HIGH PERFORMANCE DESALINATION USING GRAVITY-ASSISTED DISTILLATION ON A CHIP

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Abstract: *We herein present a fully integrated microscale distiller in agreement with the setup of conventional flash distillation. Our chip showed ability to perform gravity-assisted distillations because the high dimensions of the distillation chamber (roughly 900 μL), which was obtained by 3D printing. Desalinations of solutions at harsh salinity (600.0 mmol L^{-1} NaCl) were achieved as a sample preparation method for subsequent analytical determinations. Such desalinations presented high salt removal efficiency (up to 99.7%) and throughput.*

Keywords*:* Lab-on-a-chip; Sample preparation; Flash distillation; 3D printing.

Introduction: desalination is a key sample preparation technique for quantitative chemical assays. For instance, the performance of analyses by mass spectrometry and atomic spectroscopy is undermined at high ionic strength conditions. Additionally, the use of microfluidic platforms adds advantages by decreasing the formation of waste and improving the precision and efficiency of the sample preparation.[1] The fabrication of microfluidic chips used to reduce the concentration of salt involves time-consuming, complex, and high cost routines that are related to cleanroom-assisted steps of photolithography, etching, and thin film deposition. Considering the relevance of the microfluidic desalination as sample preparation and the limitations of such devices as aforesaid, we show for the first time a totally integrated microscale distiller in agreement with the setup of conventional flash distillation. The chip was composed of a single piece of PDMS. Its fabrication was rapid, simple, and low cost avoiding the use of cleanroom facilities, the bonding step, and laborious processes to engrave the channels.[2] Besides, our distillation chip exempts the use of membranes and electrodes, which are used in desalination methods reported in literature.[1] It further streamlines the prototyping process. These functional units can produce problems such as liquid leakage, membrane fouling, and electrode contamination. Termed distillation-on-a-chip (DOC), this method ensured high performance desalinations at harsh salinity conditions.

Experimental: the technique used to obtain the chip relied on sequential steps of polymerization and scaffold removal (PSR).[2] The scaffold used to fabricate the DOC device was composed of permanent and sacrificial pieces. Heating resistor and condenser were permanently integrated into the microchip. The resistor consisted of three surface-mount device (SMD) components in parallel (R_{eq} of 16.7 Ω), constructed on a plate of alumina by welding. The condenser was based on a stainless steel tube with inner diameter of 700 μm. This tube was rolled producing spiral-shaped channels. Sample injection, distillation chamber, and distillate collect were obtained by sacrificial scaffolds. The scaffolds of the sample injection and distillation chamber were fabricated in acrylonitrile butadiene styrene (ABS) by 3D printing. This arrangement was glued on the resistor after simply wetting the ABS in acetone. Finally, the scaffold of the collection channel consisted of a nylon wire (800 μm diameter) glued on the top of the distillation chamber (**Fig. 1(a)**). Then, PDMS was poured onto the pool with the scaffold and cured at a laboratory oven. Next, the wire of nylon that defined the collection channel was rapidly withdrawn out. The removal of the nylon accelerated the ABS piece dissolution in acetone. Such step lasted approximately 2 h in ultrasonic bath.

Gravity-assisted separations were successfully attained by creating a distillation chamber with somewhat high size (900 μL) through 3D printing. Herein, the gravity overcame the surface forces, thus driving the distillation. To evaluate the DOC performance, the system was applied in the desalination of aqueous solutions at harsh salinity conditions that simulated the amount of salts in seawaters (NaCl 600.0 mmol L^{-1}). The sample volume transferred to the chamber was 400 μL in all of the analyses. After, the resistor was connected to a DC power supply and the distillations were conducted for 1 h applying different voltages. The distillate volume was collected in Eppendorf® tubes. Tests were realized with air-cooled (Acc) and water-cooled condensers (Wcc). In this latter case, water was pumped into the condenser in two directions, up-to-down (W_{CC}^{U}) and down-to-up (W_{CC}^{D}). The performance of the desalinations was mathematically evaluated as a function of the efficiency of salt removal (ESR) and throughput.

Results and discussion: concerning the operation of the DOC, when the liquid in the bottom of chamber reaches its boiling temperature, it starts to vaporize. Once PDMS shows a low thermal conductivity (0.16 W m^{-1} K^{-1}), the top walls of the distillation chamber are at temperatures lower than the bottom. This gradient led to the production of droplets at top walls. Maintaining the heating, the droplets form distillate plugs that pass through the collection channel because of the capillarity phenomena and vapor pressure that is built up into the chamber (**Fig. 1(b)**). The

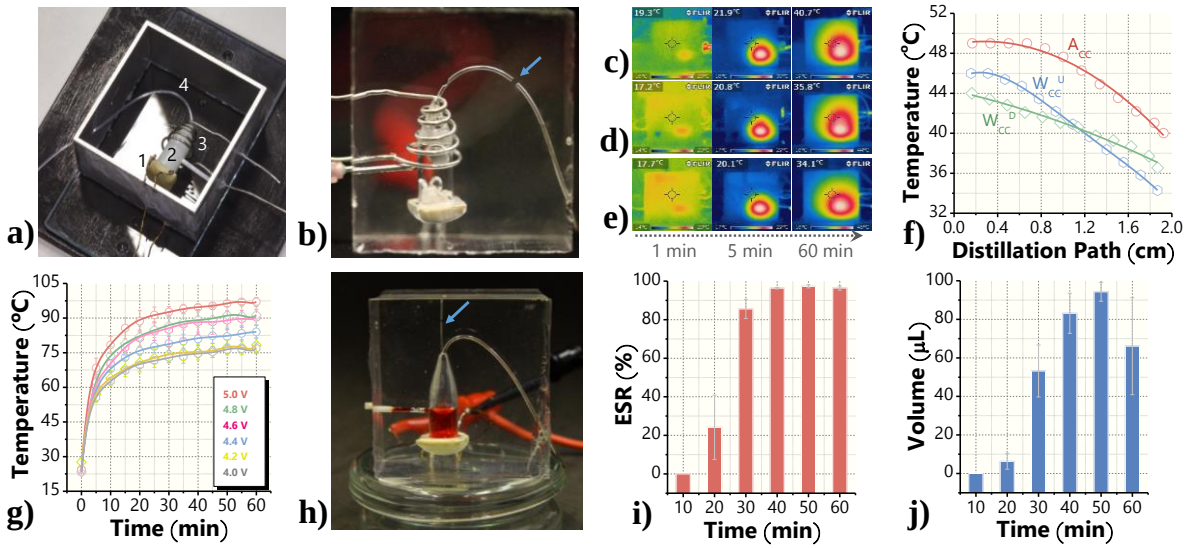

Figure 1. DOC chip. Assembled scaffolds: 1; heating resistor, 2; ABS to define distillation chamber and sample injection, 3; condenser, 4; and nylon microwire to create the collection channel **(a)**. Photo of the device showing the stage of evaporation/condensation at the distillation chamber **(b)**. Infrared images of the microdistiller surface for A_{CC} **(c)**, W_{CC}^{U} **(d)**, and W_{CC}^{D} after 1, 5, and 60 min **(e)**. Temperatures estimated from the infrared images in the region of the distillation path, which extends from the bottom to the top of the distillation chamber **(f)**. Real temperatures of the liquid phase during 60 min of distillation at different voltages **(g)**. Device constructed to improve the throughput **(h)**. Distributions of ESR **(i)** and distillate volume **(j)** as a function of the time for this new chip.

vertical temperature gradient was confirmed by recording infrared images of the device external surface after 1, 5, and 60 min of distillation at 4.8 V for three operation modes, namely A_{CC}, W_{CC}^{U}, and W_{CC}^{D} (**Fig. 1(c-e)**). Taking the temperatures associated with these images after 60 min as a function of the distillation path (**Fig. 1(f)**), we can conclude the temperatures at the top of the chamber were quite lower than the values observed at the bottom for all of the situations. As expected, W_{CC}^{U} and W_{CC}^{D} modes generated the lowest temperatures compared with A_{CC}. The NaCl solution distillation was observed only in A_{CC} likely because excessive condensations at W_{CC} modes.

As a next step, the real temperatures of the vapor and liquid (NaCl 600.0 mmol L^{-1}) phases inside the distillation chamber were monitored during the application of diverse voltages. The temperatures attained for the liquid phase (**Fig. 1(g)**) increased with the applied voltage. The distillations presented values of ESR of approximately 99%, except the data at 5.0 V when bumping (distillate contamination by the sample) was verified. With regard to the throughput, its maximum value was only 28.7 µL that was obtained at 4.8 V. This parameter was improved through simple changes on the chip. Basically, the distillation chamber was based on a more elongated top and a second channel with 400-µm diameter was engraved on the top of the chamber using nylon scaffold for its prototyping (**Fig. 1(h)**). This additional microchannel decreased the vapor pressure inside the distillation chamber, inhibiting the bumping phenomenon. Thus, biggest voltages could be used for driving the distillation. The voltage applied in these tests was 6.0 V and the temperature of the liquid phase was roughly 85 ºC after 20 min. With the use of this high voltage, the condensation did not happen at distillation chamber top as observed above, but into the collection channel. After some seconds or minutes, liquid plugs of the distillate were generated and then rapidly collected by the action of capillarity and vapor pressure enhancing the throughput. Considering the ESR distribution throughout distillations utilizing the new device (**Fig. 1(i)**), ESR was poor up to 20 min. Otherwise, such parameter was 96% taking up only the volumes collected after 30 min. Discarding the volume obtained up to this time, the throughput was 243 ± 10 µL h^{-1} (**Fig. 1(j)**). Such value is still substantially higher than the throughput produced by the previous DOC device.

Conclusion: a microscale distiller in agreement with the apparatus of conventional flash distillation and, thus, with ability to drive gravity-assisted distillations was described for the first time. While the liquid (sample) and vapor phases were separated by gravity, the distillate was driven through capillarity and vapor pressure inside the distillation chamber. Such process promoted high performance desalination of solutions at harsh salinities. Finally, our approach may contribute for a further growing of distillation-based microfluidic platforms with the intend to perform the preparation of diverse samples.

References:

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