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## Review

# Trends in analysis of explosives by microchip electrophoresis and conventional CE

The continuous upsurge in terrorist activity has generated tremendous demand for innovative tools capable of detecting nitrated organic, inorganic, and peroxide-based explosives. This article directly extends the previous exhaustive review (*Electrophoresis* 2006, 27, 244–256) and overviews the research activity in the field of microchip and conventional capillary electrophoresis for analysis of a variety of explosive compounds and mixtures in the past two years (middle 2005–middle 2007), with the focus on world-to-chip interfaces and detection techniques.

**Keywords:**

Explosives / Industrial / Lab-on-a-chip / Microchip electrophoresis

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## 1 Introduction

This review gives an overview of analysis of explosives by microfluidic and conventional CE from middle of year 2005 to middle of year 2007. The previous review on analysis of explosives by microchip and conventional CE was published in early 2006 [1] and covered the period from 1990 until middle of 2005. In the last review, we noted the last terrorist activity London public transportation bombing on 7.7.2005. Since then, the security situation has not calmed down; on the contrary, we witnessed several major terrorist attacks outside of war zones. It was the Bali bombings on 1.10.2005 and Mumbai train bombings on 11.7.2006 which took lives of several hundreds of people. Mass murder on much bigger scale was fortunately discovered before it took place in London in August 2006, when terrorists wanted to blow up several airliners, possibly killing several thousands of people (so-called “transatlantic aircraft plot”). In the Bali and Mumbai bombings, the terrorists used “traditional” explosive mixtures, cyclotrimethylene trinitramine (RDX) and ammonium nitrate while in the London 2005 public transportation attacks and 2006 transatlantic aircraft plot the terrorists used or planned to use organic peroxide explosives, showing increasing the importance of analysis of these

“unconventional” explosives (these explosives are not used for quarrying or military purposes because they are highly unstable).

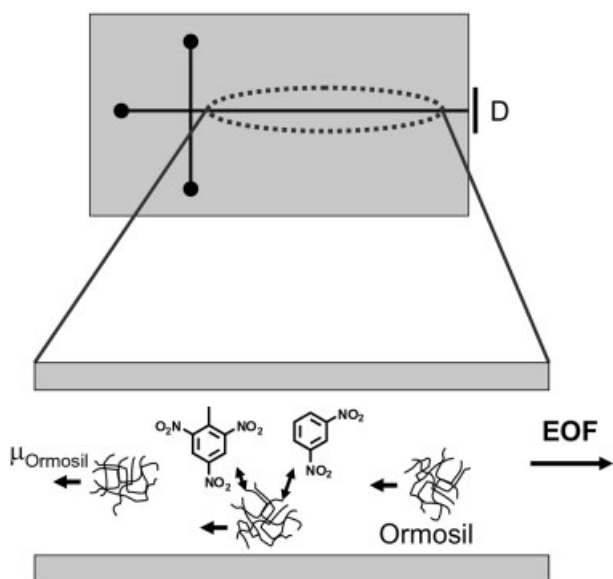
The aim of this article is to overview the progress which has been made toward the development of electrophoretic methods for on-site and fast detection of explosives in the past two years [1]. This paper will review the possibilities, opportunities, and challenges of developing mobile electrophoretic laboratory and portable lab-on-a-chip device for remote screening of explosives. I would like to point out three important complementary reviews: Readers with broad forensic analysis interests should note the review on recent advances in the applications of CE to forensic science by Tagliaro and Bortolotti [2] and by Brettell *et al.* [3], while those with a specific interest in electrochemistry of explosives are encouraged to read the excellent review by Wang [4].

## 2 Nitrated organic explosives

A new method for separation of nitroaromatic explosives by microchip electrophoresis was introduced by Pumera *et al.* [5]. The selectivity of microfluidic separation of explosives was greatly improved by the presence of organically modified silica (Ormosil) sols in the run buffer. The neutral explosives 2,4,6-trinitrotoluene (TNT) and 1,3-dinitrobenzene (DNB) interacted with negatively charged *N*-(trimethoxysilylpropyl)ethylenediamine triacetic acid (TETT)-based sol and they were separated based on their different partitioning between the TETT sol and running buffer (see Fig. 1). Unlike micellar additives that require a minimum surfactant concentration, such concentration limitation does not exist for

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**Abbreviations:** TETT, *N*-(trimethoxysilylpropyl)ethylenediamine triacetic acid; TNT, 2,4,6-trinitrotoluene



**Figure 1.** Schematic diagrams of Ormosil sol-explosive interactions in a microfluidic channel. The neutral explosives interact with negatively charged TETT sol and are they are separated based on their different partitioning between the TETT sol and running buffer. Unlike micellar additives that require a minimum surfactant concentration, such concentration limitation does not exist for Ormosil sol running buffer additives. Adapted from ref. [5] with permission.

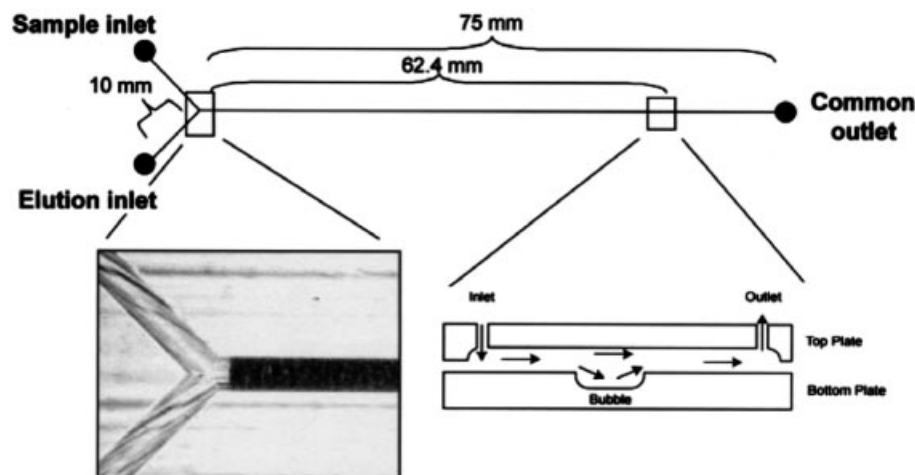
Ormosil sol running buffer additives. The diverse chemistry of Ormosil sols should prove to be extremely useful for tailoring the selectivity of wide range of microchip electrophoresis separations of nitroaromatic explosives [5].

The sol-gel method was used also by Collins and co-workers [6]. They developed microchip-based electrochromatography of nitroaromatic and nitramine explosives using silica-based sol-gel stationary phases from methyl- and ethyl-trimethoxysilane precursors. Unlike the previous work

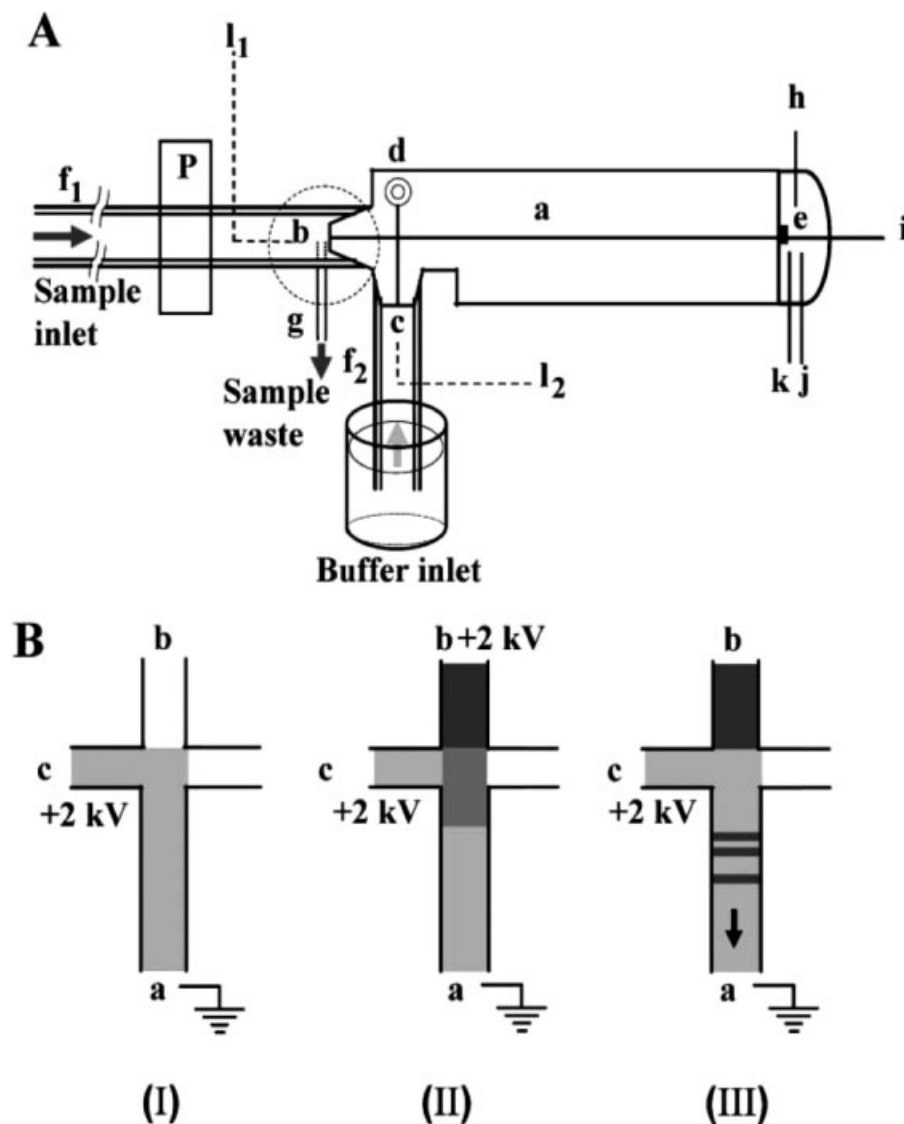
where Ormosil nanoparticles were used as pseudostationary phase [5], here sol-gel is used as stationary phase (see Fig. 2) [6]. Collins and co-workers [6] carefully explored the effect of increasing sol-gel hydrophobicity on the separation of nitroaromatic and nitramine explosives by creating hybrid gels from methyl- and ethyl-trimethoxysilane precursors. They found that increasing the alkyl-chain length significantly improved the resolution and peak capacity and allowed the separation of up to seven analytes. The sol-gel enhanced microchip electrochromatography was also applied by the same authors to the detection of nitroaromatic and nitramine explosives in seawater for confirmation in the presence of underwater mines [7].

An interface for continuous monitoring of explosives in aqueous solutions with microfabricated CE chip devices was developed by Wang *et al.* [8] (see Fig. 3). The new interface relied on mounting the sample tubing onto a sharp inlet tip and allowed rapid, convenient, and reproducible electrokinetic loading from a continuously flowing stream directly into the narrow separation microchannel. The performance of the new interface was illustrated for online microfluidic/electrochemical monitoring of explosive compounds. Conditions simulating continuous long-term monitoring, led to a highly stable response for a 15 ppm TNT solution (RSD = 3.7%,  $n = 40$ ). Such ability to continuously introduce flowing samples into micrometer channels makes “lab-on-a-chip” devices highly compatible with real-life monitoring applications.

While analysis of postexplosive sites does not usually suffer from lack of analytical samples, the more important analysis of pre-explosive sites in order to detect explosive device and prevent explosive event certainly suffers from low amounts of sample available. Therefore, the methods for highly sensitive detection of explosives are urgently needed. Very low detection limit (without preconcentration step) on microfluidic device (7 ppb) was achieved with mercury/gold amalgam electrochemical detector [9] (see Fig. 4). However, it should be noted that such low detection limit



**Figure 2.** Sol-gel stationary phase for microchip electrochromatography of nitroaromatic explosives. Drawing of the Y-configuration microchip (top). Conceptual representation of the extended pathlength detection bubble (bottom). The total pathlength through the bubble is approximately 100  $\mu\text{m}$ . The injection and separation channels were etched to an approximate depth of 50  $\mu\text{m}$ . Reprinted with permission from ref. [6].



**Figure 3.** World-to-chip interface for continuous monitoring of explosives. (A) Structure of the microfluidic chip system with online continuous monitoring capability. The separation channel (a) is joined by a sharp sample inlet tip (b), a side sharp running-buffer inlet tip (c), unused reservoir (d), and a detector compartment (e). The sample is introduced by pumping from the reservoir with a peristaltic pump (P) through the Tygon tubing (f<sub>1</sub>) onto the separation channel through a sharp inlet tip. The sample solution is drained through a plastic tubing (g) that is placed 1 mm from the sample inlet tip. The running buffer is introduced by capillary action through the plastic tubing (f<sub>2</sub>). The detector compartment (e) is designed to accommodate the platinum wire ground electrode (h), the screen-printed carbon working electrode (i), platinum wire auxiliary electrode (k), and the Ag/AgCl wire reference electrode (j). Two platinum wires (l<sub>1</sub>, l<sub>2</sub>) are inserted into the plastic tubing (f<sub>1</sub>, f<sub>2</sub>), respectively, serving as contacts to the high voltage power supply. (B) Steps involved in the new microchip assay: Plug patterns during: (I) the introduction of the running buffer into the channel; (II) sample injection; (III) sample separation and detection. Reprinted with permission from ref. [8].

was achieved only in flow injection mode and Hg/Au detector was poisoned when the SDS containing running buffer was used [9].

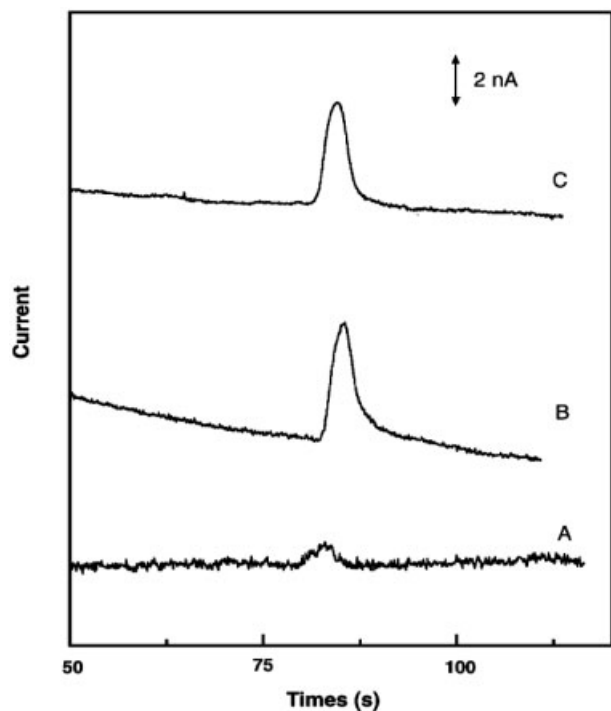
To improve electrochemical detection limits for separation of several explosives when using SDS containing buffer, Chen and co-workers [10] fabricated microchip CE–amperometric detection system by integrating a two-dimensionally adjustable electrophoresis microchip and amperometric detection cell containing a one-dimensionally adjustable disk detection electrode in a Plexiglas holder. It facilitated the precise 3-D alignment between the channel outlet and the detection electrode without a complicated 3-D manipulator. Such precise alignment of the microchip and the detector allowed very sensitive detection down to 12 ppb.

Very low detection limits (in low ppb level) offers a CE-MS system. Hawari and co-workers [11] used commercial Agilent <sup>3D</sup>CE system. They coupled sulfobutyl ether-β-CD/ammo-

nium acetate separation buffer and Bruker Esquire 3000+ quadrupole IT mass detector *via* a commercially available ESI interface with ACN sheath flow. The CE-MS system was applied in negative ionization mode for the resolution and detection of nitroaromatic and polar cyclic nitramine explosives was carried out in real marine sediment samples [11].

### 3 Inorganic explosives

Novel method for analysis of inorganic explosives focused mainly on gun powder-based explosives in the past two years. Hopper and McCord [12] published article on the CE analysis of inorganic ions present in smokeless and muzzle loading powders. In this report [12], seven commercially available smokeless powders were analyzed as unburned powder and burned residue. The results demonstrated that ionic profiles



**Figure 4.** FIA microchip response of different detector materials for a 200 ppb of TNT solution. (A) Carbon thick-film electrode, (B) gold disk electrode, and (C) amalgam mercury/gold disk electrode. Reprinted with permission from ref. [9].

(“fingerprints”) could be used to characterize smokeless powders. Five different smokeless powder samples as well as Pyrodex®RS were collected for analysis subsequent to deflagration in 15 plastic pipe bombs. The relative ion concentrations between these powders can be used to illustrate the differences between open burning and pipe bomb deflagration.

Since there is interest in analysis of gun powder-based explosives, there is also need for reference standard material to help forensic and military laboratories assure the quality of smokeless powder measurements. MacCrehan and Bedner [13] developed a stable and homogeneous material for CE which provides reference concentrations with relative uncertainties lower than 5% for the characteristic additives nitroglycerin, diphenylamine, *N*-nitrosodiphenylamine, and ethyl centralite. The use of such reference material can help assure the quality of measurements in a number of ways including validating analytical methods, testing of explosives detection equipment, training and evaluating the performance of laboratory personnel, assessing and documenting overall laboratory proficiency, and establishing the equivalence of measurements of different laboratories [13].

#### 4 Peroxide-based explosives

Organic peroxide-based explosives (namely triacetone triperoxide and hexamethylene triperoxide diamine) are currently

very popular among the terrorists, especially in the Western hemisphere, due to their simple fabrication from easily obtainable reagent supply (hydrogen peroxide and acetone, available as components of cosmetics in any drug store), see Section 1. Therefore, it is more than surprising that no effort toward development of electrophoretic system for their rapid analysis has been done in the past two years. There has been recent report on development of a highly sensitive electrochemical sensor for trace liquid peroxide explosives, using Prussian-blue “artificial-peroxidase” modified electrode by Wang’s group [14, 15] (but not in connection with CE). The analysis of peroxide-based explosives is yet to be carried out on CE or microchip electrophoresis platform.

#### 5 Conclusion and outlook

The last two years of development of electrophoretic systems for analysis of explosives witnessed two trends. First, the very important move from conventional CE instrumentation toward microfluidic systems can be clearly seen, which is central for portable, timely, “point-of-emergency” sample analysis. However, it should be noted that while most researchers prefer to develop lab-on-a-chip systems, the mobile forensic laboratories still depend on more reliable conventional systems [16]. Even more important is the clear shift toward development of real world-to-chip interfaces and analysis of real samples, which is again crucial for real life/situation analysis. We should hope that more methods on peroxide-based explosives will be developed. It is also clear while analysis of postblast sites usually does not suffer from lack of sample and sampling capabilities of both microchip and conventional capillary electrophoretic formats are well developed in this sense, the more crucial pre-explosive analysis remains an enormous challenge for detection of explosives *via* electrophoretic methods.

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