

## Supporting Information

### *NEMS resonator fabrication and measurement*

The cantilever resonators were fabricated from 100-nm thick, low stress silicon nitride films grown on silicon substrates. A metal film was patterned on the nitride surface through a combination of electron-beam lithography, physical vapor deposition, and lift-off methods. The metal, typically a 30-nm gold film, served a dual role as an etch mask for the NEMS release, and then later as a piezoresistive strain sensor for integrated transduction of the mechanical motion. The NEMS devices were released through a combination of anisotropic plasma etching through the nitride and isotropic silicon undercut etching.

To functionalize the released device, the chip was first treated with hexamethyldisilazane (HMDS) to improve the adhesion of the polymer film. DKAP and PCL polymers were dissolved in toluene at a concentration of  $0.5 \text{ mg ml}^{-1}$ . Using a micropipette, a droplet of polymer solution was then applied onto the chip surface, and the chip was dried in a gentle flow of  $\text{N}_2$  (g). Two sets of cantilevers that were 2.5 mm apart on the chip were thus coated with different polymers. The resulting coating thickness typically varied from a few nm to 10 nm, as confirmed by measurement of the changed resonance frequency of the cantilever before and after the coating process, as well as by atomic force microscopy.

The coated cantilevers used in the experiments were typically  $2.5 \text{ }\mu\text{m}$  long and  $0.8 \text{ }\mu\text{m}$  wide, with a designed resonance frequency of 8 MHz. In air, the resonance quality factor was 150-200, and was approximately 50% higher in  $\text{H}_2$  due to the decreased gas viscosity. To actuate the NEMS, the device chip was mounted on an extremely thin ( $\sim 100 \text{ }\mu\text{m}$ ) piezoceramic “shaker” disc that could be operated at  $>100 \text{ MHz}$ . The resonance frequency of the NEMS resonator was

tracked in real-time with a phase-locked feedback loop circuit, such that the actuation frequency was maintained at the center frequency of the resonance. The obtainable fractional-frequency resolution in a 1 Hz bandwidth was better than  $5 \times 10^{-7}$  ( $\sim 4$  Hz for an 8 MHz resonator), mostly limited by short-term environmental fluctuations of the temperature, pressure and/or carrier gas flow rates. For the fast GC measurements, the phase-locked loop provided insufficient bandwidth to resolve the short peaks that eluted from the column. Instead, the NEMS was operated in open-loop mode, using an oscilloscope with a 1 kHz sampling speed to resolve short-term excursions of the resonance frequency as analytes were exposed to the device. While this approach enabled very high-speed operation, it accordingly increased the noise, and reduced the frequency resolution from the 1 Hz bandwidth number quoted above.

The gas microfluidic flow volume was fabricated by etching a patterned channel in a glass chip. The channel consisted of a shallow groove along one surface of the glass chip, with two machined through holes comprising a gas inlet and outlet, respectively. The groove dimensions were 20  $\mu\text{m}$  in depth, 250  $\mu\text{m}$  in width, and 2.5 mm in length. The glass chip was flip-attached to the device chip and sealed with vacuum epoxy, encapsulating the NEMS array inside the channel.

#### *Gas chromatography measurement*

A Hewlett-Packard 5890 gas chromatography system was used for the gas chromatography. Fused silica columns (Restek Rtx-5, inner diameter of 0.1 mm, coating thickness of 0.1  $\mu\text{m}$ ) were utilized for the separations. The oven, housing both the column and the NEMS device package, was set at 40  $^{\circ}\text{C}$ . Temperature-programmed analysis was used to obtain the fast chromatograms. A fast temperature ramp of 20  $^{\circ}\text{C s}^{-1}$  was run on the column, by applying a step-function profile of 40 W power to a Ni-Cr wire heater that was coaxially located

with the column inside an insulating glass fiber sleeve. For typical fast GC operation, the H<sub>2</sub> carrier gas flow rate through the column was 5.0 cm<sup>3</sup> min<sup>-1</sup>, with an injection split ratio of 1:200. The injector headspace pressure was 30 psi and, in each analysis, 1 µl of sample solution was injected using an automatic syringe injection unit.

#### *Preparation of tested chemicals*

Toluene (TOL), octane (C8), dimethyl methylphosphonate (DMMP), heptanol (C7OH), 2-chloroethyl ethyl sulfide (CEES), octanol (C8OH), diethyl methylphosphonate (DEMP), diethyl chlorophosphate (DCP), di-n-butyl sulfide (DNBS), diisopropyl methylphosphonate (DIMP), undecane (C11), dichlorohexane (DCH), and methyl salicylate (MS), were used as received. To obtain the chromatograms in Figs. 2 and 3, all of the analytes were dissolved in diethyl ether to produce a mass concentration of 0.5%.