MEMS and NEMS Group
Room A210 - Session MN-MoA

Microfabricated Systems for Gas Chromatography and Nanomechanical Mass Sensing

Moderators: Robert Davis, Brigham Young University, Christian Zorman, Case Western Reserve University

1:40pm **MN-MoA1 Micromachined Silicon Micro-pillar Arrays for Liquid and Gas Chromatography**, ***Gert Desmet,*** Vrije Universiteit Brussel, Belgium **INVITED**

The present contribution aims at illustrating and demonstrating how micro-machining technology can give a boost to High Performance Liquid Chromatography (HPLC). Currently, HPLC is routinely used in nearly every chemical analysis lab. Despite its high degree of maturity, the technique however suffers from serious performance limitations when faced to the complex samples that need to be separated to solve the current state-of-the-art problems in the biological and pharmaceutical research (e.g., proteomics and metabolomics), the food and environmental analysis, etc.

The currently used packed bed HPLC columns are clearly underachieving because of the packing disorder and the concomitant large degree of band broadening. To solve this packing disorder problem, the present contribution will focus on the possibilities of advanced photolithographic etching techniques such as the Bosch-process to produce perfectly ordered porous support columns with optimized hydrodynamic shape and optimized external porosity.

At the conference, we will demonstrate the possibility of rapid multi-component separations and the possibility to achieve very high separation efficiencies with a microfabricated column in pressure-driven liquid chromatography. In addition, we have also extended the concept to gas chromatography (GC), where the micromachining allows to make designs that combine fast separation kinetics with a high mass loadability, two factors with opposite requirements in the current commercial format for GC.

2:20pm **MN-MoA3 An Integrated Passive µPreconcentrator with Progressively-Heated µInjector for µGC**, *R. Hower, C. Zhan, M. Akbar, N. Nuñovero, J. Wang, J. Potkay,* ***Edward Zellers,*** University of Michigan **INVITED**

We report on a new device designed to serve as a universal 'front-end' for gas chromatographic microsystems (µGC) for remote, long-term monitoring of vapor-phase chemical threats or environmental pollution. This small, low-power, Si/glass-micromachined device, dubbed a micro-collector/injector (µCOIN), combines a passive micro-preconcentrator (µPP) with a progressively heated micro-injector (µPHI). The µPP samples vapors at known rates by molecular diffusion and transfers them under active flow via thermal desorption to the µPHI, which, in turn, injects them to a downstream (µGC) separation column via progressive (sequential) heating. Most testing to date was performed with discrete devices, both of which contain tandem cavities packed with granular carbon-based adsorbents of different specific surface areas. Carbopack B (CB, 100 m^2/g) and Carbopack X (CX, 240 m^2/g) were used for most compounds. But CX was used with Carboxen 1003 (C3, 1000 m^2/g) for more volatile compounds. Using a conventional GC for downstream analyses, we have found that the µPP (CX/CB) can collect vapors of widely different volatility at a nearly constant effective sampling rate for up to 24 hrs (low concentrations) and over a 2,500-fold concentration range (0.25-hr samples). Effective (compound-specific) sampling rates ranged from ~0.25 to 0.69 mL/min, most of which agreed with theoretical predictions. Desorption/transfer efficiencies from the µPP were > 87% (most > 94%) at 5 mL/min and 250 °C for 60 sec. For the µPHI (CX/CB) bolus challenges of compounds at 5mL/min, mimicking transfer from the µPP, resulted in > 90% capture efficiency for up to 3.6 µg of lower volatility compounds. More volatile or highly polar compounds required the CX/C3-loaded device. Back-flushed progressive heating of the µPHI produced injection bands < 250 ms wide at flow rates < 0.5 mL/min. In separate tests, remarkable selectivity for polar compounds was achieved by applying an ionic-liquid surface modifier to the carbon adsorbents (tests in the µPP and µPHI are pending). The monolithically integrated µCOIN (0.23 cm^3) has not yet been tested. But, a hybrid-integrated µCOIN (capillary connections) provided good preliminary performance, including efficient sampling, transfer, and injection of multi-component mixtures. Valveless flow modulation was implemented to avoid backflow to the µPP. Using typical power levels for each device, two valves, a pump, an interconnect heater, and supporting electronics, the energy consumption was only 320 J per cycle for the hybrid µCOIN. Thus, the µCOIN shows promise as a component in future ultra-low-power µGC systems for analyzing complex vapor mixtures.

3:00pm **MN-MoA5 Developments and Challenges in Full-range Microchip Gas Chromatography**, ***Abhijit Ghosh,*** Honeywell UOP, Des Plaines, IL, USA.; *M.L. Lee,* Brigham Young University

This year (2019) marks the 40th anniversary of microchip gas chromatography (GC). In these four decades of investigations, many avenues, as well as challenges, have been encountered by researchers to produce microchip columns that are as efficient as fused silica open tubular columns in GC. Although there are exciting theoretical possibilities, in reality many practical constraints remain that limit their widespread commercialization and use. The main challenges are difficulty in static coating, unwanted dead volumes and inadequate interfacing technologies, which all affect both column performance and range of applications. This presentation emphasizes some of the challenges and key developments in the field of microchip gas chromatography, as well as novel approaches that are currently being investigated

3:20pm **MN-MoA6 Fabrication of Thermally Isolated micro-Column for Gas Chromatography**, ***James Harkness,*** *H. Davis, A.C. Davis, R.C. Davis, B.D. Jensen, R.R. Vanfleet,* Brigham Young University

Micro gas chromatography (GC) has suffered from poor separations due to short column length and stationary phase pooling, however introducing a thermal gradient along a GC micro-column has been shown to enhance separations. We will present a thermally isolated micro-column for thermal gradient GC, fabricated using a two-wafer deep silicon etch/bond/etch process. Desired thermal isolation was achieved by forming suspended micro-columns that enable low-power thermal control using passive and active elements.

4:00pm **MN-MoA8 Control of Surface Geometry and Chemistry to enable integration of Microfabricated Structures into High Performance Microscale Gas Chromatography Systems**, ***Henry Davis,*** *D. McKenna, J. Harkness, D. Kane, R.R. Vanfleet, R.C. Davis,* Brigham Young University

There are a variety of microfabricated structures, materials and devices that could enable high performance microscale gas chromatography systems, such as micro pillar arrays and porous resonant mass detectors. However, integration of these structures into microscale gas chromatography systems will require a high degree of control over surface geometry and surface chemical functionalization. Here we will describe processes using liquid deposition of silsesquioxanes and oxide atomic later deposition for control of surface chemistry and geometry of micro and nanoscale structures.

4:20pm **MN-MoA9 Constructive Utilization of Nonlinear Dynamics in MEMS/NEMS**, ***Hanna Cho,*** The Ohio State University **INVITED**

During the last decades, we have witnessed that MEMS/NEMS revolutionized fundamental and applied science. However, due to small size and low damping, these devices often exhibit significant nonlinearity and thus the operational range of these impressive applications shrinks. Therefore, understanding the mechanisms leading to nonlinearity in such systems will eliminate obstacles to their further development and significantly enhance their performance. Motivated by the need to advance current capabilities of MEMS/NEMS, our research has been focused on the implementation of intentional intrinsic nonlinearity in the design of MEMS/NEMS resonators and proved that harnessing intentional strong nonlinearity enables exploiting various nonlinear phenomena, not attainable in linear settings, such as broadband resonances, dynamic instabilities, nonlinear hysteresis, and passive targeted energy transfers. We developed a comprehensive analytical, numerical, and experimental methodology to consider structural nonlinearity as a main design factor enabling to tailor mechanical resonances and achieve targeted performance. We investigated the mechanism of geometric nonlinearity in a non-prismatic microresonator and suggested strategies to tailor the various types of nonlinear resonance. Our recent works focus on exploiting nonlinearity and multimodality simultaneously by internally coupling two or more modes through the mechanism of internal resonance or combination resonance. This talk will introduce various types of nonlinearity realized in micro/nanomechanical systems and discuss their unique behavioral features that can be exploited in the field of MEMS/NEMS.

5:00pm **MN-MoA11 Frequency Stabilization in a MEMS Oscillator Via Tunable Internal Resonance*, Jun Yu*, *H. Cho,*** The Ohio State University

Micro-Electro-Mechanical Systems (MEMS) oscillators are being considered as substitutes of quartz oscillators since these microscale oscillators are easier to be integrated in electronics. As a timing device, one of the most important functionalities of MEMS oscillators is to provide a reference frequency with a minimal frequency fluctuation. The mechanism of internal resonance (IR) was proposed to stabilize the frequency by Antonio et al. in 2012 [1]. Here, we report a MEMS resonator that is specifically optimized to provide 1:2 relationship between its modal frequencies and, thus, implement 1:2 IR in its dynamic response. We also tune the frequency ratio precisely by adjusting the applied DC voltage to achieve an ideal IR characteristic for frequency stabilization.

In this study, a clamped-clamped silicon microbeam resonator shown was designed and fabricated to enforce a 1:2 ratio between its second and third flexural modes. We first characterized the thermal-mechanical noise of the resonator under different DC biases using a Laser Doppler Vibrometer. Its modal frequencies can be tuned with DC bias, because the DC bias influences the mid-plane stretching of the microbeam structure. Thereby, the ratio between second and third flexural modes can be finely adjusted around the 1:2 commensurate condition and eventually achieve exact 1:2 ratio when the DC bias is 21V. Under this IR condition, a well-documented M-shape, typically occurring in a 1:2 IR system. The externally resonated (ER) curve represents the oscillation amplitude at the excitation frequency, while the internally resonated (IR) curve represents the oscillation amplitude at the twice of the excitation frequency. We further studied the frequency stabilization by exploiting the energy transfer mechanism of internal resonance. We measured the frequency fluctuations from the MEMS oscillator implementing this resonator in the cases without and with IR. When IR was triggered, the frequency fluctuation was diminished by more than 20 times to be 5.72 ppm. The Allan deviations is also reduced by about 30 times when the IR is activated.

[1] D. Antonio, D. H. Zanette, and D. López, “Frequency stabilization in nonlinear micromechanical oscillators,” *Nat. Commun.*, vol. 3, no. 1, Jan. 2012.

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