C-6, allowing the selectivity adjustment to reach full separation of the three cations. Table 1 presents the different studies involving analysis of explosive-related cations by CE.

As it appears in Table 1, anion and cation determinations were usually performed with different BGEs, whereas both anion and cation analysis are required for characterizing the explosive, which was either costly or time-consuming and laborious. Also, simultaneous analysis of explosive-related anions and cations needed to be developed. One approach could be the use of ethylenediaminetetraacetic acid (34) or 2,6-pyridinedicarboxylic acid (35) to form anionic complexes with cations and thus simplified the analysis of anions and cations into a single anion analysis. Nevertheless, these well-known complexing agents were not relevant in the explosive field, because they did not form any complex with the targeted cations, such as ammonium, potassium or MMA.

Another approach consisted of generating a high-magnitude EOF allowing the detection from the same injection end of some anions and cations, having both their apparent velocity directed to the detection end (36). However, no chromophore was used, precluding the UV detection of

TABLE 1 Separation of Explosive-Related Ions by CZE

Compounds	BGE	Detection	LOD (ppm)	Matrices	Ref.[a]
Anions					
Cl^-, NO_3^-, ClO_3^-, NO_2^-, SO_4^{2-}, SCN^-, ClO_4^-, Br^-	2 mM borate, 40 mM boric acid, 1.8 mM sodium dichromate, 1 mM DETA[b], pH 7.8	ind[c] UV 280 nm dir[d] UV 205 nm	1	pipe-bomb residues	(23)
Cl^-, ClO_3^-, NO_3^-, ClO_4^-	5 mM chromate, 5 mM Nice Pack (Waters)	ind UV 254 nm	N/A[e]	residues	(24)
Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, SCN^-, ClO_3^-, OCN^-	2 mM borate, 40 mM boric acid, 18 mM sodium chromate, 1 mM DETA, pH 7.8	ind UV 280 nm	0.7–8.5	powder, residues	(25)
Cl^-, $S_2O_3^{2-}$, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, SCN^-, ClO_3^-, OCN^-, F^-, ClO^-, HPO_4^{2-}, HCO_3^-, CH_3COO^-, $C_6H_5COO^-$	10 mM CrO_3, 10 mM Na_2CrO_4, 40 mM Tris, pH 8.1	ind UV 370 nm	0.2–1.2	residues	(15)
Cl^-, $S_2O_3^{2-}$, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, SCN^-, ClO_3^-, OCN^-, F^-, ClO^-, HPO_4^{2-}, HCO_3^-, CH_3COO^-, $C_6H_5COO^-$	70 mM Tris, 70 mM CHES[f], pH 8.6	CCD	0.027–0.24	residues	(30)
ClO_3^-, ClO_4^-, NO_2^-, NO_3^-, SO_4^{2-}	2 mM tetraborate, 40 mM boric acid, 18 mM dichromate, pH 8.6 adjusted with TMAOH[n]	ind UV 254 nm	0.1–1.9	soil	(26)
Cl^-, $S_2O_3^{2-}$, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, SCN^-, ClO_3^-, N_3^-, HPO_4^{2-}, HCO_3^-,	25 mM CrO_3, 25 mM Na_2CrO_4, 100 mM TRIS, 6% EtOH, pH 8.2	Ind UV 254 nm	0.1–0.8	soil, cloth, paper, swab, plastic, metal, detonator	(27)
Cations					
NH_4^+, Na^+	5 mM UVCat1, 6.5 mM HIBA, 2 mM 18-C-6	ind UV 214 nm	N/A	residues	(24)
K^+, NH_4^+, Ba^{2+}, MMA, Sr^{2+}, Na^+, Ca^{2+}, Al^{3+}, Mg^{2+}, Li^+, Co^{2+}, Zn^{2+}	6 mM imidazole, 17.5 mM HIBA, 4 mM 18-C-6, 5% ACN[g], pH 4.4	ind UV 215 nm	0.5	black powder, residues	(29)
NH_4^+, K^+, Na^+, Mg^{2+}	16 mM imidazole, 17.5 mM HIBA, 4 mM 18-C-6, pH 4.4	ind UV 215 nm	1–11	residues	(25)

(*Continued*)

TABLE 1 (Continued)

Compounds	BGE	Detection	LOD (ppm)	Matrices	Ref.[a]
MMA, NH_4^+, EA[h], K^+, Na^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}	10 mM chrysoidine in MeOH[i], 0.7% glacial acetic acid	ind UV 470 nm	0.1–2.3	residues	(15)
MMA, NH_4^+, EA, K^+, Na^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}	10 mM histidine, 50 mM acetic acid, 1 mM HIBA, 0.7 mM 18-C-6, pH 4.2	CCD	0.031–0.240	residues	(30)
K^+, NH_4^+	10 mM pyridine, 3 mM 18-C-6, pH 4.5	ind UV 254 nm	0.1–0.3	soil	(26)
Simultaneous detection					
NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Br^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, ClO_3^-, SCN^-, CN^-	6 mM imidazole, 15 mM HIBA, 4 mM 18-C-6, 3 mM NTS, 5% ACN, pH 6.5 adjusted with TMAOH[j]	ind UV 235 nm (anions) 208 nm (cations)	10–15 (anions) 0.5–5 (cations)	residues	(28)

[a] Ref: reference; [b] DETA: diethylene triamine; [c] ind: indirect; [d] dir: direct; [e] N/A: not available; [f] CHES: cyclohexylaminoethanesulfonate; [g] ACN: acetonitrile; [k] EA: ethylammonium; [i] MeOH: methanol; [j] TMAOH: tetramethylammonium hydroxide.

TABLE 2 Separation of Nitrated Explosives by CE

Compounds	Separation mode	BGE	Detection	LOD (ppm)	Matrices	Ref.[a]
DBP, DEDPU, DEGDN, 1,3-DNN, 1,5-DNN, 1,8-DNN, 2,3-DNT, 2,4-DNT, 2,6-DNT, 3,4-DNT, DPA, EGDN, HMX, 2-nDPA, N-nDPA, NG, NGU, 2-NN, 2-NT, 3-NT, 4-NT, PA, PETN, RDX, Tetryl, TNT	MEKC	2.5 mM borate, 25 mM SDS, pH 7.8–8.9	UV (220 nm)	0.1–1	plastic explosives	(37)
4-ADNT, DNB, 2,6-DNT, HMX, NB, 2-NT, 4-NT, RDX, Tetryl, TNB, TNT	MEKC	2.5 mM borate, 12.5 mM boric acid, 25 mM SDS, pH 8.5	UV (230 nm)	100–10000	soils	(38)
EGDN, HMX, NG, NGU, PETN, RDX, Tetryl, TNT	MEKC	2.5 mM borate, 25 mM SDS, 1 μM fluoresceine, pH 8.5	LIF (488 nm)	10–40	N/A[b]	(39)
DNB, 2,4-DNT, 2,6-DNT, HMX, NB, NG, 2-NT, 3-NT, 4-NT, PETN, RDX, Tetryl, TNB, TNT	MEKC	25 mM phosphate, 50 mM SDS, pH 7	UV (254 nm)	0.31–1.42	detonating cord, explosives	(40)
2-ADNT, 4-ADNT, DNB, 2,4-DNT, 2,6-DNT, HMX, NB, 2-NT, 3-NT, 4-NT,RDX, Tetryl, TNB, TNT	MEKC	25 mM phosphate, 50 mM SDS, pH 7	UV (254 nm)	N/A	water	(41)
1,4-DNB, 1,2-DNB, 1,3-DNB, 2,3-DNT, 2,4-DNT, 2,6-DNT, 3,4-DNT, 2-NT, 3-NT, 4-NT	MEKC	10 mM SB-β-CD, 30 mM SDS, 20 mM borate pH 9, 10% ACN[c]	UV (214 nm)	N/A	N/A	(42)
2-ADNT, 4-ADNT, 1,4-DNB, 1,2-DNB, 2,4-DNT, 2,6-DNT, 3-NT, 3,4-DNT, 2,3-DNT, HMX, NB, RDX, TNT	MEKC	15 mM borate, 25 mM SDS, pH 8.7	EC (Ag/Au)	0.07–0.11	soil, water	(43)
2-ADNT, 4-ADNT, 2,6-DANT, 2,4-DANT, 2-HADNT, 4-HADNT, TAT, TNT	MEKC	2.5 mM borate, 12.5 mM boric acid, 50 mM SDS, pH 8.5	UV (225 nm)	0.1–0.2	sludge	(44)
HMX, MNX	MEKC	2.5 mM borate, 12.5 mM boric acid, SDS 50 mM, pH 8.5	UV (230 nm)	N/A	soil, plant	(45)

(*Continued*)

TABLE 2 (Continued)

Compounds	Separation mode	BGE	Detection	LOD (ppm)	Matrices	Ref.[a]
HMX	MEKC	2.5 mM borate, 12.5 mM boric acid, 50 mM SDS, pH 8.5	UV (230 nm)	N/A	soil, plant	(46)
2,3-DNT, 2,4-DNT, 2,6-DNT, 3,4-DNT, HMX, 2-NT, 3-NT, 4-NT, PETN, RDX, Tetryl, TNT	MEKC	10 mM borate, 50–60 mM SDS, pH 8.4–8.6	UV (195 nm)	1	N/A	(47)
2-ADNT, 4-ADNT, 1,3-DNB, 2,4-DNT, 2,6-DNT, HMX, NB, 2-NT, 4-NT, 3-NT, RDX, Tetryl, 1,3,5-TNB, TNT	MEKC	10 mM borate, 55 mM SDS or 80 mM cholate	UV (254 nm)	0.2–0.8	seawater	(48)
	CEC	10 mM Tris, 45% ACN	UV (254 nm)	0.1	seawater	
2-ADNT, 4-ADNT, 1,3-DNB, 2,4-DNT, 2,6-DNT, HMX, NB, 2-NT, 3-NT, 4-NT, RDX, Tetryl, 1,3,5-TNB, TNT	MEKC	7.5 mM NaH_2PO_4, 7.5 mM H_3PO_4, 150 mM SDS in water/MeOH[d]/ACN (7:2:1, v/v)	UV (210 nm)	0.003–0.006	soil	(49)
CL20, HMX, MDNA, MNX, RDX	CD-EKC[e]	0,1 mM acetate buffer, 10 mM SB-β-CD, pH 5	UV (230 nm)	0.2	N/A	(50)
CL20, HMX, RDX, TNB, TNT	CD-EKC	10 mM acetate buffer, 10 mM SB-β-CD, pH 6.9	MS	0.025–0.5	soil, sediment	(51)
2-ADNT, 4-ADNT, DNB, 2,4-DNT, 2,6-DNT, HMX, NB, 2-NT, 3-NT, 4-NT, RDX, Tetryl, TNB, TNT	CEC	15% MeOH, 85% 10 mM MES with 5 mM SDS	UV (254 nm)	N/A	N/A	(52)
4-ADNT, 2-ADNT, DNB, 2,6-DNT, 2,3-DNT, HMX, NB, 2-NT, 4-NT, 3-NT, RDX, TNB, TNT	CEC	30% MeOH, 70% 10 mM MES with 7 mM SDS	EC (Au)	0.07–0.11	soil, water	(53)
2-ADNT, 4-ADNT, DNB, 2,4-DNT, 2,6-DNT, HMX, NB, 2-NT, 4-NT, 3-NT, RDX, Tetryl, TNB, TNT	CEC	20% MeOH, 80 % 10 mM MES with 5 mM SDS and 5 µM Cy-5	LIF (635 nm)	1–10	N/A	(54)

[a]Ref.: reference; [b]N/A: Not available; [c]ACN: acetonitrile; [d]MeOH: methanol; [e]CD-EKC : cyclodextrin-based electrokinetic chromatography.

TABLE 3 Analysis of Explosives by Chip Electrophoresis

Compounds	Separation mode	BGE	Detection	LOD (ppb)	Analysis time (s)	Ref.[b]
Explosive related ions						
K^+, Na^+, Ba^{2+}, Li^+; Cl^-, SO_4^{2-}, F^-, CH_3COO^-, PO_4^{3-}	CZE	20 mM histidine, 20 mM MES, pH 6.1	CCD	100–250	40; 100	(65)
K^+, NH_4^+, Na^+, MMA; NO_3^-, Cl^-, ClO_4^-	CZE	20 mM histidine, 20 mM MES, 7.5 mM 18-C-6, pH 6.1	CCD	10	25 (each)	(66)
K^+, NH_4^+, Na^+, MMA; NO_3^-, Cl^-, ClO_4^- (simultaneously)	CZE	20 mM histidine, 20 mM MES, pH 6.1	CCD	N/A[p]	60	(67)
NH_4^+, Na^+, MMA, NO_3^-, Cl^-, ClO_4^- (simultaneously)	CZE	20 mM histidine, MES 20 mM, pH 6.1	CCD	1500	60	(68)
Organic explosives						
DNB, 2,4-DNT, 2,6-DNT, 4-NT, TNT	MEKC	15 mM borate, 25 mM SDS, pH 8.7	EC (carbon)	600–2000	210	(70)
2,4-DNT, 2,6-DNT, 2,3-DNT, RDX, TNT	MEKC	15 mM borate, 25 mM SDS, pH 8.7	EC (Au)	110–200	400	(71)
2-ADNT, 4-ADNT, DNB, 2,4-DNT, 2,6-DNT, HMX, NB, NT, RDX, tetryl, TNB, TNT	MEKC	50 mM borate, 50 mM SDS, 5 μM Cy7, pH 8.5	Indirect LIF	1000	60	(62)
2,4-DNT, 2,6-DNT, 2,3-DNT, TNT	MEKC	15 mM borate, 25 mM SDS or 25 mM MES, pH 8.7	EC (Au)	24–36	130	(72)
2-ADNT, 4-ADNT, DNB, 2,4-DNT, TNB, TNT	MEKC	15 mM borate, 20 mM SDS, pH 9.2	EC (carbon)	60	150	(73)
Tetryl, TNB, TNT	NACE[c]	ACN[d] – MeOH[e] (87.5/12.5), 2.5 mM NaOH, 1 mM SDS	UV 505 nm	60–220 or 0.19–0.34 (SPE)	20	(74)
1,3-DNB, 2,4-DNT, TNT,	MEKC	15 mM borate, 15 mM SDS, pH 9.2	EC (diamond)	70–110	45	(75)
DNT, TNB, TNT	MEKC	15 mM borate, 15 mM SDS, pH 9.2	EC (carbon)	450–800	140	(63)
DNB, TNB, TNT	MEKC	15 mM borate, 15 mM SDS, pH 9.2	EC (carbon)	N/A	170	(64)
TNT	CZE	15 mM borate, pH 9.2	EC (Au, Hg/Au, carbone)	7	24	(76)

(*Continued*)

TABLE 3 (Continued)

Compounds	Separation mode	BGE	Detection	LOD (ppb)	Analysis time (s)	Ref.[b]
TNT	CZE	10 mM borate, pH 10.5	EC	10000	N/A	(77)
2,4-DNT, NB, 4-NT TNT	MEKC	15 mM borate, 15 mM SDS, pH 9.2	EC (carbon)	12–52	120	(78)
1,3-DNB, 2,4-DNP, 2,4-DNT, PA, TNB, TNT	IA[f]	phosphate buffer, pH 7.6	LIF	1	50	(79)
TNT	IA	acetate buffer, Tris, EDTA, pH 8.2	LIF	1	55	(80)
DNB, 2,4-DNT, 3-NT, RDX, 1,3,5-TNB, TNT	CEC	20 mM Tris, 40% ACN, pH 10	UV 254 nm	N/A	150	(81)
DNB, TNT	sol in BGE	40 mM phosphate, 13% MeOH, 175 mM TETT[g]-based sol, pH 10.1	EC	120	650	(82)
Inorganic and organic explosives						
MMA, NH_4^+, Na^+, TNB, TNT, 2,4-DNT, 2-ADNT	CZE /MEKC	20 mM histidine, 20 mM MES, 15 mM LiDS, pH 6.1	CCD + EC (carbon)	10	120	(69)

[a]Ref: reference; [b]N/A: not available; [c]NACE: non-aqueous capillary electrophoresis; [d]ACN: acetonitrile; [e]MeOH: methanol; [f]IA: immunoassay; [g]TETT: N-(trimethoxysilylpropyl)ethylenediamine triacetic acid.

numerous anions that could be solved by employing a conductivity detector. Another alternative is to simultaneously inject into both sides of a single capillary, named dual-opposite injection. This was used for the simultaneous analysis of anions and cations in explosive residues (28). In this dual-opposite injection mode, a novel BGE was developed containing HIBA as the buffer, imidazole as cationic chromophore, 1,3,6-naphthalenesulfonic acid (NTS) as anionic chromophore, 18-C-6 as a cation selectivity modifier, and acetonitrile (5%) as an organic modifier. The pH was adjusted at 6.5 using tetramethylammonium hydroxide, which is also an EOF modifier. Reversed polarity was used for separating the anions using the normal injection side (longer migration distance) because a wide variety of anions must be separated for explosive residue characterization. The HIBA, imidazole, and NTS concentration and pH values were optimized in order to reach complete resolution in the same run of 6 cations and 9 anions in less than 6 min, as presented in Figure 2. LODs ranged from 0.5 to 5 ppm for anions and from 10 to 15 ppm for cations.

All the methods for CE explosive-related anion and cation analysis published in literature presented good figures of merit, especially the relative standard deviations for migration times remaining less than 2% and for peak areas, always inferior to 5 or 10% over numerous successive runs. Various matrices were analyzed, such as powders, soils, metallic pieces, and water samples. A recent paper evaluated the potential effect of various matrices (cotton, soil, cloth, paper, plastic, and metal) on figures of merit and quantitations obtained by CE analysis, and observed that it was negligible in all cases (27). Whereas sample collection had to be meticulous, sample preparation was always fast and simple, consisting of water extraction at ambient or high temperature or in wiping matrices with moistened swabs, which were themselves next extracted with water.

MOBILE LABORATORY

The recent Bali bombings demonstrated that a "mobile laboratory" was the only effective and efficient way to process large numbers of samples and assist investigators with relevant information in a very short time (16). Consequently, Hutchinson et al. developed protocols for CE separation of 15 anions in less than 9 min and 12 cations in less than 9.5 min (15). A commercialized portable CE instrument was modified for use with a LED detector to enable sensitive indirect photometric detection. Indeed, LED provided a highly stable narrow-spectrum, low-noise output, required low power, could be purchased quite cheaply, was small in size, and had very long lifetime in comparison with other light sources. LODs ranged from 0.2 to 1.2 ppm for anions and from 0.1 to 2.3 ppm for cations.

Use of the portable instrumentation in the field was demonstrated by analyzing post-blast residues in a mobile laboratory immediately after

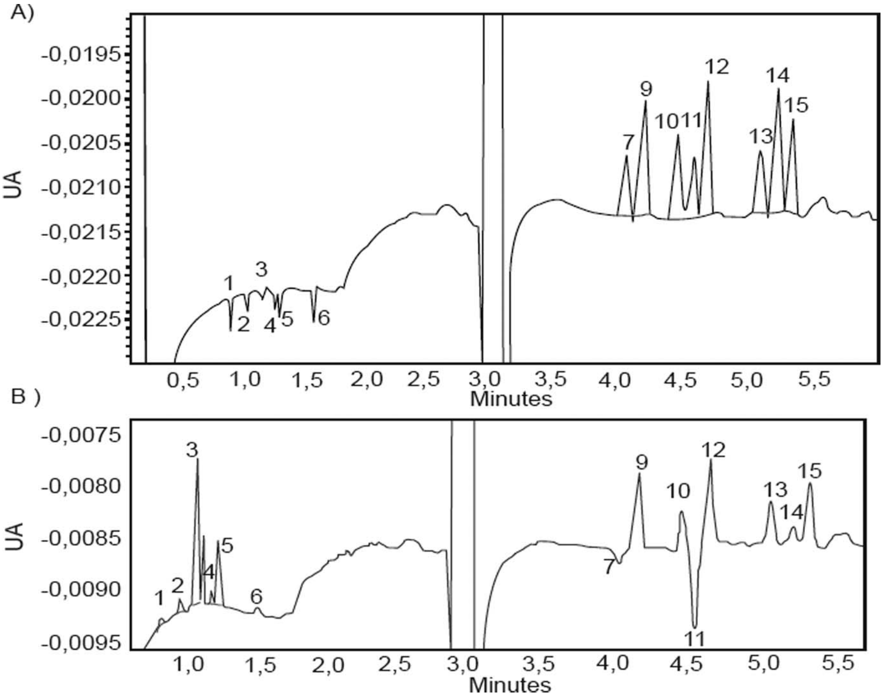

FIGURE 2 CE separation of a 10 ppm cation and anion standard mixture in ultra-pure water at (A) 235 nm and (B) 208 nm. Bare fused-silica capillary, 50 μm I.D. × 40,2 cm (detection at 30 cm). BGE: 4 mM 18-C-6, 5% (v/v) acetonitrile, 15 mM HIBA, 3 mM NTS, and 6 mM imidazole adjusted at pH 6.5 with tetramethylammonium hydroxide. Separation voltage: 10 kV. Hydrodynamic injection, 50 mbar, 7 s (inlet) and 5 s (outlet). Peak assignment: 1, ammonium; 2, potassium; 3, sodium; 4, calcium; 5, magnesium; 6, strontium; 7, bromide; 9, chloride; 10, nitrite; 11, nitrate; 12, sulfate; 13, perchlorate; 14, thiocyanate; 15, chlorate. From (28).

detonation of the explosive devices. Complete profiling of the ionic composition of the residues allowed identification of the chemicals initially used. The same CE portable instrumentation approach was next evaluated with a contactless conductivity detection, which improved the LODs by a factor of 10 (cf. Table 1) (30). Low conductivity BGEs were used and 15 anions or 11 cations were analyzed in less than 7 min. A selection of 10 deemed most important anions could even be separated in 45 s on a short capillary (30.6 cm).

The developed methods were successfully field tested for post-blast residues obtained from the control of homemade devices. The resulting electrophoregrams are shown in Figure 3. Thus, CE is a highly relevant separation technique for inorganic explosive analysis, and its miniaturized and portable features are perfectly adapted for field analyses, which are necessary within the terrorism context, but may be also highly useful for forensic or environmental purposes.

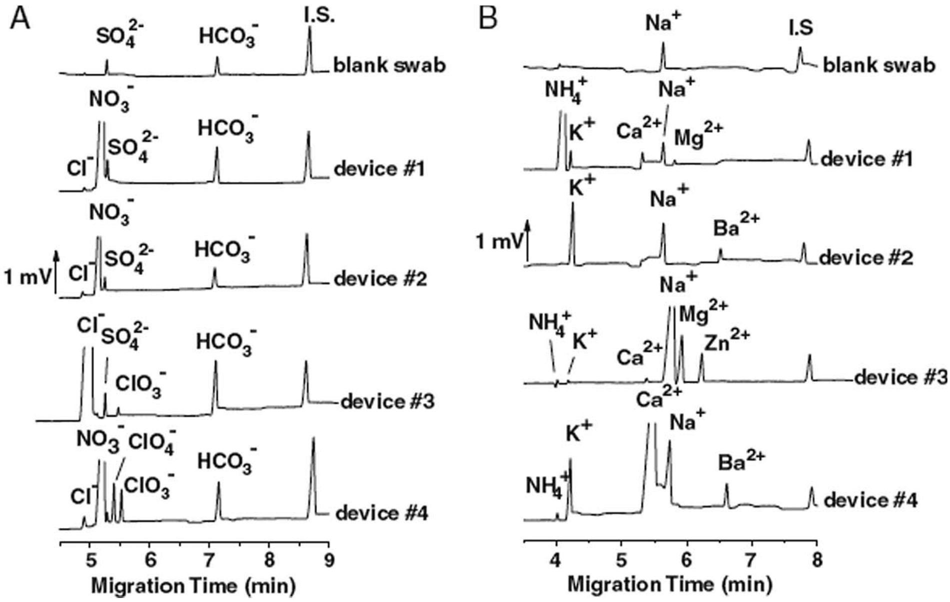

FIGURE 3 Analysis by CE-CCD of (A) anions and (B) cations extracted from post-blast residues resulting from the detonation of four inorganic homemade explosive devices and present in blank swab. (A) Fused-silica capillary modified with hexadimethrine bromide, 75 μm I.D. × 90 cm (detection: 82 cm). BGE: 70 mM TRIS, 70 mM CHES, pH 8.6. Separation voltage: −25 kV. Hydrodynamic injection, 1 psi, 5 s. Internal Standard: hexanesulfonate. (B) Fused-silica capillary, 75 μm I.D. × 73 cm (detection: 65 cm). BGE: 10 mM His, 50 mM acetic acid, 1 mM HIBA, 0.7 mM 18-C-6, pH 4.2. Separation voltage: 25 kV. Hydrodynamic injection, 1 psi, 5 s. Internal Standard: benzylamine. From (30).

Analysis of Organic Explosives by CE

Even if the nitroaromatic, the nitramine, and the nitrate ester compounds are neutral compounds, capillary electrophoretic techniques have been demonstrated to be fully relevant for organic explosive analysis, as it appears in Table 2.

SEPARATION MODES

Micellar electrokinetic chromatography (MEKC) involving the introduction of charged surfactants, most often sodium dodecylsulfate (SDS), above its critical micellar concentration (CMC) was extensively used for the separation of neutral compounds (55,56). The partitioning of the neutral analytes between the micelles cavity and BGE, depending on both the analyte and micelle natures, allows their separation. Identification of organic explosive constituents by MEKC was presented for the first time by Northrop et al. in 1991 (37). The effects of the SDS concentration, pH, addition of a tetraalkylammonium salt, capillary diameter, and injection time were studied.

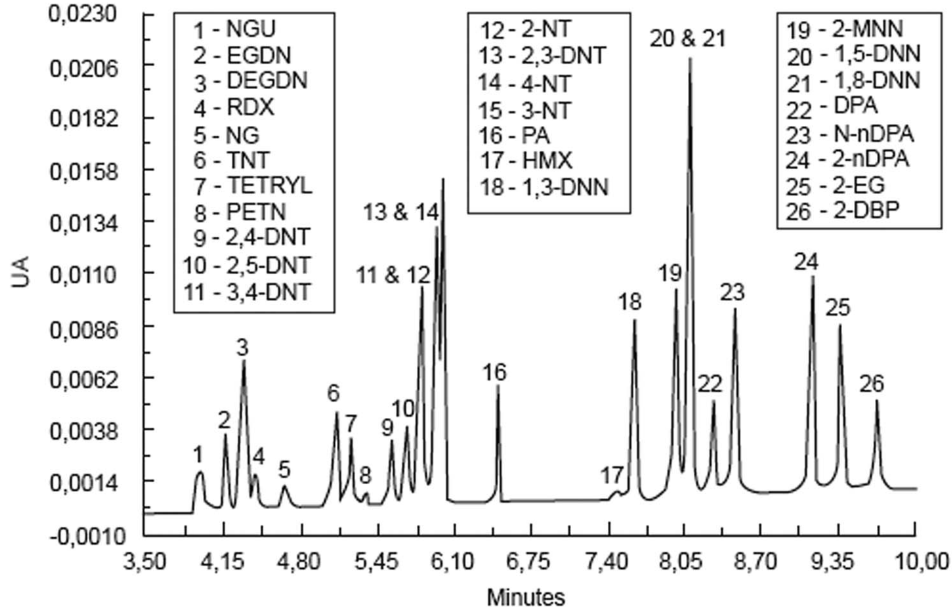

FIGURE 4 MEKC separation of 26 gunshot and high-explosive constituents. Fused-silica capillary, 100 µm I.D. × 67 cm (detection: 62 cm). BGE: 2.5 mM borate, 25 mM SDS. Separation voltage: 20 kV. Electrokinetic injection: 5 kV, 2 s. UV detection at 220 nm. From (37).

Figure 4 presents the separation of 26 compounds in less than 10 min, with a borate buffer containing 25 mM SDS. Some compounds were not fully resolved, such as 3,4-DNT and 2-NT. The use of a phosphate buffer at pH 7.0 instead of the previous borate buffer at pH 8.0 allowed Oehrle to completely resolve 14 explosive compounds including 3-NT and 4-NT (40). This electrolyte was used for the analysis of high-explosives, such as C-4, and detonating cord (40), but also various waste water samples generated from an ammunition plant (41). LODs about 1 ppm were obtained.

MEKC was compared to HPLC for the determination of explosive residues in real extracts, and more especially in soils (38). MEKC offered high resolution, allowing for fingerprinting of complex soil extracts, was fast and cost-effective, and generated little organic waste compared to HPLC. Small sample sizes were easily handled, and LODs were close to those obtained by HPLC. In addition, MEKC provided easy removal of interfering humic substances extracted from complex soil matrices, because they were highly retained by micelles and migrated at the very end of the electrophoregram. Other environmental real matrices were then analyzed by MEKC for the determination of high-explosive compounds and their degradation products, allowing the determination of their degradation patterns and environmental fates (41,45,46).

Numerous experimental parameters affect MEKC separations and a large number of experiments may be required to reach the optimum experimental conditions. For this purpose, multivariate approach and artificial neural networks were employed by Casamento et al. for the optimization of the separation of 12 explosives by MEKC (47).

The use of cyclodextrins (CDs) alone or mixed with SDS was also evaluated in order to improve selectivity. The CDs form inclusion complexes with the analytes, exhibiting different stability constants according to the explosive molecule and leading to different selectivities for the explosives compared to SDS. Luong and Guo involved a mixed pseudo-stationary phase combining SDS and negatively charged sulfobutyl ether-β-CD (SB-β-CD) to obtain a satisfactory separation of positional isomers of some nitroaromatic compounds (42). Groom et al. used SB-β-CD alone (without SDS) to rapidly resolve CL-20, HMX, and RDX plus their related degradation intermediates in environmental samples with UV detection (50) or MS (51).

Another electrokinetic separation technique well adapted to the separation of neutral compounds is capillary electrochromatography (CEC). CEC can be viewed as a hybrid technique between HPLC and CE where a solid stationary phase is present in the capillary and a mobile phase is driven through this stationary phase using EOF. Neutral species are separated on the basis of differential partitioning between the mobile and stationary phases. Bailey and Yan were the first ones to involve CEC for the separation of explosive compounds (52).

A separation with baseline resolution was achieved for 14 nitroaromatic and nitramine explosives (the US EPA standard mixture) in under 7 min with efficiencies over 500,000 theoretical plates/m. They also developed a fast CEC separation of these compounds in less than 2 min with a very short column, 12 cm, packed with non-porous 1.5 μm C18-bonded particles and a hydro-organic mobile phase. Next, Bailey and Wallenborg, for the first time, developed the hyphenation of a CEC separation with indirect laser-induced fluorescence (LIF) detection and applied it to the complete separation of the US EPA standard mixture (cf. Figure 5) (54).

Monolithic stationary phases may advantageously replace particle-based stationary phases for CEC applications, as columns in the capillary format are easily prepared by in situ synthesis and no longer require the presence of frits, which are often sources of troubles. CEC of explosive mixtures using sol-gels prepared from methyltrimethoxysilane was evaluated (48). It was observed that CEC was not as powerful as MEKC in terms of resolving power but allows for extended injection times for concentrating analytes contained in seawater at the top of the separation column. LODs below 100 ppb were reached.

DETECTION MODES

Aromatic explosives possess a chromophore moiety allowing their direct UV detection, which is most often satisfactory. Nevertheless, due to the short

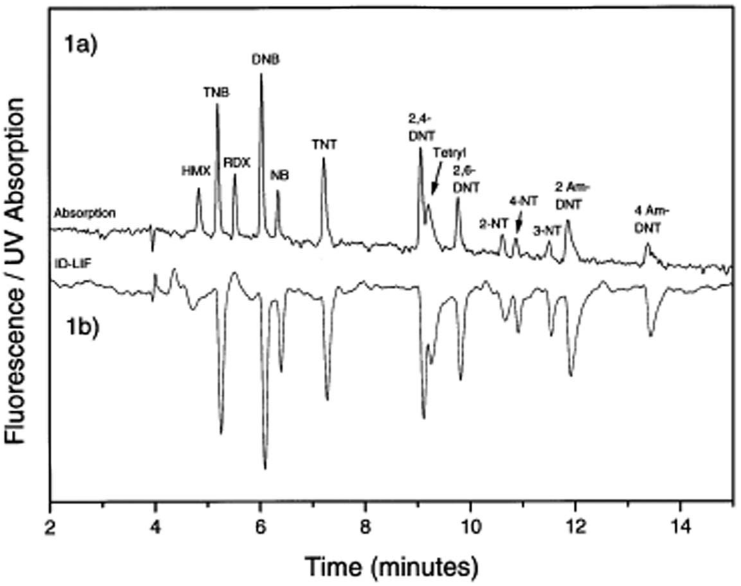

FIGURE 5 CEC separation of US EPA 8330 standard mixture with tandem UV absorption and indirect laser induced detection. Fused-silica capillary, 75 μm × 44 cm, 30 cm of which was packed with 1.5 μm non-porous C18-bonded particles. Mobile phase, 20% methanol and 80% 10 mM MES, 5 mM SDS and 5 μM Cy-5 (v/v). Separation voltage, 15 kV. Electrokinetic injection, 1 s at 8 kV of a 20 mg L^{-1} (each component) sample. UV detection at 254 nm. Fluorescence detection excitation, 635 nm. From (54).

optical path length in CE compared to HPLC, the LODs are around some ppm in CE, whereas it is rather some ppb in HPLC (57). When more sensitivity is required, it is possible to select a capillary with a wider internal diameter, but this solution is limited by Joule effect. The capillary may also be replaced by one fitted with an extended path length, i.e., the inner diameter is increased only at the detection window, offering the sensitivity of a wider inner diameter capillary and the low current generation of a narrow one (47). However, sensitivity may be improved likewise by only a factor between 3 and 5. A Z-shape detection cell may also be connected, allowing a gain of about 10, but it has not been exploited yet for the detection of explosives.

To solve the potential problem of low concentration sensitivity in CE, several techniques have been developed. One approach consists in on-line sample preconcentration, which can be easily performed in CE without any modification of the apparatus and keeping automation of the system. Yang et al. developed an on-line sweeping preconcentration step (picking and accumulating analytes by a pseudo-phase passing through the large sample zone during voltage application) coupled to a MEKC separation for the determination of the US EPA mixture compounds in soil extracts (49).

LODs were improved down to as low as 3.1–6.5 ppb. Another approach is the use of high sensitivity detectors such as LIF, in a direct or indirect mode (58). Kennedy et al., for the first time, developed LIF detection for explosives (39). As indirect detection was used, a fluorophore (fluoresceine, eosin, anthracene, or rhodamine B) was added to the MEKC buffer system. The mechanism by which the analytes were detected is based on the fact that analytes perturb the partitioning of the fluorophore between the aqueous and micellar phases, knowing that one of the properties of the micelles is their ability to alter the fluorescence quantum yields.

Electrochemical (EC) detectors, which promise high sensitivity, simplicity, and low cost, have been also coupled with CE to detect explosives, since nitroaromatic ones are known to exhibit well-defined redox behavior. Indeed, these compounds such as TNT are readily reduced at various electrodes. Reduction of nitrotoluene occurs in a single four-electron step to form hydroxylamines, which is followed by a two-electron reduction to corresponding amine. The MEKC separation followed by amperometric detection was used to determine the explosive content of soil extracts and groundwater (43). The electrochemical reactivity of TNT and analogs, and thus performance of the working electrode is strongly influenced by the type of electrode.

Authors evaluated platinum, nickel, silver, gold, and silver-plated gold working electrodes (43). Preliminary results eliminated platinum and nickel electrodes options because of their rapid fouling. Then, it appeared that the use of gold electrode could be problematic since its response to acetonitrile, the sample solvent used in the study, was significant. Best results were finally obtained with a silver-plated gold electrode and LODs of about one hundred ppb were reached for 13 explosives. The response signal is also strongly influenced by the electrode position. Here, precise alignment was not necessary due to the large diameter of the detecting electrode in comparison with that of the separation capillary. Amperometric detection was also coupled to CEC separation of explosives for their successful determination in environmental samples (53).

It is noteworthy that LIF and EC detection modes are characterized not only by a high sensitivity but also by a high selectivity, which provides high suitability for the analysis of explosives at trace-levels in complex matrices. As an example, in soil extracts and groundwater, a majority of potential interferents such as humic acids are neither fluorescent nor electro-active.

Finally, CE can be hyphenated with MS to combine the excellent separation capabilities of CE and the sensitivity of MS associated with its power in analyte identification for structure elucidation or additional selectivity (59–61). Groom et al. used a CE-MS system for the analysis of explosives in environmental samples and offered potential for the identification of highly polar or charged degradation products (51). CDs were added in the CE buffer to allow the separation of the explosive compounds and the potential effect of the presence of CD on analyte mass spectra was studied. The CD concentration was optimized such as the nature of the sheath liquid flow. Soils from an ammunition manufacturing site and contaminated marine sediments were next analyzed leading to LODs of 25 ppb for 6 explosive compounds.

ANALYSIS OF EXPLOSIVES IN ELECTROPHORETIC MICROSYSTEMS

CE microchip systems are of considerable recent interest owing to their high degree of integration, portability, minimal solvent and reagent consumption, speed, cheapness, consistency with multidimensional separations, disposability. These micro total analytical systems hold great promise for biomedical and pharmaceutical analysis, but also for environmental monitoring and forensic investigations in the explosive field. For explosive separation protocols on chip, all the developments were first performed in the capillary format and then transferred to the chip format. Thus, what mainly characterizes the state of the art of CE chip for explosive analysis is either the difficulty to transfer the capillary separation methods to a shorter separation length or the technical development of chip, such as the hyphenation of the separation step with the detection one, the miniaturization of the detection step or the introduction of macro-world sample to microfabricated separation devices without manual intervention.

Chips involved in explosive analysis are generally made of glass. Cross-injector design was mainly involved, even if some authors also evaluated offset double-T design for increasing the injected volume (62). It is noteworthy that the development of the methods for the separation of explosive compounds on chip has completely followed, and sometimes even induced, instrumental or conceptual evolutions with time, rendering the literature about the chip analysis of explosives rich and highly relevant. As an example, a newly designed CE chip with a simple and efficient sample introduction interface was described, and its performance was demonstrated with the MEKC analysis of three explosives (TNT, TNB, and DNB) (63).

The idea consisted in fabricating a chip with a sharp inlet shape that can penetrate into a vial of either the sample solution or BGE (Figure 6A). It led to reproducible and simple introduction of multiple discrete samples without memory effects, complex channel layouts, and numerous voltage controls. This idea was next extended to achieve the direct coupling of hydrodynamically flowing stream to a CE chip for continuous assays, and thus, monitoring explosives (64). It was achieved with two sharp inlets as presented in Figure 6B. With a sample having a hydrodynamic flow-rate in the range 0.2–1.8 ml min^{-1}, a long sequence of 40 consecutive measurements was carried out over a total time of 125 min and gave relative standard deviations inferior to 4% for the current response and migration time.

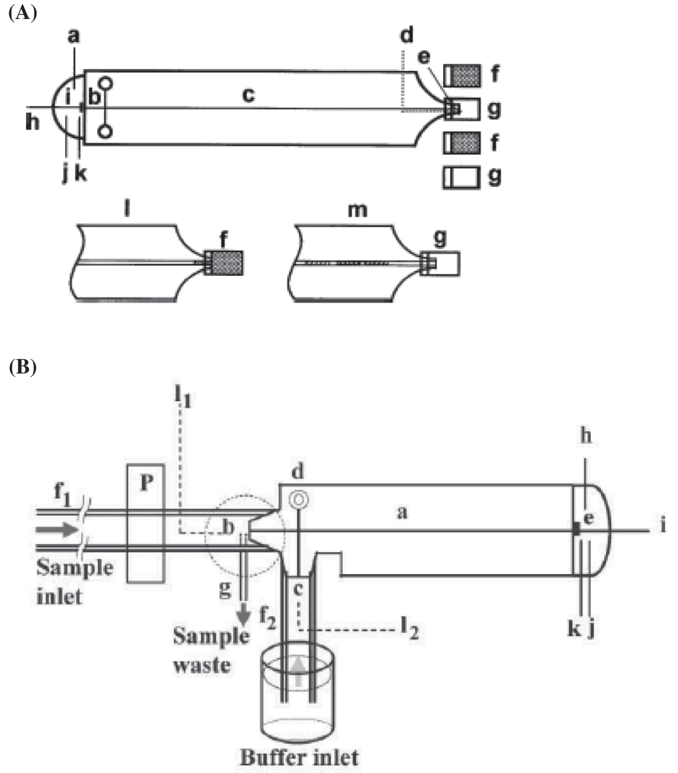

FIGURE 6 Schematic diagram of the sharp CE chip for (A) simplified sample introduction and (B) on-line continuous monitoring capability. (A) The separation channel (c) is connected to a sharp inlet tip (e) and a detection cell (i). The sample or running buffer is introduced by placing the sharp inlet into a vial of either the sample solution (f) or BGE (g). The detection cell (i) comprised a Pt wire grounding electrode (a), screen-printed carbon working electrode (h), Pt wire auxiliary electrode (j), and the Ag/AgCl wire reference electrode (k). A Pt wire (d) serves as contact to high voltage power supply. From (63). (B) The separation channel (a) is connected to a sharp inlet tip (b), a side sharp BGE inlet tip (c), unused reservoir (d) and a detector compartment (e). The sample is introduced by pumping with a peristaltic pump (P) from the reservoir through the tubing (f_1) to the separation channel. The sample solution is drained through a plastic tubing (g) that is placed 1 mm from the sample inlet tip. The BGE is introduced by capillary action through the plastic tubing (f_2). The detection cell (i) comprised a Pt wire grounding electrode (h), a screen-printed carbon working electrode (i), a Pt wire auxiliary electrode (k), and the Ag/AgCl wire reference electrode (j). Two Pt wires are inserted into the plastic tubings (f_1, f_2), respectively, serving as contacts to high voltage power supply. From (64).

Analysis of Inorganic Explosives in Electrophoretic Microsystems

The analysis of ionic explosives by chip electrophoresis has received much less attention than the nitroaromatic ones, and only one group worked on the development of chip electrophoresis for low-energy explosives (65–69)

(Table 3). Nevertheless, a very significant work was performed. An original and miniaturized CCD was described by Pumera et al. (65). The contactless approach allows the direct detection of ionic solutes and precludes problems associated with the electrode-solution contact (fouling, unwanted reactions), offers isolation of the detection system from the high separation fields, does not compromise the separation efficiency, and simplifies the detector fabrication.

Indeed, two planar sensing aluminum film electrodes were placed on the outer surface of a chip and the impedance of the solution in the separation channel was then measured. This design was applied to the analysis of cationic and anionic explosives pertaining to pre- or post-explosion mixtures (66). The low EOF generated in polymethylmethacrylate channels made it easier the rapid switching between cationic and anionic analyses within the same channel and using the same BGE, without any EOF modifier.

The CCD arrangement was next improved by moving the detector along the separation channel via sliding the electrode holder (67). Placing the detector at different locations along the channel offered insights into the separation process and may help in optimizing resolution/channel length/separation voltage parameters. The system also enabled rapid switching between total (fast screening) or individual (fingerprinting) signals while placing the detector at the channel inlet or outlet. The analysis time can also be decreased by changing the detector position during the analysis, after the detection of the first fast migrating ions.

These improvements were illustrated with some low-energy ionic explosives. CCD detection was also used for the simultaneous measurement of six low-energy explosive-related anions and cations (68). Dual electrokinetic injection from both ends of the separation channel was performed, thanks to the presence of injection crosses on both extremities of the chip. Since the EOF of the PMMA channel is low, anions and cations moved in opposite directions in the separation channel upon applying electric field and were detected by the CCD placed around the middle of the separation channel.

Recently, for the first time, Wang et al. reported an end-column "hybrid" CCD for microchips (83). It was based on a hybrid arrangement where the receiving electrode is insulated by a thin layer of insulator and placed in the bulk solution of the chip detection reservoir, whereas the emitting electrode is in contact with the solution flowing out from the channel in a wall-jet arrangement. A 10-fold sensitivity enhancement was obtained as compared with usual chip CCD arrangement for the detection of 3 explosive-related cations (ammonium, methylammoniun, and sodium) and the peak shapes were improved in comparison with the contactless mode. This approach would allow spatial integration with amperometric detection, allowing easy and sensitive simultaneous detection of inorganic and organic explosives, as will be described in more details later.

Analysis of Organic Explosives in Electrophoretic Microsystems

As previously pointed out, neutral organic explosives are most often electrokinetically separated by MEKC- or CEC-based mechanisms. For MEKC separation, no developments were made on the electrolyte media in chips. Most authors used a borate buffer containing 15–50 mM SDS (Table 3). Whereas MEKC separations developed in the capillary format can be easily transfered to chip format, this is slightly more complex for CEC analysis, where the stationary phase is used for both preconcentration and separation purposes. Giordano et al. synthesized a stationary phase directly in the channel by a sol-gel process using methyl-based precursors to yield a hydrophobic phase (81).

To keep the overall separation resolution obtained with the capillary format while transferring to the chip format with reduced separation length, the authors increased the hydrophobicity of the stationary phase by producing hybrid gels from methyl- and ethyl-trimethoxysilane precursors. It is worthwhile to notice that a simple Y configuration was used, rather than the traditional cross one, as the injection of a discrete plug of sample was not necessary because preconcentration was performed at the head of the stationary phase, precluding for the need of a sample waste reservoir.

For the first time in chip format, Pumera et al. evaluated an organically modified negatively-charged sol added to the BGE and acting as a pseudostationary phase for tuning selectivity, as the analyte mobilities were modified thanks to sol-solute interactions (82). Indeed, the introduction of negatively charged sol in a phosphate buffer allowed the separation of TNT and DNB. It is worthwhile to note that the presence of sols in the BGE did not alter the EC detection. The linearity and the precision of the response were satisfactory. A decrease in current intensity was observed in the presence of the sol, indicating lower diffusion coefficients in the sol-modified buffer. The sols were found to be stable for more than 6 months whereas the stability of micellar phases is limited, and a minimum surfactant concentration is not required in contrast to CMC thresholds.

Chips were also involved for immunoassay of TNT, in the direct, competitive, displacement or sandwich formats, immobilizing anti-TNT antibodies onto the surface of the chip (84). Determinations of TNT were achieved with LODs between 1 and 20 ppb according the immunoassay formats. Another study extended the application to TNT analogues for measurement of binding and dissociation rate constants (79). High-throughput immunoassays were next implemented, thanks to a radial array electrophoretic chip comprising 96 channels (80).

As in capillary format, UV detection can be used in chips, especially with a deuterium lamp coupled to an optical fiber and a UV transmission microscope objective to collect the light at 254 nm (81). The path length was increased to 100 μm by the design of a bubble cell on the chip, whereas injection and separation channels were etched to an approximate depth of 50 μm. Another study reported the spectrophotometric determination of three trinitroaromatic explosives (TNT, TNB, and tetryl) in the presence of 10 other explosives and explosive derivatives by non-aqueous zone electrophoresis (74).

The electrolyte was composed of 2.5 mM NaOH in acetonitrile-methanol mixture (87.5/12.5, v/v), which reacted with the three trinitroaromatic compounds to form ionized red-colored derivatives that were detected using a green light emitting diode (LED) on the chip. All other explosives and degradation products were colorless throughout this wavelength range. The color formation seemed to be especially sensitive to trinitroaromatic compounds. Acetonitrile was selected as solvent, as it promoted the chemical reaction with sodium hydroxide and methanol was added to increase the NaOH solubility in the medium.

As conductivities are significantly lower in acetonitrile than in aqueous electrolytes, deeper channels could be employed (100 μm instead of 20 μm), permitting simple absorbance detection to be made with a LED. Some SDS (1 mM, i.e., below the CMC value) was also added to the electrolyte in order to improve the separation selectivity thanks to solvophobic interactions between the surfactant and analyte molecules. The applicability of the procedure was demonstrated with the off-line SPE and chip analysis of trinitroaromatic compounds dissolved at trace levels in seawater.

With electrophoretic chips, more sensitive detection modes, such as LIF or electrochemical detection, were also used. Even if LIF has dominated the detection in microchips, in the case of explosives, EC has received much more attention, thanks to the oxido-reductive properties of the nitroaromatic compounds (85). Indeed, EC detection offers great advantages for chip systems such as high sensitivity, inherent miniaturization of both the detection and control instrumentations, and low cost. Therefore, the first paper published on CE chip dedicated to explosive analysis involved an electrochemical detection (70). It combined a separation chip and a thick-film carbon strip, a planar screen-printed carbon line electrode mounted perpendicularly to the flow direction.

Such coupling obviates the need for permanent attachment of the detector and allows easy and fast replacement of the working electrode, which can be particularly advantageous with applications that induce severe electrode fouling. Different carbon inks were evaluated, and the best one gave a LOD of about 0.06–0.2 ppm. An improvement in sensitivity was needed as in insulation between separation and detection electric field, because an increase in the electric field strength induced a decrease in migration times and peak heights, as expected, but also an increase in background noise, revealing incomplete insulation, which constitutes the bottleneck of the hyphenation of CE separation and EC detection.

This chip was implemented in repetitive fast and total analysis for screening purposes of nitroaromatic explosives to provide a timely warning, and was able to switch to a separation mode when harmful compounds were individually detected for fingerprinting identification (73). Switching between the screening and separation modes was accomplished by rapidly exchanging SDS-free for SDS-containing buffers in the separation channel, likewise switching from zone electrophoresis to MEKC mode. Even if this chip was not used with real samples, the paper demonstrated the ability to use a single-channel chip for both the individual and total explosive compound determination, with analysis rates of 30 and 360 per hour, respectively. The high specificity of EC detection was there a key point for preventing from false alarm. This thick-film detector design could also be used to perform linear-scan, square-wave, and adsorptive-stripping voltammetric protocols for determination of TNT (77).

The performance of the working electrode is strongly influenced by the electrode nature. A diamond electrode was evaluated and compared to the thick-film carbon arrangement used previously (75). It offered some enhanced sensitivity, lower noise levels, and, moreover, improved resistance to surface fouling (negligible adsorption of organic compounds) and greater insulation from high separation voltages. Wang and Pumera also compared thick-film carbon, gold, and mercury/gold amalgam electrodes (76). The thick-film carbon electrode resulted in a higher background signal, compared to the two other electrodes. Most favorable signal-to-noise ratios were observed on Hg/Au amalgam electrode. The Hg/Au electrode displayed linear response over 20–100 ppb range and a very low LOD of 7 ppb for TNT.

For the first time in chips, Hilmi and Luong carried out an electroless deposition procedure for fabricating gold electrodes just at the outlet of the separation channel to serve as working electrode (72). They use this setup for the separation and determination of 4 nitroaromatic compounds. This approach obviates the need for a coupling mechanism or tedious alignment procedures that is indeed often problematic, but this is not useful for applications that require frequent surface cleaning or electrode replacement due to severe surface fouling. This is why, rather than fixing or integrating the detector permanently to the chip, these authors also developed a specially designed detection cell allowing to remove the gold electrode from its sensing area just at the outlet of the separation channel (71).

Because of the large diameter of the detecting electrode (0.3 mm) as compared with the internal width of the separation channel (50 μm), good electrochemical efficiency was achieved without a precise alignment procedure. However, to ensure repeatable measurements, the distance between the electrode and the channel outlet must be controlled. This was performed by monitoring the detector background current before sample introduction. A new approach for the separation channel-electrode alignment was presented by Yao et al. (78). It involved Plexiglas holders for housing the separation chip, and the detection reservoir was fitted with three electrodes allowing their convenient replacement and reproducible positioning.

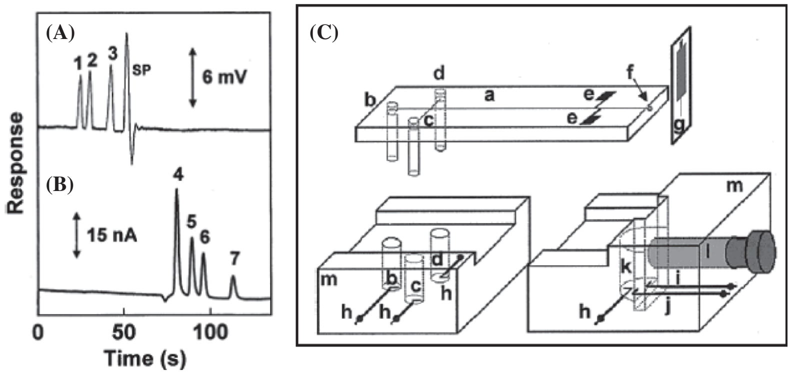

FIGURE 7 Electrophoregrams showing the simultaneous measurement of low- and high-energy explosives, as recorded with conductivity (A) and amperometric (B) detectors. BGE: MES/His buffer (20 mM, pH 6.1) containing 15 mM LiDS. 1, ammonium. 2, methylammonium. 3, sodium. 4, TNB. 5, TNT. 6, 2,4-DNT. 7, 2-ADNT. SP, system peak. Explosive concentration, 2 mM (1,2,3) and 15 ppm (4,5,6,7). (C) microchip system with a dual amperometric/conductivity detection system: (a) glass microchip, (b) run buffer reservoir, (c) sample reservoir, (d) unused reservoir, (e) aluminum electrodes for contactless conductivity detection, (f) channel outlet, (g) thick-film working electrode for amperometric detection, (h) high voltage power electrodes, (i) counterelectrode, (j) reference electrode, (k) outlet reservoir, (l) plastic screw, (m) Plexiglas holder. From (69).

Finally, Wang and Pumera combined both previously presented approaches for low- and high-explosives: they carried out the simultaneous electrophoretic analysis of nitroaromatic and cationic explosives, involving a chip with a dual detection system based on simultaneous conductivity and amperometric measurements (69). The analysis of a mixture containing 4 nitroaromatic explosives (TNB, TNT, 2,4-DNT, and 2-ADNT) and the explosive-related ammonium, methylammonium, and sodium ions was performed in less than 2 min (Figure 7), which offers great promise for obtaining the desired forensic information in a fast and simple manner. Therefore, the literature about the chip analysis of explosives is rich and highly relevant.

CONCLUSION

This review is intended to illustrate that electrophoretic techniques are perfectly well-adapted for explosive determination, in a capillary or chip format. The development of the methods for the separation of explosive compounds has completely followed the instrumental evolutions of electrophoretic techniques with time. Indeed, depending on the nature of explosives, ionized or neutral compounds are concerned, requiring CZE, MEKC or CEC-based separation mechanisms, and the environmental or terrorist context has created a recurrent demand for up-to-date electrophoretic methods. No doubt that this evolution will keep on going.

Currently, one of the targeted key points is a "mobile laboratory" where miniaturization is highly required and the question is: chip or capillary format? It seems that a capillary approach has outstanding advantages, including simplicity, ease of capillary replacement and low cost. It involves most often very short capillaries (<10 cm) mounted on platforms that form devices often similar to microfluidic chips that allow integration with other functional parts such as injection and detection (86). Therefore, all the new technologies developed in one given field (chips, portable CE, and even sensors (87)) may keep on going to improve electrophoretic approaches of explosive analysis for environmental or forensic purposes.

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