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Fast detection of triazine herbicides on a microfluidic chip using capillary electrophoresis pulse amperometric detection

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ABSTRACT

We report simple and rapid capillary electrophoresis (CE) separation followed by in-channel pulsed amperometric detection (PAD) of three common triazine herbicides: simazine, atrazine and ametryn that are used to control broad leaf weeds and annual grasses. For their detection in soil and groundwater samples, a CE–PAD microfluidic chip was fabricated using standard photolithography methods. Cyclic voltammetry was conducted on these herbicides that exhibited a characteristic cathodic peak at −0.70 V for simazine or atrazine and −0.80 V for ametryn, without any anodic peak at reverse scan, indicating that the cathodic peaks were irreversible electron transfer processes. For effective CE–PAD separation of triazine complex, the capillary was filled with 1.5% agarose. The pulsed amperometric detection of these chemicals ensured better sensor response and low electrode fouling. The average electropherogram of simazine, atrazine and ametryn showed single peaks at 58, 66 and 74 s, respectively at 20 V/cm separation potential. A mixture of all three herbicides showed similar separated peaks. HPLC was also conducted in a soil spiked with these pollutants to compare the method. The results hold the promise of detecting triazines within a very short time.

1. Introduction

Simazine (2,4-bis-ethylamino-6-chloro-1,3,5-triazine), atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and ametryn (2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine) are atrazine herbicides used to control broadleaf weeds and annual grasses. The widespread use of these herbicides can cause groundwater contamination [1] leading to acute health effects including congestion of the heart, lungs and kidneys; hypotension; antidiuresis; muscle spasms; weight loss, adrenal, retinal and cardiovascular damage; carcinogenicity and long term exposure may even lead to Parkinson's disease [2,3]. Because of the increase in incidence of mammary gland tumors in female laboratory animals exposed to triazine herbicides, these compounds are classified in Group C, and are therefore considered as possible human carcinogens [4].

The analysis of these herbicides are usually carried out by gas chromatography (GC); mass spectrometric detection; high performance liquid chromatography (HPLC) [5]. However, these methods require sample pretreatment, enrichment or extraction steps. Therefore, they are mostly laborious and time-consuming, and require complicated cleanup procedures and sophisticated technical equipment. Beside these analytical technologies, methods based on biological or electrochemical principles are available to certain extent for sample analysis of these pollutants, e.g., biosensor [6,7], square wave voltammetry with the hanging mercury drop electrode (HMDE) [8], etc. Compared to these methods, capillary electrophoresis (CE) coupled with optical and electrochemical detection methods is becoming an advantageous tool for determining pesticide residues in environmental matrices because of its advantages, such as shorter analysis times, higher separation efficiency and very small consumption of expensive reagents and toxic solvents [9,10]. Initially introduced as a technique for separation of biological macromolecules, CE has since attracted much interest in other application areas, including pesticide-residue determination [11]. The capability to conduct analysis in a miniaturized format (microchip technology) is interesting for the routine analysis of samples containing hazardous pesticides. However, most of these reported CE–AD devices suffer the drawbacks of low separation efficiency for closely related analytes and often have low detection sensitivity and non-reproducibility in small microchannel configuration. While addressing some of the drawbacks related to CE–AD devices, we fabricated a microfluidic chip for the detection and separation of three most common triazines. Cyclic voltammetry was conducted due to accurately resolve different detection voltage of structurally similar compounds. The sensing principle of this microfluidic sensor is based on the

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capillary electrophoresis pulsed amperometric detection (CE–PAD), while maintaining a sieving medium (agarose) for their effective separation prior to detection which is an improved and modified version of our previous CE–AD studies [12–14]. The pulsed amperometric technique of detection, rather than the common amperometric method was to ensure better sensor response and prevent electrode fouling during continuous CE operation. The proposed method was also compared with existing HPLC method while analyzing the herbicides in soil samples.

2. Materials and methods

2.1. Device design and fabrication

The devices were fabricated using standard photolithographic techniques as per the schematics shown in Fig. 1. The chip consisted of two reservoirs acting as inlet and outlet along with a microchannel made from PDMS. The dimensions of each microchannel were 200 μm (width) × 200 μm (height) × 5 cm (length). The configuration of the microfluidic chip is shown in Fig. 2. For fabrication of microchannels, 200 μm-thick photoresist (SU-8 2075) was spin-coated and patterned on the silicon wafer. The PDMS layer was fabricated by pouring a degassed mixture of Sylgard 184 silicone elastomer and curing agent (10:1) onto a molding master, followed by curing for at least 1 h at 72 °C. The cured PDMS was separated from the mold, and reservoirs were made at the end of each channel using a 3 mm circular punch. At the same time, gold electrodes were fabricated on a glass substrate using standard photolithographic methods. The three electrodes namely working, reference and counter electrodes were fabricated by thermal evaporation. Finally, bonding of PDMS layer on glass substrate containing the electrodes was performed with UV-Ozone cleaner to get improved bond strength.

2.2. Device operation and electrochemical measurements

Cyclic voltammetric (CV) and Amperometric measurement were performed using CHI 800B electrochemical workstation. A three-electrode system comprising a platinum wire as auxiliary,

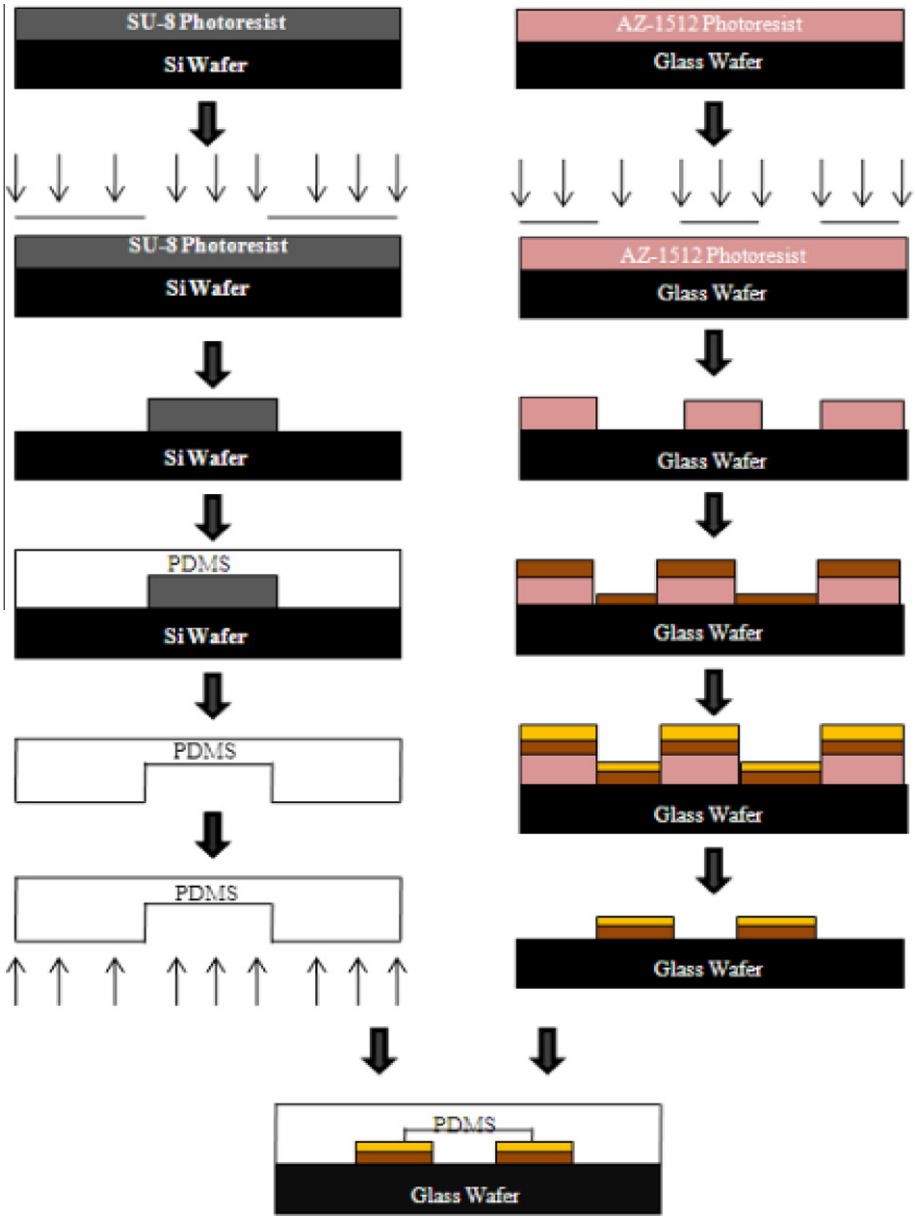

Fig. 1. Schematics for the fabrication process of the microchip.