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Authors	Wang, Yineng;Messina, Walter;Cao, Xi;Hogan, Anna;van Zalen, Ed;Moore, Eric J.
Publication date	2016-11-01
Original Citation	Wang, Y., Messina, W., Cao, X., Hogan, A., van Zalen, E., and Moore, Eric (2016) 'A novel CE microchip with micro pillars column & double-L injection design for Capacitance Coupled Contactless Conductivity detection technology'. Journal of Physics: Conference Series, 757 (1):012042-1-012042-6. doi: 10.1088/1742-6596/757/1/012042
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.1088/1742-6596/757/1/012042
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A novel CE microchip with micro pillars column & double-L injection design for Capacitance Coupled Contactless Conductivity detection technology

Yineng Wang[1], Walter Messina[1], Xi Cao[1], Anna Hogan[1], Ed van Zalen[2], Eric Moore[1*]

[1]Tyndall National Institute, University College Cork
[2]CBRN Program Director, Netherlands Forensic Institute

*eric.moore@tyndall.ie

Abstract. This novel capillary electrophoresis microchip, or also known as μTAS (micro total analysis system) was designed to separate complex aqueous based compounds, similar to commercial CE & microchip (capillary electrophoresis) systems, but more compact. This system can be potentially used for mobile/portable chemical analysis equipment. Un-doped silicon wafer & ultra-thin borofloat glass (Pyrex) wafers have been used to fabricate the device. Double-L injection feature, micro pillars column, bypass separation channel & hybrid-referenced C4D electrodes were designed to achieve a high SNR (signal to noise ratio), easy-separation, for a durable and reusable μTAS for CE use.

1. Project background

The use of Chemical, Biological, Radiological and Nuclear (CBRN) reagents is an ever growing threat to today's society, and this drives the need for innovative tools capable of fast and efficient analysis techniques at incident crime scenes [1]. CBRN warfare has been developed since the early 1900's [2] and incidents related to their use can also be classified as accidental or intentional. Accidental incidents are those caused by human error, natural occurrences or technological reasons examples being spills, leakages or accidental release of agents [3]. These are referred to as HAZMAT (hazardous materials) or DG (dangerous goods) accidents [4]. Naturally occurring biological incidents are those involving outbreaks of diseases such as SARS, Ebola or influenza pandemics. Intentional CBRN incidents are those that involve the:

- Illegal release/ dumping of hazardous materials to avoid regulatory requirements.
- The ill-intentioned poisoning of one or more individuals [3-4].
- Acts of terrorism

Other consequences caused by CBRN incidents and: mass casualty/loss of life; potential long term consequences; formation of a dangerous environment [5]; narrow time frames for life saving treatment/interventions; potential to use a variety of specialised detection equipment; need of

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specifically trained and equipped service personnel. This research has been developed within the EU FP-7 project GIFT-CBRN which aims to fabricate a forensic toolbox for investigating CBRN incidents. This toolbox provide：

- Procedures, sampling methods and detection of CBRN agents at the crime scene.
- Traditional forensic laboratory methods for contaminated evidence.
- Laboratory methods for profiling the CBRN agents released at the incident.

The procedures and methods will be set up and validated according to ISO17025 and the system validation will be performed by a final exercise. Procedures for chain of custody and quality control (QC) to ensure the integrity of the investigations done on the evidences collected at the crime scene will be developed. An education and training curriculum will be designed and progressed to implementation.

In response to terrorist activities there is an urgent demand for rapid and reliable methods for the determination of chemical warfare agents (CWA) and HAZMAT (hazardous materials) and their degradation products. Tyndall National Institute is participating to the GIFT project consortium and is responsible for the fabrication of devices for chemical agents (Chemical substance of CBRN) detection. The objective is to develop an integrated portable μTAS device capable of performing analysis of suspicious substances at the crime scene. CE (capillary electrophoresis), especially in its miniaturized design (lab-on-a-chip/microfluidics), offers great possibilities to create portable, field deployable, rapidly responding and reliable devices, allowing the authorities to take important decisions with respect to the public safety.



Figure 1. EU FP-7 project GIFT.

2. Target reagents & detection technique

A micro-capillary electrophoresis (MCE) microfluidic system for project GIFT was designed at Tyndall National Institute for sensing chemical weapons (mainly nerve agents) at the crime scene. Nerve agents affect the nervous system; nerve agents relevant to the group of organophosphorus compounds will be tested during this project. They are stable and they easily diffuse in air or water, highly toxic and have rapid influence the human body through the skin or respiration [6]. The development of on-site techniques and devices capable of detecting organophosphate nerve agents and their degradation products is a challenge that needs to be undertaken sooner rather than later. Three typical CWA (chemical weapons agents), Sarin, Soman, and VX, contain the alkyl methyl-phosphonate moiety [7-8]. Rapid identification of their degradation products will allow first responders to make important decisions concerning the evacuation or the decontamination of a terrorist attack site and prevent becoming victims themselves [9]. UV fluorescence and Ion chromatography have been traditionally used for monitoring these CWA products [7-8]. More recently, conventional capillary electrophoresis (CE) systems based on the C4D (Capacitively-Coupled Contactless Conductivity Detection) [10-12] technique have been introduced for monitoring the breakdown products of organophosphate nerve agents.

Unlike the traditional UV detection method which needs UV lamps, reflection mirror sets, sophisticated semi-conductor sensor for UV sensing and its power supply system, C4D technology make all the components compact and more efficient. The C4D technology has proved to be able to achieve similar performances to those of the conventional UV detection [13].

Joseph Wang et al. have described the use of a low-cost PDMS MCE chip using the contactless conductivity method to separate organophosphate materials and their bread-down substance in early stage. His experiments described the combination of a CE microchip with a contactless conductivity detection method for monitoring organophosphate nerve agent degradation products. He also demonstrated a well-defined concentration dependency for CWA degradation products. The ability to sense the nerve agents and their breakdown-products is beneficial in terms of speed, efficiency, portability, sensitivity, cost and sample volume compared to conventional capillary electrophoresis or ion chromatography systems [9].

A series of organophosphate compounds like methyl paraoxon (MPX), ethyl paraoxon (EPX), methyl parathion (MPT), fenitronthion (FT), and ethyl parathion (EPT) will be used as reagents to test the MCE devices fabricated at Tyndall.

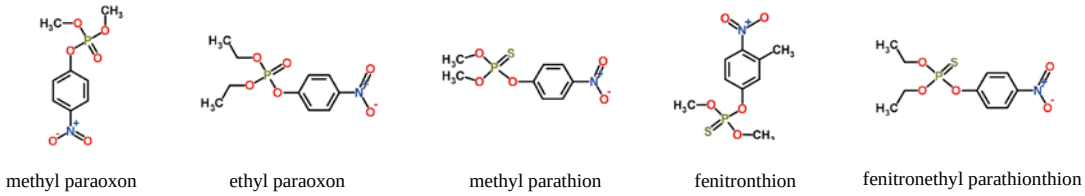


Figure 2. Target reagents for Tyndall's MCE system.

3. Device features

It was decided to fabricate the MCE chip using silicon wafers, because the surface of the oxidised silicon microchip (silicon dioxide) can guarantee high stability from the chemical perspective. Moreover, the silica capillary channel is able to generate the surface double-electric layer, which is similar to the conventional CE-UV detection technique [14].

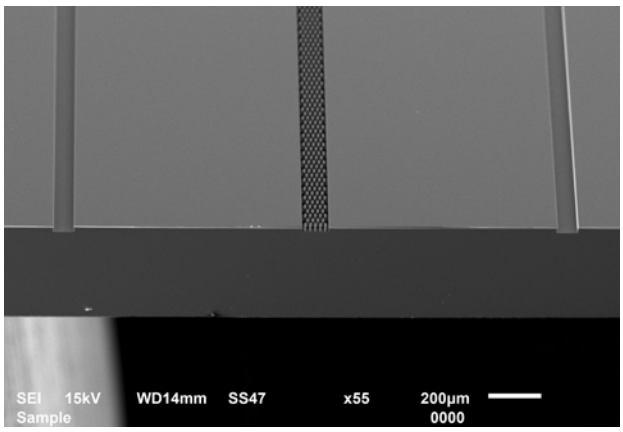


Figure 3. Micro-Pillars column via SEM observation.

Dry etching technique was applied to fabricate a clean, sharp, low-defects and high-quality "Micro-Pillars" column structure with an ultra-thin Pyrex glass wafer bonding for seal all the channels. This offers a 3D design which increases the total surface area inside the microfluidic channel (as the channel with "Micro-Pillars" columns has increased about 2.75 times its effective surface area).

Around 4500 pillars have been built within 4cm length channel on an un-doped silicon wafer. Only 3 pillars were damaged during the fabrication process (0.000666% damage rate), after an observation via a CCD microscope. Based on the novel micro-pillars column, a larger surface area-to-volume ratio is beneficial for Joule heat transfer which can be compared with the conventional capillary under same dimension [14].

According to the capillary zone electrophoresis theory, a simple 2D-model has been built to estimate the differential electrophoresis performance between this novel MCE system and conventional capillary system. From Debeye-Huckel-Henry's Capillary zone electrophoresis (CZE) theory, the electrophoretic mobility in a homogeneous buffer solution and constant field strength throughout the length of the capillary can be approximated.

$$\mu_{ep} = \frac{v_{ep}}{E} = \frac{q}{6\pi\eta R} \quad \textbf{(1)}$$

The electrophoretic mobility ($\boldsymbol{\mu_{ep}}$) , the electrophoretic velocity ($\boldsymbol{v_{ep}}$) , and the electric field strength ($\boldsymbol{E}$) , the net charge ($\boldsymbol{q}$) , the capillary radius (**R**) , and ($\boldsymbol{\eta}$) is the viscosity. These relationships between these factors are shown in Equation 1.

If we consider c as the perimeter of this 2D-model's section, we have Equation 2 and 3:

$$\mu_{ep} = \frac{q}{2\pi R \cdot \eta} = \frac{q}{c \cdot \eta} \quad \textbf{(2)}$$

$$v_{ep} = \frac{qE}{c\eta} \quad \textbf{(3)}$$

Comparison of an MCE (section area 90um*40um) and an ordinary capillary (50um diameter):

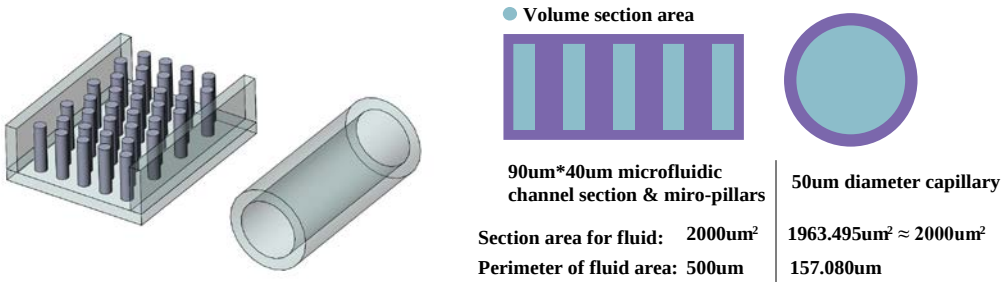


Figure 4. 2D-model of MCE (with micro-structure) and CE comparison.

$$\frac{v_{ep\ MCE}}{v_{ep\ Capillary}} = \frac{157.1}{500} = \frac{1}{3.15} \quad \textbf{(4)}$$

This 2D-model shows that under the same net charge ($\boldsymbol{q}$), electric field strength ($\boldsymbol{E}$), and viscosity ($\boldsymbol{\eta}$) condition; higher total surface area (with the 3d-micro structure) will bring lower electrophoretic velocity or longer separation time. A MCE device with "Micro-Pillars" column is equivalent to a longer capillary under same volume condition.

This MCE chip has two different designs for the separation cross: one is designed as a conventional simple cross, while the other one includes a double L injection technique which reduces sample leakage in comparison to the traditional one [15]. In future experiments, the authors will compare the performances of the two of types:

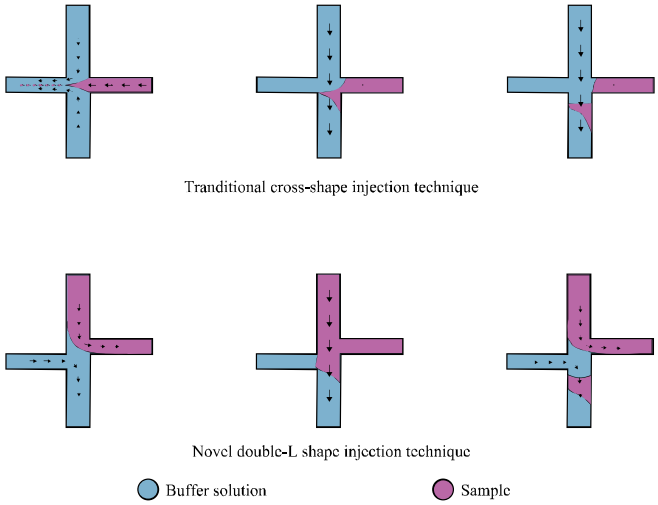


Figure 5. Traditional & novel injection technique.

In this novel MCE system the electrodes won't be in direct contact with the liquid, which will avoid any contamination to the samples or buffer solutions. "Lab-on-chip" technology offers tremendous potential for obtaining the desired forensic information in a faster, simpler, and less costly manner compared to traditional laboratory-based instruments. Particularly attractive for on-site counter-terrorism and compliance applications is the high-performance, small-footprint, high throughput, versatility of microchip devices.

4. Preliminary test

"NanoPort" assembly connector (Model: N-333, IDEX Health & Science LLC, USA) were bonded to the MCE chip to connect the chip to a 1/16" tube. A 5ml syringe (TERUMO, Leuven, Belgium) was used for manual aspiration (Figure 6.) to purge the DI water throughout the channel. A CCD microscope (BX51 microscope, DP71 CCD digital camera, Olympus, Japan) was used for observation. Figure 7. shows that, after keeping continuous aspiration for 10 minutes, most of the water has gone through the channel with the micro-structure; however there are still some air bubbles between the "Micro-Pillar" columns. Despite this bubble defects, all the liquid (DI water) has flown through without blockages.

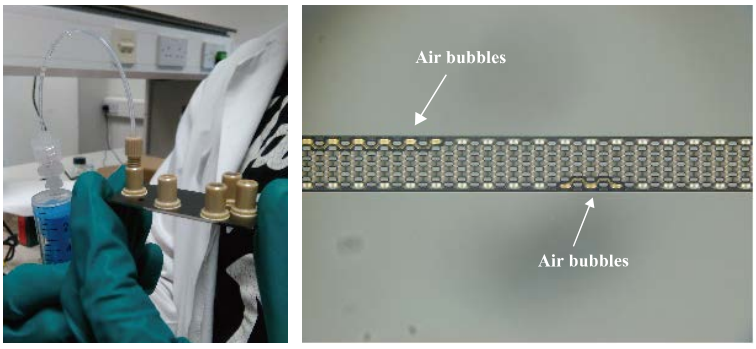


Figure 6 (left) and **7** (right). DI water purges test and observation under persistent aspiration.

5. Discussion

The microfluidic platforms developed here uses a novel "Micro-Pillar" column to enhance the electrophoresis separation performance and gives longer separation time based on the Debeye-Huckel-Henry's Capillary zone electrophoresis (CZE) theory calculation. During the preliminary DI water purge test, bubbles appeared in the "Micro-Pillars" column. Author will attempt to use sonication to solve these negative effects from the "Micro-Pillars" column in the future experiments.

Acknowledgements

The 7th Framework Programme, European Commission are acknowledged for the research funding. The Tyndall National Institute and the Netherlands Forensic Institute are acknowledged for hosting this research in their laboratories and for the consultations. The help and kindness of Dr. Anna Hogan at the Department of Chemistry, University College Cork was highly appreciated.

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