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Gravity-assisted distillation on a chip: Fabrication, characterization, and applications

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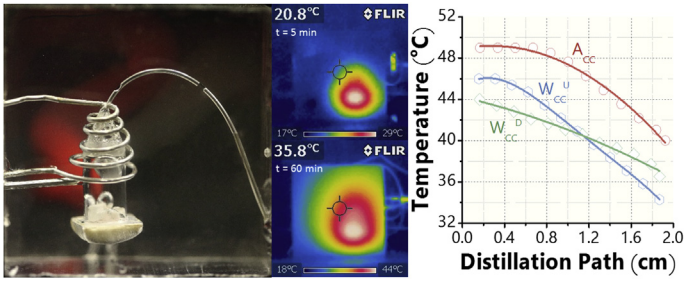
HIGHLIGHTS

- PDMS microdistiller was constructed according to conventional flash distillation.
- Sample chamber engraved by 3D printing ensured gravity-assisted distillations.
- Low thermal conductivity of PDMS assured generation of vertical temperature gradient.
- The chip provided distillations with high efficiency of salt removal and throughput.

Accurate determinations of ethanol in alcoholic beverages was possible.

GRAPHICAL ABSTRACT



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ABSTRACT

Distillation is widely used in industrial processes and laboratories for sample pre-treatment. The conventional apparatus of flash distillation is composed of heating source, distilling flask, condenser, and receiving flask. As disadvantages, this method shows manual and laborious analyses with high consumption of chemicals. In this paper, all these limitations were addressed by developing a fully integrated microscale distiller in agreement with the apparatus of conventional flash distillation. The main challenge facing the distillation miniaturization is the phase separation since surface forces take over from the gravity in microscale channels. Otherwise, our chip had ability to perform gravity-assisted distillations because of the somewhat large dimensions of the distillation chamber (roughly 900 μL) that was obtained by 3D-printing. The functional distillation units were integrated into a single device composed of polydimethylsiloxane (PDMS). Its fabrication was cost-effective and simple by avoiding the use of cleanroom and bonding step. In addition to user-friendly analysis and low consumption of chemicals, the method requires cost-effective instrumentation, namely, voltage supply and analytical balance. Furthermore, the so called distillation-on-a-chip (DOC) eliminates the use of membranes and electrodes (usually employed in microfluidic desalinations reported in the literature), thus avoiding drawbacks such as liquid leakage, membrane fouling, and electrode passivation. The DOC promoted desalinations at harsh salinity (NaCl 600.0 mmol L^{-1}) with high throughput and salt removal efficiency

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(roughly 99%). Besides, the method was used for determination of ethanol in alcoholic beverages to show the potential of the approach toward quantitative purposes.

1. Introduction

The distillation process is widely used in industrial processes and laboratories for sample pre-treatment. The conventional distillation apparatus is usually composed of four units, namely, heating source, distilling flask, condenser, and receiving flask. As disadvantages, this technique presents chemical-consuming and laborious assays that undermine parameters such as precision, simplicity, cost, and green chemistry compatibility. In this regard, the macro-to-microscale conversion is a powerful alternative. The safety represents other advantage of the microsystems on their macroscale analogues since some species can explode under the distillation conditions [1–3]. Despite the relevance of the distillation and the consequent gains with the miniaturization, little attention has been paid to develop microscale distillers. The major challenges for distillation process miniaturization are phase separation and vapour driving, integration of the functional steps in a single device, complexity and cost of microfabrication, and separation efficiency. In microchannels, surface forces such as viscosity, wall friction, and surface tension take over from the gravity [1–8]. Accordingly, alternatives to gravitational forces are needed to provide the phase separation and controllably drive and collect the vapour within a microscale channel.

The alternatives to gravity for microdistillations include the use of inert carrier gas or vacuum pump in membrane distillation [6,7,9]. In this case, the vapour is separated from sample by microporous and hydrophobic membranes and the temperature gradient is vertically reached by placing a microfluidic chip on a heating source and flowing cooling water above the sample channel. As hurdles, the separation efficiency is poor because of the concentration polarization in the membrane across the liquid phase side and further steps for gas-liquid separation are required when carrier gas is employed. Another type of microfluidic distillation, called zero-gravity [1–5], performs the phase separation in a horizontal microchannel that is either heated or cooled at its ends to attain a temperature gradient. Micropillars around the distillation channel separate the liquid from vapour by capillary force. The micropillars establish fractional distillations with improved separation efficiency by increasing the number of vaporization-condensation equilibria (plates). However, the use of these micropillars requires a pre-treatment step, namely, the sample should be previously degassed to get rid of any entrapped air [2–4]. Moreover, both the aforesaid microchips involve a complex, high-cost, and time-consuming fabrication. The zero-gravity microdevices are obtained by standard photolithography, dry or wet chemical etching, and thermal or anodic bonding procedure that needs long time and high temperatures. With regard to the membrane distillation, the fabrication is further laborious since the membrane surface is thermally uniform, thus requiring the generation of a vertical temperature gradient. Such fabrication relies on photolithography with multiple and subsequent steps of film deposition, UV exposure, resist development, and adhesive bonding in UV-curable resins [7,9,10]. Additionally, the membrane and zero-gravity microdistillers presented non-integrated functional components making it impossible to construct lab-on-a-chip platforms, i.e., systems with multifunctional units incorporated into a single device.

Considering the relevance and downsides of the microscale-based distillation processes, we describe in this paper for the first time a totally integrated microdistiller in agreement with the apparatus of a conventional flash distillation. The chip was composed of a single piece of polydimethylsiloxane (PDMS) and its fabrication was rapid, simple, and cost-effective by avoiding the use of cleanroom facilities and bonding step. Such technique was based on sequential steps of polymerization and scaffold removal (PSR) [11–13], which granted the simple incorporation of the components of flash distillation (heating resistor, distillation flask, condenser, and distillate collector) into a single chip. This integration contributed for automation and operation simplicity of the system that was termed distillation-on-a-chip (DOC). Gravity-assisted separations were attained through the 3D printing of a distillation chamber with somewhat large size (approximately 900 μL). In this regard, the gravity overcame the surface forces, thus driving the distillation. The 3D printing technology has generated a new revolution in the fabrication of microfluidic chips by creating 3D structures in a simple and single-step way [14–16]. While the phases were separated through the gravity, the distillate was driven by capillary force and vapour pressure in a microchannel. As proof of concept applications, the DOC was successfully used in i) desalination for sample pre-treatment and ii) determination of ethanol in alcoholic beverages. Desalinations at harsh salinity conditions (NaCl 600.0 mmol L^{-1}) were obtained with high throughput and salt removal efficiency (roughly 99%). Finally, the concentrations of ethanol obtained in real samples using the microdistiller were in agreement with those results recorded by gas chromatography.

2. Experimental

2.1. Chemicals

Sodium chloride (NaCl), acetone, 1-butanol, and ethylene glycol were supplied from Labsynth (São Paulo, Brazil), whereas ethanol was supplied from Merck (Darmstadt, Germany). Sylgard 184 silicone was purchased from Dow Corning (Midland, MI). Deionized water (Milli-Q, Millipore Corp., Bedford, MA) was obtained with resistivity no less than 18 MΩ cm. Alcoholic beverage samples were acquired from a supermarket in Campinas, Brazil, which included whiskey, vodka, rum, and cachaça (typical Brazilian distilled beverage made from sugarcane).

2.2. Microfabrication

The main steps of the PSR method are the preparation of the scaffold, addition of PDMS, its cure, and scaffold removal as illustrated in Fig. 1 [11–13]. The scaffold used to fabricate the microdistiller was composed of permanent and sacrificial pieces. Heating resistor and condenser were permanently integrated into the chip. The resistor consisted of three surface-mount device (SMD) components in parallel, which were constructed over a plate of alumina (13 mm × 13 mm × 1 mm) by welding. Each resistor presented 47 Ω resulting in an equivalent resistance of 16.7 Ω. All the resistors were coated with Torr Seal® epoxy resin. The condenser relied on a stainless steel tube with inner diameter of 700 μm that was rolled producing spiral-shaped channels. Sacrificial scaffolds defined the

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