Capillary-Driven μPAD's for Lab on a Chip Screening of Explosive Residues in Soil

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Abstract

A novel microfluidic paper-based analytical device (μPAD) was designed to filter, extract, and pre-concentrate explosives from soil for direct analysis by a lab on a chip (LOC) device. The explosives were extracted via immersion of wax-printed μPADs directly into methanol soil suspensions for 10 minutes, whereby dissolved explosives travelled upwards into the μPAD circular sampling reservoir. A chad was punched from the sampling reservoir and inserted into a LOC well containing the separation buffer for direct analysis, avoiding any further extraction step. Eight target explosives were separated and identified by fluorescence quenching. The minimum detectable amounts for all eight explosives were between 1.4 and 5.6 ng with recoveries ranging from 65 to 82 % from the paper chad, and 12 to 40 % from soil. This method provides a robust and simple extraction method for rapid identification of explosives in complex soil samples.

Keywords: explosive detection, lab on a chip, μPADs

Highlights:

- *A microfluidic paper-based analytical device was developed to extract explosives in soil*
- *Explosives were directly extracted from the paper fibers and analysed via Lab on Chip*
- *μPads combined with Lab on a Chip are a fast and simple way to detect 8 explosives*

1. Introduction

The development of rapid on-site soil analyses of explosives is essential for the identification of hazardous sites from decommission of facilities that have previously been involved in military production and testing [1-3]; detection of landmines and unexploded ordnances; and investigation of terrorism-related bombings [4-6]. On-site analyses are challenging as the most commonly used secondary explosives such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [6-8] have low volatilities and are typically present at very low concentrations in soil [9].

Collection of samples for processing by specialised laboratories is time-consuming and does not facilitate rapid decision-making processes by first responders during explosive-related emergencies. Typically, 70-90% of the soil samples taken at an explosive site do not hold detectable amounts of explosives leading to unnecessary laboratory based tests. These inefficiencies may be mitigated by on-site screening procedures, miniaturisation of instrumentation [10], and rapid sample through-put methods which are simple, inexpensive, sensitive.

The most common analytical procedures for the on-site detection of explosives are based on colorimetric reactions or immunoassays [7]. More recently, novel on-site explosive detection methods such as surface-enhanced Raman scattering (SERS) [11, 12], continuous flow immunosensing [13], immunochemical assays [14], assays based on fluorescence quenching [15] or silicon nanowire arrays [10] have been introduced.

Alternative on-site methods rely upon miniaturised instrumentation based on microfluidics including portable CE [16] and microchip capillary electrophoresis, also known as "lab on a chip" (LOC) devices [17-20]. Advanced microchip designs are capable of handling more than one sample [21], and can integrate multiple functions such as filtration, concentration and separation [22]. However, most of these methods require difficult and tedious sample preparation, or have limited utility and capability such as detection of only specific single explosive compounds.

The direct analysis of soil for explosives is problematic due to its complex matrix which contains many non-volatile and semi-volatile compounds that may confound analyte detection. For example, humic acids present in soil interfere with colourimetric methods of detection [23]. Therefore, it has been common practice to apply a sample preparation step prior to analysis to prevent such interferences [9]. Various extraction techniques have been explored for the removal of energetic materials from soil samples. Routine sample clean-up

methods prior to analysis include liquid extraction (LE) with sonication [24], centrifugation [17], accelerated solvent extraction (ASE), supercritical fluid extraction (SFE) and pressurized fluid extraction (PFE) [3, 23, 25]. These procedures are in general time consuming, require an expert operator and are consequently are more difficult to perform on-site [26, 27].

We have developed a simple, rapid explosive extraction system based on a wax-printed microfluidic paper-based analytical device (μPAD) that has the additional advantage that it can be directly analysed by a commercial LOC instrument (Agilent Bioanalyzer 2100). μPADs are a relatively new generation of microfluidic system [28, 29], and show high potential for portable detection technologies due to their relatively low cost, ability to function without the use of pumps, and easy storage and disposal. Although there are several methods for fabrication of hydrophobic barriers on paper [30], we used the simplest method of "wax printing". Barriers were printed on filter paper with a wax-printer and heated with a press [15, 31] forming hydrophobic channels that compartmentalise and control direction of liquid flow. This article describes a new μPAD device designed to filter, extract and pre-concentrate explosive residues from soil and directly identify them using a LOC system.

2. Materials and methods

2.1. Reagents

Explosive standards: trinitrobenzene (TNB), 1,3-dinitrobenzene (DNB), 2,4,6-trinitrotoluene (TNT), methyl-2,4,6-trinitrophenylnitramine (Tetryl), 3,4-dinitrotoluene (3,4-DNT), 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT), 4-amino-2,6-dinitrotolune (4-A-2,6-DNT), 2,4-dinitrotoluene (2,4-DNT) were obtained from AccuStandard (New Haven, CT, USA) at a certified concentration of 1000 μg/mL in acetonitrile. These explosives were chosen as they are common dinitro and trinitro aromatic explosives. Analytical grade methanol was purchased from ChemSupplies Pty Ltd (Gillman, SA, Australia). Sodium dodecyl sulphate (SDS) was obtained from Sigma-Aldrich (St. Louis, MO, USA) and sodium tetraborate from Fluka (Switzerland).

2.2. μPAD fabrication

The μPADs were designed with CorelDraw 5 software (Corel Corporation, Ontario, Canada) and printed using a Fuji Xerox ColorQube 8870 printer (Xerox, Australia). The designs were printed on Whatman® qualitative filter paper Grade 5 using the cyan colour

cartridge, which has previously been shown to produce high quality hydrophobic barriers when compared against other colours, with minimal colour bleeding when in contact with an organic solvent [15]. The µPAD was heated using a swing-away heat press (GEO Knight & Co, Inc) at 150 °C for 30 seconds to melt the wax into the filter paper fibers to create hydrophobic barriers. The µPAD was then cut to shape. The fabrication process is illustrated in Figure 1(a). The µPAD was a 2.7 cm long and 0.5 cm width strip with a circular 0.7 cm diameter sample reservoir. Three 1.0 mm length barriers were printed between the strip and the sample reservoir resulting in four channels of 0.33 mm width (Figure 1(b)).

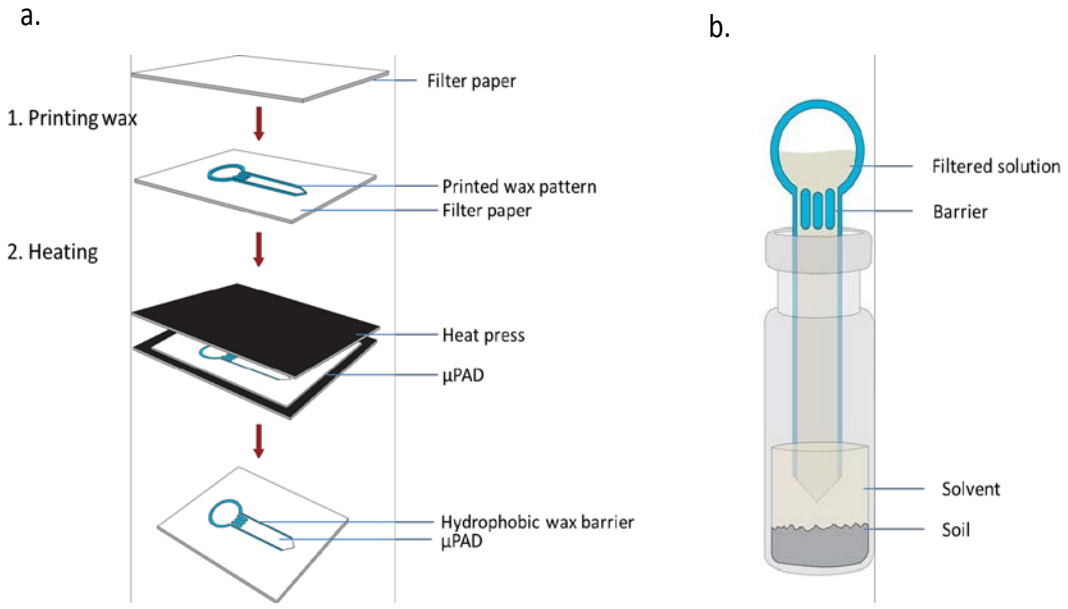

Figure 1: (a) µPAD fabrication process involving printing the desired pattern using wax on the paper and heating it using a heat press; (b) the set-up used for the extraction of explosives from soil samples.

2.3. Standards analysis

All standard solutions of mixed explosives were prepared by dilution of individual stock solutions into sodium tetraborate buffer (10mM; pH 9.2) containing 50 mM sodium SDS. The explosive solutions were stored in glass containers at 4°C in an explosion proof fridge.

Calibration curves were constructed by pipetting 9 µl of mixed standard directly into the chip sample wells at 1, 2, 5, 10, 15 and 20 ng/µl. Explosive recoveries from the µPAD chads were determined by pipetting 9 µL of a 20 ng/µl (n=3) mixture of the explosives directly on the µPAD sample reservoir. After a one minute drying time chads were hole-punched from the µPAD (5 mm diameter). The entire chad was then folded twice, in order to

fit into the sample reservoir, and placed directly into the lab on a chip injection well containing 5 µL of 10 mM borate/50 mM SDS buffer to prevent the filter paper absorbing buffer from the channels. After insertion of the paper chad an additional 4 µL of electrolyte was added to obtain a final volume of 9 µL (Figure 2).

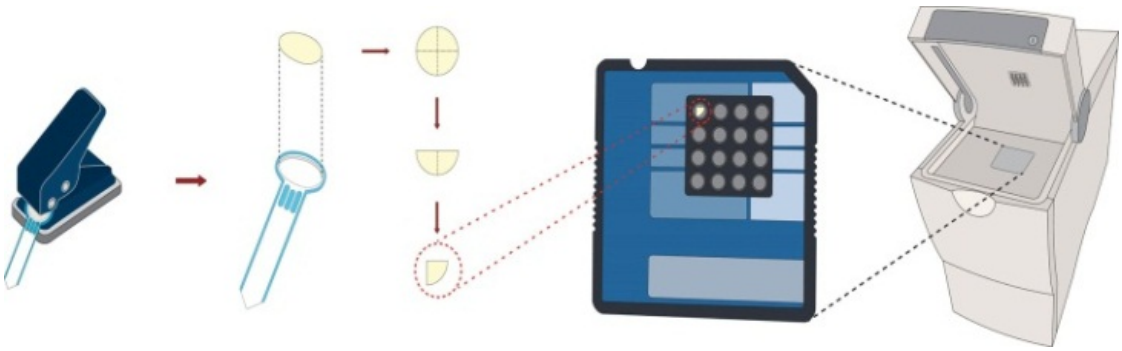

Figure 2: The process used to analyze explosives from soil samples. After extraction the µPAD was hole-punched. The chad was folded twice and inserted directly into the sample well of the Caliper DNA chip containing 5 µL of buffer. After insertion, 4 µL of buffer was added to the filter paper and the sample was analysed.

2.4. Soil analysis

Calibration curves for each explosive were constructed by µPAD extraction of standard solutions at 5, 10, 15 and 20 ng/µl. After 10 minutes the µPAD was removed from the vial and hole-punched immediately. As before, the explosives were electrophoretically extracted from the paper chad inserted into the sample well of the microchip.

Soil samples were collected from garden areas in Ultimo, Sydney, Australia and were representative of different soil matrices. Soil 1 was a sandy clay soil; soil 2 was a rocky soil with a large particle size; soil 3 was sandy with low moisture content and soil 4 was moist, with comparatively high organic content. 0.200 grams of each soil sample was spiked with 62.5 ng of each explosive (equivalent to 313 ng/g) and placed in a 1 mL polypropylene vial. Methanol, ethanol, acetonitrile and acetone were compared as extraction solvents. Each solvent was added to the sample and shaken for 10 seconds. The explosives were extracted by insertion of the µPAD into the 1ml vial and analysed with the LOC instrument as described above.

2.5. Lab on a chip instrumentation

All separations were performed on an Agilent 2100 Bioanalyzer, equipped with a red laser fluorescence detection system with excitation and emission wavelengths of 630 nm and 680 nm, respectively. Data was collected with the Agilent 2100 Expert software (Agilent technologies, Waldbronn, Germany). The chip was manufactured from borate silica glass and

was designed by Caliper for the analysis of DNA allowing the analysis of 12 samples per chip. The separation channel lay between wells A4 and C4, while B4 and D4 were used for waste. The microchannels which interconnect 12 sample wells have a depth of 10 mm and width of 50 mm. The separation channel length was 15 mm, and a new chip was used for each sample run. The background electrolyte comprised of 10 mM sodium tetraborate, 50 mM SDS, at pH = 9.2, and 2% v/v of Agilent DNA 1000 dye®. 2 % v/v of DNA dye was the optimal concentration providing the best signal response. The background electrolyte was sonicated for 15 minutes and filtered using a 0.45 µm Minisart® syringe filter (Sartorius AG, Goettingen, Germany) prior to priming the chip. The chip was primed by pipetting 9 µl of the background electrolyte into the priming well. Air pressure was applied for 60 seconds using a chip priming apparatus. Explosive standards and/or samples were then added to the remaining wells for analysis. During injection, 100 V was applied in A4 and C4 simultaneously to avoid sample diffusion to the main channel. A 1400 V potential difference was applied for 40 seconds for injection and the same voltage was used for separation.

3. RESULTS AND DISCUSSION

3.1. Lab on a chip analysis of explosive standards

The separations of the explosives in the microchip were performed by micellar electrokinetic chromatography (MEKC), in which the addition of a surfactant to the electrolyte formed micelles to act as a pseudo stationary phase to allow the separation of neutral molecules [17]. A background electrolyte of 10 mM sodium tetraborate, 50 mM SDS, and 2 % v/v of the DNA dye produced consistent baselines across all standard and sample runs. The explosives appeared as negative peaks in each of the electropherograms due to fluorescence quenching. Figure 3 (I) shows the separation of 9 µl of a 20 ng/ µl mixture of eight explosives pipetted directly (in the absence of a µPAD) into a sample well of the chip. The minimum detectable masses of the selected explosives were calculated from the LODs as 3.3 σ / slope of the calibration curve where σ = error in the slope [32], and are shown in Table 1. The solution LODs were comparable to more traditional methods, such as LC-MS, ranging from 0.04 to 1.06 ng/µl, and 0.11-2.30 ng/ µl by CE [34].

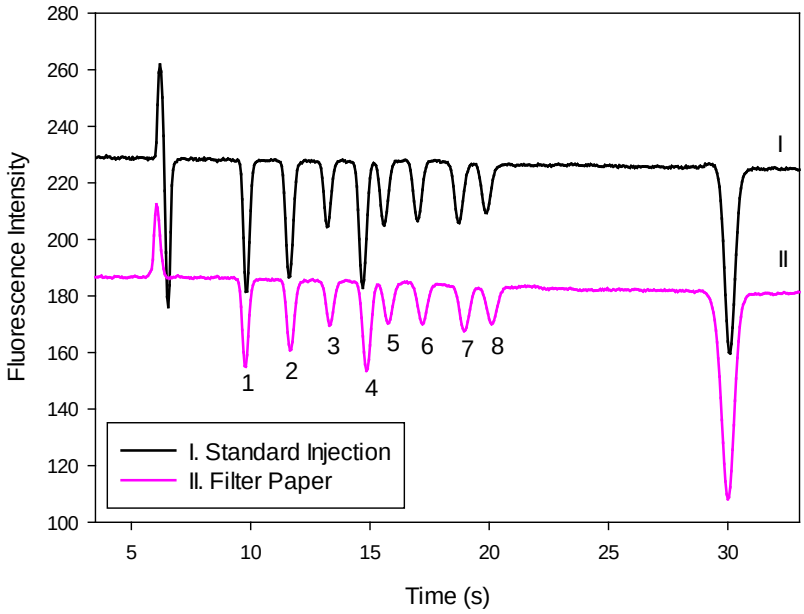

Figure 3: (I) Lab on a chip analysis of explosive standards (180 ng on chip): 1: TNB, 2: DNB, 3: TNT, 4: Tetryl, 5: 2,4-DNT, 6: 3,4-DNT, 7: 2-A-4,6-DNT and 8: 4-A-2,6-DNT in buffer. (II) µPAD chad spiked with 9 µl of 20 ng/µl of each explosive, dried and inserted onto the chip vial containing 9 µL of the running buffer. Experiments were performed using the Agilent Bioanalyzer 2100 (injection 1400 V/40 s, separation 1400 V). Running buffer, 10 mM Borate/50 mM SDS buffer, pH= 9.2 with 2 % fluorescent DNA Dye®.

Figure 3 (II) shows the separation of the eight explosives when 9 µl of a 20 ng/µl mixture was applied directly to the µPAD collection area, dried for 1 minute and analysed as illustrated in Figure 2. This experiment demonstrated that the paper chad inserted into the sample wells did not block the channel or interfere with the sample separation, avoiding an extra step for the extraction of the explosives. No differences in separation were observed when compared against direct injection, with recoveries ranging from 65 to 83 % (Table 1).

Table 1: Average recovery from the paper chad of the eight explosives in order of elution compared to the liquid injection, along with minimum detectable masses of the explosives from the paper chad and recovery of explosives from soil samples.

Explosive	Average Recovery [%] from paper chad (n=3)	Minimum detectable mass [ng] direct injection	Minimum detectable mass [ng] from paper chad	Average Recovery [%] from soil samples (n=3)
TNB	82	2.4 ± 0.2	3.5 ± 1.4	24
DNB	71	2.9 ± 0.2	4.0 ± 0.7	39
TNT	81	3.6 ± 0.3	1.4 ± 0.6	16
Tetryl	78	2.0 ± 0.3	4.9 ± 1.8	12

2,4-DNT	65	2.4 ± 0.4	2.5 ± 0.4	19
3,4-DNT	67	3.3 ± 0.6	4.2 ± 1.2	23
2-A-4,6-DNT	74	3.6 ± 0.7	3.8 ± 2.1	22
4-A-2,6-DNT	52.6	3.4 ± 1.1	5.6 ± 3.5	40

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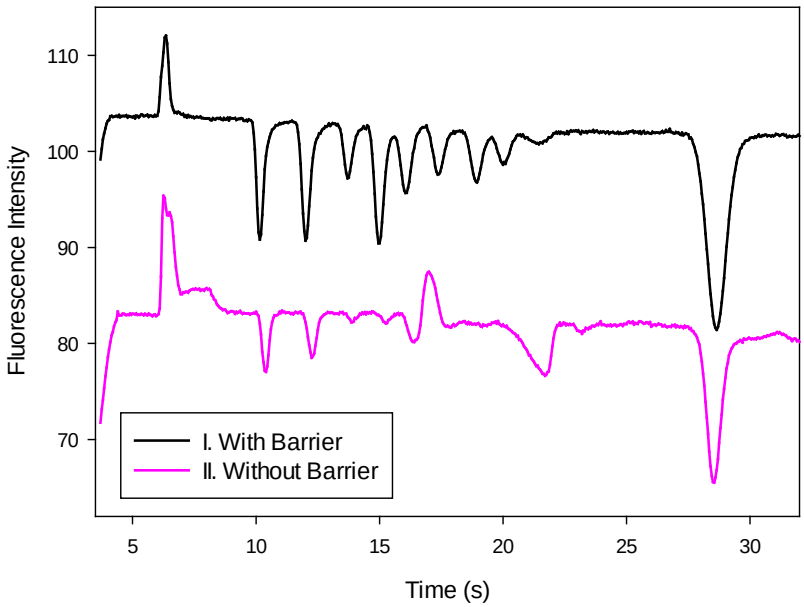
207 *3.2. Spiked soil analysis*

208 A preliminary design for the µPAD consisted of a 0.5 cm sampling strip terminating
209 with a sample collection area. This design rapidly adsorbed the solvent from the soil
210 extraction vial and saturated the sample collection area within approximately 60 s. However
211 undesirable baseline fluctuations in the electropherograms rendered the analysis unreliable
212 (Figure 4 II). Therefore, the design of the µPAD was optimised via incorporation of a three-
213 line barrier pattern in the main channel (Figure 1b) which slowed the flow of the extraction
214 solvent and increased the time for saturation of the sampling reservoir by approximately 1
215 minute, eliminating subsequent baseline perturbations (Figure 4 I). The barriers further
216 improved the percentage recoveries of all of the explosives. The most likely reason for this is
217 that the slower flow of the extraction solvent allowed the filter paper to retain the interfering
218 compounds in the sampling strip, whilst allowing the explosives to migrate to the sample
219 reservoir.



220
221 Figure 4: Lab on a chip analysis of explosive standards using (I) µPAD with barriers present and (II) µPAD
222 without barriers. Experiments were performed using the Agilent Bioanalyzer 2100 (injection 1400 V/40 s,
223 separation 1400 V). Running buffer, 10 mM Borate/50 mM SDS buffer, pH= 9.2 with 2 % fluorescent DNA
224 Dye®.
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Four soil extraction solvents were examined: methanol, ethanol, acetonitrile and acetone. Methanol had the best overall performance with regards to recoveries, speed of extraction and drying of the chad prior to analysis by the lab on chip device, and was used in all further experiments. This is also in agreement with previous reports [9]. Figure 5 shows the electropherograms of blank and spiked soil (313 ng/g) samples extracted with the µPADs. The minimum detectable amounts are shown in Table 1. The µPAD functioned as a selective extraction and sample clean-up device with percentage recoveries ranging from 12 to 40 % (Table 1). The differences observed between the recoveries of each explosive type were most likely associated with variation in their affinities for the mobile phase (methanol) and stationary phase (filter paper). These recoveries were independent of soil types which ranged from sandy clay, rocky soil with large particle sizes, sandy soil with low moisture content, and soil with high organic content.

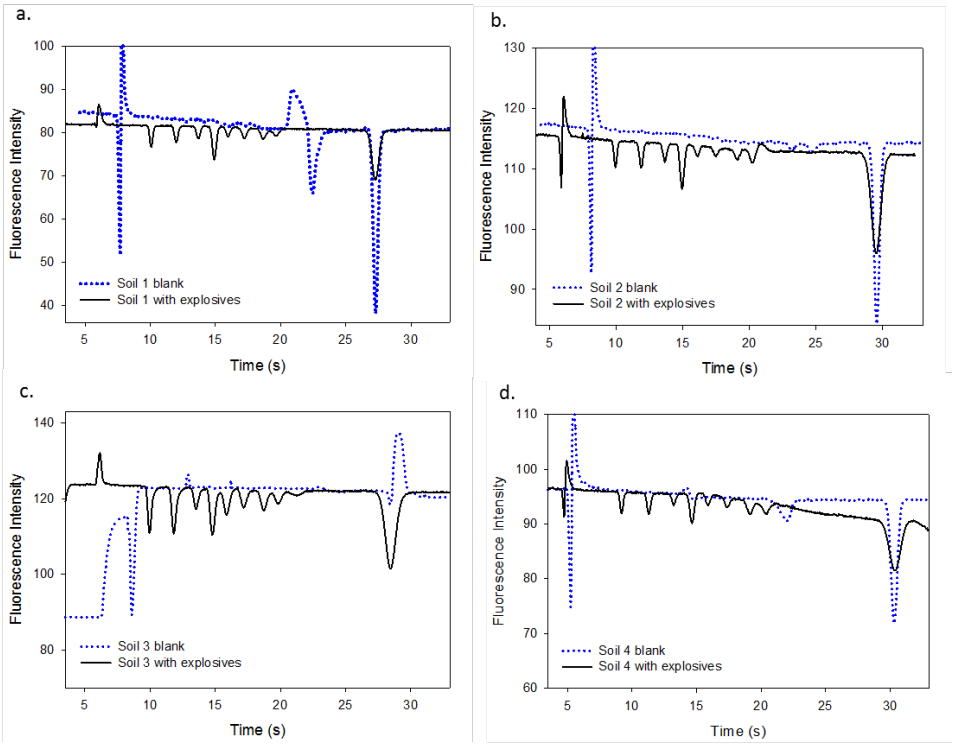

Figure 5: Lab on a chip analysis of four different soil samples spiked with 62.5 ng of each of the eight explosives along with a soil blank (soil without the presence of explosives). The explosives were extracted from soil (0.2 g + 400µL of MeOH) using the µPAD as described in Figure 1 and inserted into the lab on a chip well for direct electrokinetic extraction.

4. Conclusion

The combination of a µPAD and LOC for sample preparation and analysis provides a new, fast approach for identification of explosive mixtures in soil. To the best of our

knowledge this is the first report where a filter paper device containing the sample has been directly inserted into a microfluidic device for electrokinetic extraction. This approach directly inserting the paper chad into the chip sample wells represents a significantly simplified extraction process. The LOC device does not require any pumps or gas for its operation; this along with its low weight (approximately 10 kg), small size and robust nature gives it excellent potential for portable use in mobile laboratories. The current method was optimized for the analysis of eight target explosives that were well separated and visualised using fluorescence quenching. The minimum detectable amounts for all eight explosives were between 1.4 and 5.6 ng with recoveries ranging from 65 to 82 % from the paper chad and 12 to 40 % from soil. Sample extraction and preparation may be performed in approximately 12 minutes, with up to 12 samples processed by the LOC per hour. This rapid turnaround, the ability to analyse explosive mixtures, and relatively low costs per analysis (currently ~ $4 / sample) makes this approach a viable alternative method of explosive screening [35].

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