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Electronic Supplementary Information

Rapid detection of nicotine from breath using desorption ionisation on porous silicon

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Materials and Methods

Hydrofluoric acid (HF, 48%) and undenatured ethanol (99.9%) were purchased from Scharlau Chemie (Chem-Supply, Australia). (Tridecafluoro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane (F_{13}) was purchased from Gelest (USA). Cesium iodide (CsI) was purchased from Sigma (Australia).

Fabrication of DIOS chips

As described elsewhere, DIOS substrates were prepared from monocrystalline (0.008−0.02 Ω·cm) antimony-doped n-type Si (100) wafers (Silicon Quest International). Desorption ionisation on porous silicon (DIOS) chips were fabricated by light-assisted anodic etching in a 1:1 HF/ethanol electrolyte solution. A constant current of 4 mA/cm^2 was applied across the cell for 2 min using a 2425 current source meter (Keithley). The pSi chips were then rinsed extensively with ethanol and dried under nitrogen gas. The freshly etched pSi was ozone-oxidised at a flow rate of 3.25 g/h by use of an Oxyzone T500 (Oxyzone, Australia). Subsequently, the pSi was subjected to a second pore broadening etch with 5% HF/H_2O for 30 s. The double etched surface was ozone-oxidised (as above) for a second time. The pSi was silanized with neat F_{13} (80 µL) for 30 min at 90 °C. Subsequently, the pSi chips were washed with ethanol and dried under a stream of nitrogen gas.

Small molecule standards

Nicotine standards were kindly provided by Forensic Science SA. Working solutions of nicotine (10 µg/mL) were prepared by diluting the original stock solution in ethanol. Working solutions were stored at +4 ^{o}C and prepared fortnightly. Subsequently, fresh nicotine solutions in milliQ water in the concentration range of 0-10 ng/mL were prepared on the day of analysis from working solutions. The limit of detection (LOD) was defined as three standard deviations of the calculated background signal. The background signal was calculated from six replicates that did not contain nicotine.

Collection of breath

Breath was collected from a non-smoker (control) and a habitual cigarette smoker. Two alternative procedures were used for breath collection. Procedure one involved the direct exhalation onto DIOS substrates. In this procedure the DIOS chip was inserted into a slit cut into a plastic straw (Homebrand, Woolworths, Australia) and the subject exhaled through the straw for 15 s (scheme 1a). Procedure two involved the subject exhaling through straws into a 500 µL Eppendorf vial. The resulting vapour was then resuspended in 5-20 µL of milliQ water (Millipore, Australia) and vortexed and centrifuged consecutively for 30 s. The resuspended breath (1 µL) was then directly deposited onto DIOS chips in replicates of three and analysed for small molecules.

DIOS analysis

All DIOS analysis were performed in reflectron positive mode on an ultrafleXtreme MALDI ToF/ToF instrument (Bruker Daltonics, Germany). Data acquisition used flexControl 3.4.78 with a user optimised laser fluence. Calibration was performed using CsI (10 mg/mL). MS/MS spectra were acquired using a LIFT method and processed in flexAnalysis version 3.4 (Bruker Daltonics, Germany). Spectra were also processed using mMass open source software[1].

Scanning electon microscopy (SEM)

SEM imaging was carried out using a Zeiss Gimini crossbeam 540 SEM operated at 3-5 kV in “in-lens” mode. Obtained images were analysed using ImageJ V. 1.46 (open source software).

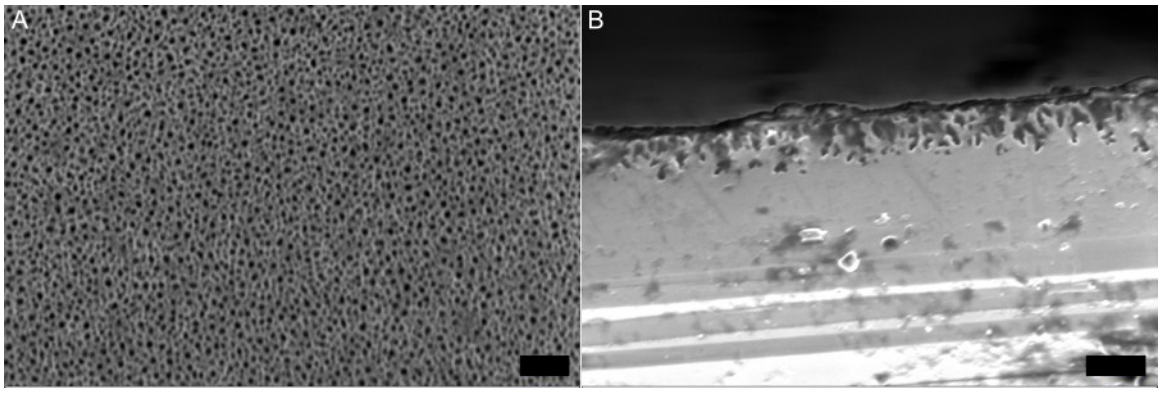

Fig. S1. SEM of a DIOS chip in A) the top view and (B) the cross-sectional view. Scale bar corresponds to 1 μm.

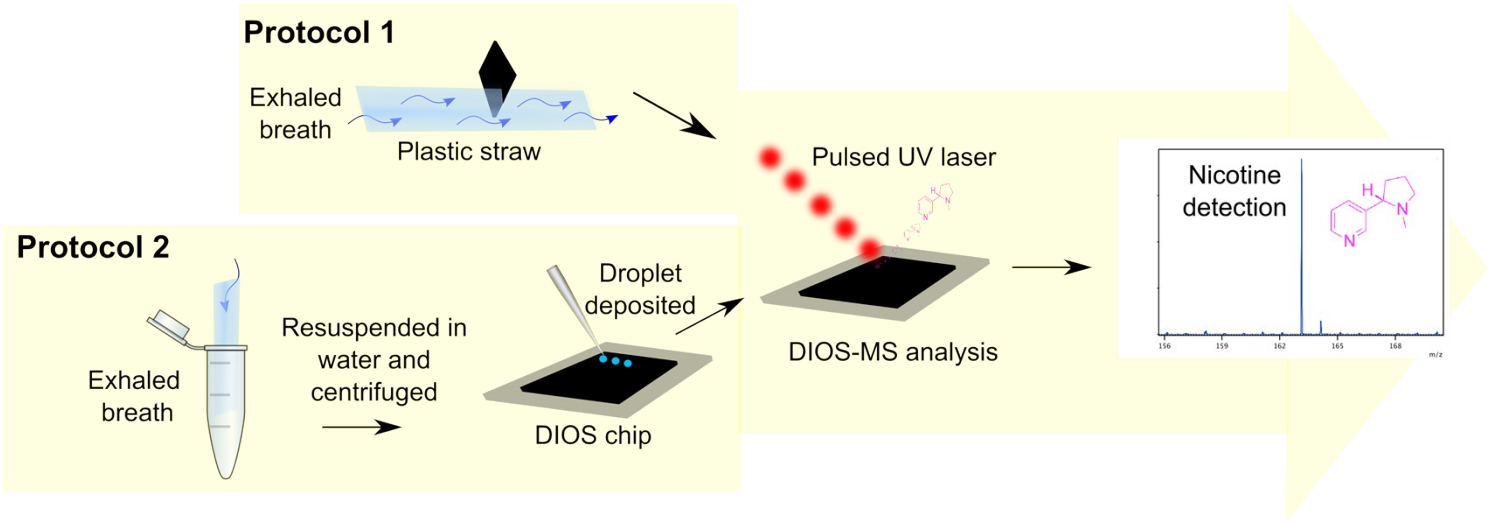

Fig. S2. Schematic of protocol 1 and protocol 2 for breath collection. For protocol 1 (top panel) exhaled breath is passed through a plastic straw for 15 s with a custom made slit to secure the DIOS chip in place. The DIOS chip is removed from the straw and immediately analysed using DIOS-MS. For protocol 2 (bottom panel) exhaled breath is passed through a plastic straw for 15 s. The straw is placed over the top of an open 500 μL Eppendorf tube. The vapour is then suspended in milliQ water and centrifuged for 2 min. 1 μL droplets are pipetted onto the DIOS chip and then analysed by DIOS-MS.

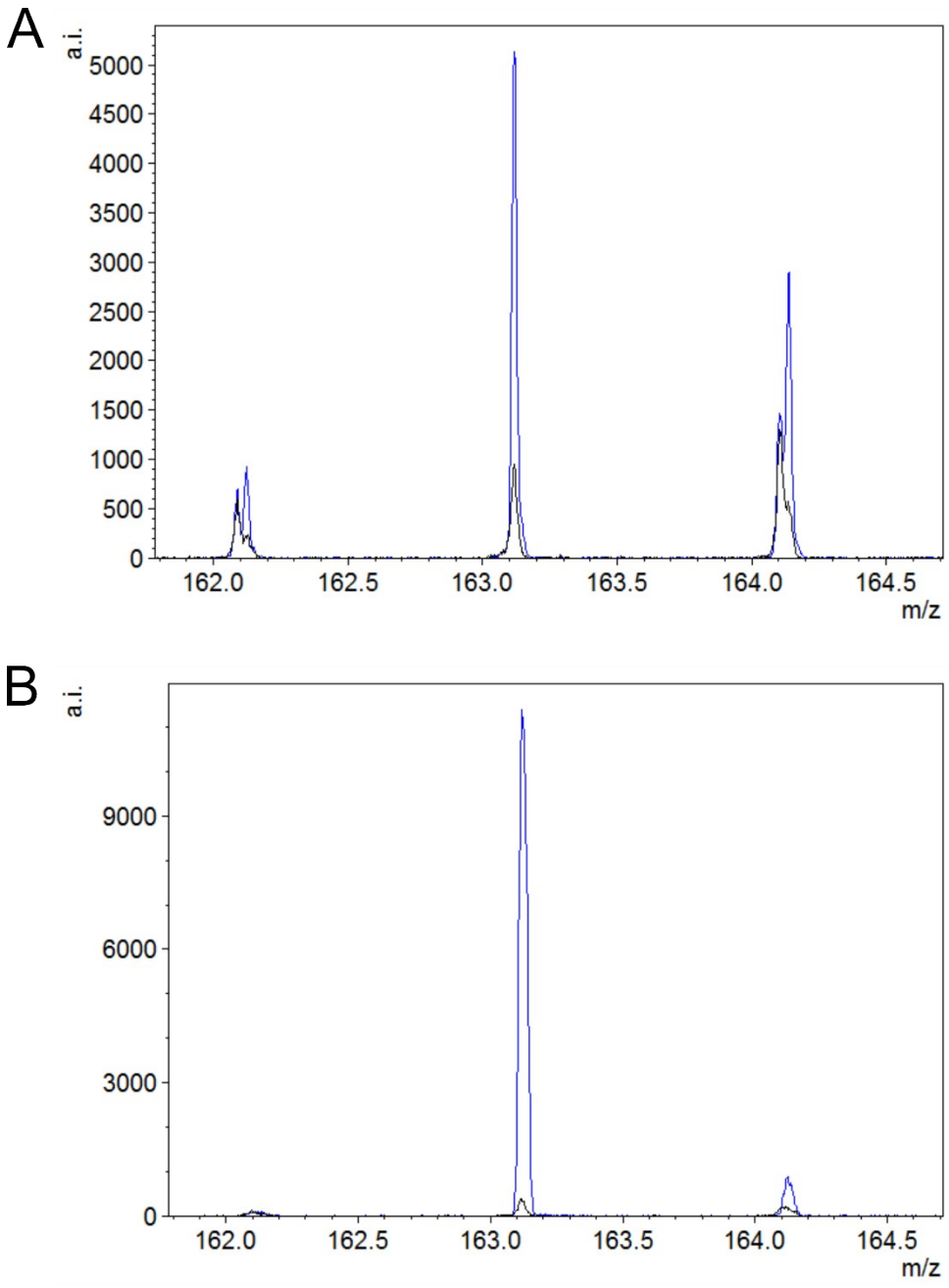

Fig. S3. Representative DIOS-MS spectra observed for A) protocol 1 and B) protocol 2, respectively. The blue and black trace represents breath analysed from a smoker and non-smoker as the control, respectively.

References

1. M. Strohalm, M. Hassman, B. Košata and M. Kodíček, *Rapid Commun. Mass Spectrom.*, 2008, **22**, 905-908.