Ion Chromatography-on-a-Chip for Water Quality Analysis

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We report progress towards developing a Micro-Electro-Mechnical Systems (MEMS)-based ion chromatograph (IC) for crewed spacecraft water analysis. This IC-chip is an offshoot of a NASA-funded effort to produce a high performance liquid chromatograph (HPLC)-chip. This HPLC-chip system would require a desalting (i.e. ion chromatography) step. The complete HPLC instrument consists of the Jet Propulsion Labortory's (JPL's) quadrupole ion trap mass spectrometer integrated with a state-of-the-art MEMS liquid chromatograph (LC) system developed by the California Institute of Technology's (Caltech's) Micromaching Laboratory. The IC version of the chip consist of an electrolysis-based injector, a separation column, two electrolysis pumps for gradient generation, mixer, and a built-in conductivity detector. The HPLC version of the chip also includes a nanospray tip. The low instrument mass, coupled with its high analytical capabilities, makes the LC-chip ideally suitable for wide range of applications such as trace contaminant, inorganic analytical science and, when coupled to a mass spectrometer, a macromolecular detection system for either crewed space exploration vehicles or robotic planetary missions.

Nomenclature

ASTID	=	Astrobiology Science and Technology Instrument Development
CD	=	conductivity detector
CCD	=	contactless conductivity detector
DRIE	=	deep reactive ion etcher
ESI	=	electrospray ionization
HPLC	=	high performance liquid chromatography
IC	=	ion chromatography
LC	=	liquid chromatography
MECA-WCL	=	Mars Electrochemistry and Conductivity Analyzer - Wet Chemistry Laboratory
MEMS	=	micro-electro-mechnical systems
MS	=	mass spectrometer
PIDDP	=	Planetary Instrument Definitition and Development Program
QIT	=	quadrupole ion trap
VCAM	=	Vehicle Cabin Atmosphere Monitor

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I. Introduction

OUR group's objective is to design, build and demonstrate a new miniaturized instrument for analysis of organic compounds in planetary materials with high sensitivity (parts-per-billion/trillion depending on target species) and accuracy, with a particular focus on detecting biomarkers previously extracted from crushed rocks, soils and ices. The ultimate goal of this research is to develop a miniaturized instrument for both robotic and human missions. The proposed work consists of the development and integration of two high TRL instruments: a complete, microfluidic High Performance Liquid Chromatograph-on-a-chip (HPLC-chip) and a miniature Paul quadrupole ion trap (QIT) Mass Spectrometer (MS) detector, based on flight heritage but modified for external ionization. As an off-shoot of the HPLC-chip, we are pursuing and ion chromatograph (IC) version of the chip for crewed spacecraft water analysis – this is the primary focus of this paper.

Until recently, HPLC systems have been considered to be unsuitable for *in situ* planetary applications due to their large mass and operational complexity. However, starting in 2004 the Caltech Micromachining Laboratory demonstrated the first complete microfluidic reverse-phase HPLC-chip instrument (pumps, injector, mixer, column), which is capable of separating a wide range of organic compounds based on their varying elution times through the separation column [1,2]. The HPLC-chip is based on Micro-Electro-Mechanical Systems (MEMS) technology and consists of a reusable microfluidic polymer chip with dimensions smaller than a quarter. The HPLC-chip integrates three electrolysis-based electrochemical pumps, one for loading the sample and the other two for delivering the solvent gradient; a static mixer; a column packed with silica-based reversed-phase support; and an electrospray nozzle (for MS) directly on the polymer chip.

There are a variety of compact detectors commonly used for HPLC: UV/VIS absorption or fluorescence, refractive index, electrochemical, conductivity, evaporative light scattering to name a few. However, none of these types of detectors can give a definitive identification of molecules nor can they identify, and in some cases, even detect unknown compounds. The coupling of LC to MS is recognized as the premier technique for any application, which requires high sensitivity, selectivity, and complete unambiguous identification of an unknown collection of chemical species. These are exactly the requirements and conditions found in a planetary robotic exploration. The coupling of LC to MS via electrospray ionization (ESI) is the terrestrial standard and is especially useful in producing ions from macromolecules because it overcomes the propensity of these molecules to fragment when ionized through other methods (e.g. electron impact, laser ionization). A further advantage for LC/MS is that the need for chemical labeling (for optical detectors) and/or derivatization (for gas chromatography) are eliminated. The clogging and reliability of prior ESI efforts will be solved in the proposed work through the inclusion of a desalting mode/valve on the HPLC-chip.

Mass spectrometry has as its basis the measurement of mass-to-charge ratios (m/z) of ions. There are many different mass analyzers that can be used in LC/MS - Single Quadrupole, Triple Quadrupole, Paul Quadrupole Ion Trap (QIT), TOF (Time of Flight) and Quadrupole-Time of Flight (Q-TOF). The principal advantages of a Paul quadrupole ion trap in chemical analysis can be summarized as follows: (i) high sensitivity, (ii) compactness and mechanical simplicity in a device which is nevertheless capable of high performance, (iii) MS^n mass spectrometry experiments are available by performing sequential mass analysis measurements, (iv) ion/molecule reactions can be studied for mass-selected ions, (v) high resolution ($m/\Delta m > 1000$ Da), (vi) ions of high mass/charge are accessible using resonance experiments, and (vii) non-destructive detection is available using Fourier transform techniques. A QIT be made into a compact or miniaturized device by suitable scaling of dimensions and potentials and this has been accomplished in the flight-proven QIT in the Vehicle Cabin Atmosphere Monitor (VCAM) recently flown on the *International Space Station* [3]. Under current NASA funding through the ASTID (and previously, PIDDP [4]) and Advanced Exploration Systems (AES) programs this QIT is undergoing further miniaturization to realize a total system mass of ~2 kg in total mass, including electronics and vacuum pumps.

In most analytical investigations, there is a need to process complex field samples for the unique detection of analytes especially when detecting low concentration organic molecules that may identify extant and extinct extraterrestrial life [5]. Sample processing for analytical instruments is time, resource and manpower consuming in terrestrial laboratories. Every step in this laborious process will have to be automated for *in situ* life detection. This front-end processing is beyond the scope of this proposal and is being covered by other instruments [6].

However, one step that would be of critical relevance to the HPLC-chip/MS system is desalting; compound mixtures isolated from natural matrices often contain considerable amounts of nonvolatile salts. The presence of such salts may interfere with the operation of electrospray ion sources by clogging the skimmer and obscuring or suppressing ionization. And, in complex environments where high levels of salts are present, e.g. Mars [7,8], front-end devices may not be efficient enough (or dedicated enough) to desalt a sample for HPLC/MS.

Therefore, as part of our work, we pursuing a desalting methodology either as an addional step (and valve) on the HPLC-chip or as a separate desalting-chip. An off-shoot of pursuing a separate chip (with a built-in conductivity detector) is that it can also act as an ion chromatograph opening up the possibility of water analysis for both human and robotic applications. This paper primarily describes our ion chromatography efforts.

The JPL lab-on-a-chip ion chromatography project adapts proven laboratory methods to the microfluidic scale to provide a compact, portable pressure-driven flow system for high-resolution inorganic chemical enumeration for in situ planetary analysis. Deployment of these sensing technologies is relevant for analysis of regolith on solid bodies following solvent extraction (e.g. Mars), or on icy planetesimals which harbor liquid water (e.g. Europa, Enceladus) where ingestion of aqueous samples from exposed ice or subsurface water can be accomplished. The relevance to Mars *in situ* science continues from the successful analyses by the Mars Electrochemistry and Conductivity Analyzer Wet Chemistry Laboratory (MECA-WCL), especially the detection of the anion perchlorate up to 0.6% by weight from water-extracted regolith [9]. Recent confirmation of the likely presence of hydrated calcium perchlorate by the Mars Science Laboratory (MSL) Sample Analysis at Mars (SAM) instrument [10] reinforces science questions regarding the presence of other oxychlorine species (e.g. chlorate, chlorite, hypochlorite) [11]. Inorganic species, such as salts and oxidants, present in water on icy planetesimals will be a critical science question once *in situ* investigations begin on these bodies.

II. Experimental Setup

The implementation plan included development of a Phase I system breadboard utilizing packed fused silica capillaries which are near identical in dimension to those planned for the microfluidic device. This breadboard system was utilized for testing of ionic separations using packed capillary columns and will be adapted for separations using the microfluidic device later. The Phase I plan is focused on column packing, integration of IC components (injector, pressure sensors, pumps and detector as well as proof-of-concept chromatographic runs. The focus on the separation system configuration is enabled by the high technology readiness of the detection method,

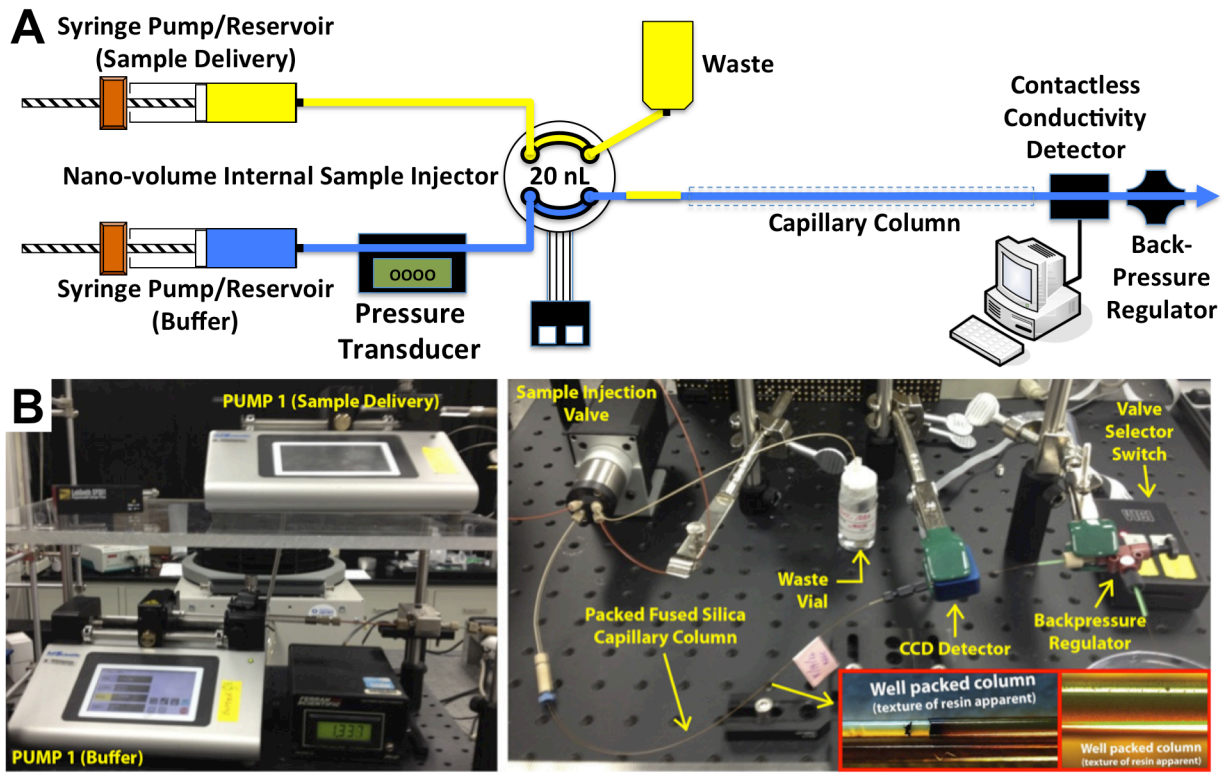

Figure 1. Breadboard setup. *(A) Block diagram and (B) photographs of the breadboard setup. Pump setup is shown on the left while fused silica capillary separation systems is shown in the right panel. The system includes dual syringe pumps (top pump for the sample, bottom pump for the mobile phase), high-pressure electronically actuated valve, capillary column, contactless conductivity detector, and pressure regulator. All components, except for the separation columns, are available commercially.*

contactless conductivity detection (CCD), which provides an effective approach for detection of ions following pressure-driven flow separation. CCD provides monitoring of the conductivity of the solution in a short length of capillary (or a local microfluidic channel section) as the solution elutes from the separation resin bed using this standoff method. This contactless approach allows for sensitive detection of ions following separation as they pass across the detection window. The Phase II system makes a number of improvements upon the Phase I system, namely the exclusive use of Caltech-fabricated microfluidic devices, enhanced use of miniaturized components, including an on-chip (contact) conductivity detector, and the planned use of integrated electrolysis pumps.

A. Preliminary Ion Chromatography in Fused Silica

The first year of the project targeted testbed development (Figure 1) to demonstrate proof-of-concept for miniaturization of an ion chromatography system. Using a Next Advance PC77 pressure injection cell, resin beads were packed inside columns with outer diameters of 365 µm and inner diameters of 250 µm. Fused silica capillary material was chosen because: (i) withstands high-pressure, (ii) provides ability to "see" resin through the column, and (iii) available in similar dimensions as microfluidic channels. KD Scientific Legato 180 syringe pumps drive buffer and load sample. A VICI electrically-driven 20 nL fixed volume sample injector loads aliquots onto the column before separation – the fused silica column is packed with ion exchange resin (5-30 µm) to resolve ionic species. An eDAQ C^4D Systems ET120 contactless conductivity detector provides detection of ions during flow through the module. A backpressure regulator provides stable operating conditions.

Test runs conducted to optimize separation conditions used tartaric acid (TA) as the eluting agent and dipicolinic acid (DPA) as a divalent complexing agent. A 4-species mixture was used for these experiments (Na^+, K^+, Ca^{2+}, Mg^{2+}), capillary columns were packed with 30 µm diameter Phenomenex weak cation exchange resin, and pressures were between 100-500 psi.

B. Ion Chromatograph Chip

The following phase of the project is the design and fabrication of a dedicated ion chromatograh chip (see Figure 5B for a schematic of the chip). The device is a glass-silicon bonded column. The technique allows for a high pressure device (above 10 MPa). The device's microchannel has a throat or filter that retains the chromatography media. Choosing a height of 3 µm for the filter permits the use of media as small as 5 µm diameter, such as Hamilton PRP-C18, or PRP-X100. With a size 80 µm x 50 µm, the microchannel can accommodate a wide range of chromatography media.

Fabrication (see Figure 2) begins by etching alignment marks on both sides of a double-sided silicon polished wafer. Oxide is then grown on the wafer. The micro channel is patterned onto the wafer using buffered hydrofluoric acid (BHF). Using the patterned oxide as a mask, the channel is then etched to the depth of the throat (3 µm) using the Bosch process in a deep reactive ion etcher (DRIE). Photoresist AZ4620 is then spun on the channel side of the wafer. It is patterned and hard baked to protect the filter portion of the channel from further etching. The wafer is once again etched with the DRIE to pattern the remaining channel. The device now contains a distinct filter and microchannel. The backside of the wafer is spun with photoresist AZ4620, the bottom oxide is patterned using BHF, and then etched through using the DRIE. Oxide is then etched-off everywhere except where in contact with the metal layers from the borosilicate wafer. Piranha solution is used to clean the wafer.

The conductivity sensor is patterned on a borosilicate wafer. The wafer is patterned with

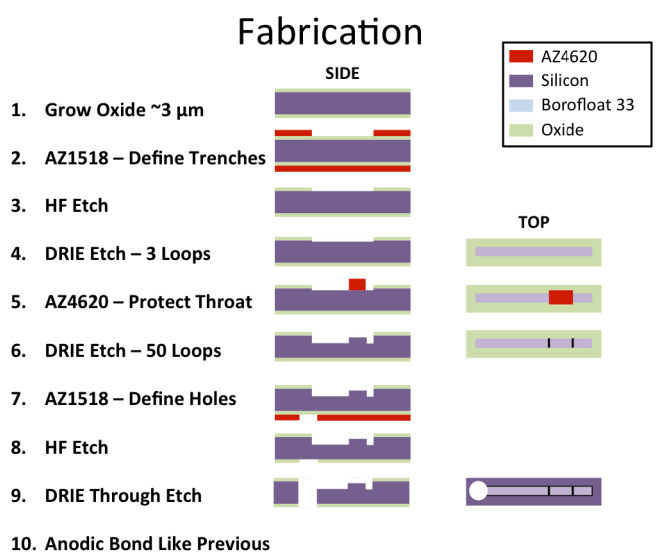

Figure 2. Fabrication process for the chip. *Silicone oxide is grown and patterned on silicon as an etching mask for the channel (steps 1-3). Step 4 shows the DRIE etch of the trench down to the height of 3 µm for the frit for the chromatography beads. Steps 5 & 6 is the application of a mask protecting the bead filter and 50 µm etching using DRIE to define the channel. Steps 7-9 show the through-hole etching. The channels are sealed by anodically bonding silicon to borosilicate glass.*

titanium-gold using a photoresist/LOR-3B lift-off process. This completes the electrodes which are externally driven. Both wafers are aligned and anodically bonded using 500 V and 440°C to the patterned silicon wafer. Dicing separates the individual devices.

The device is then placed in a chip holder, which connects the microchannel to Valco Instruments Company, Inc. (VICI) 0.005" I.D. x 1/16" O.D. tubing through Viton AppleRubber O-rings. The chip holder is capped with a transparent acrylic top allowing vision of the microchannel. This permits control over the packing. To pack the column, the media is suspended in water using a sonicator. This is then loaded into a syringe and injected into the column. The media flows into the column until stopped by the filter. Pressures around 10 MPa can be seen during packing at high flow rates (5-10 µL/min).

The electrolysis pump is comprised of microfabricated electrodes placed into an eluent containing holder. Titanium-gold electrodes are patterned onto a soda lime wafer using a photoresist LOR-3B lift-off later. These electrodes are thern planed in a holder which seals them using an o-ring. When voltage is applied, gas is produced, pushingthe liquid (eleuent) out. This technology allows for very high pressures [12]. This pump is connected with VICI 1/16" O.D. x 0.005" I.D. stainless steel tubing to the microfluidic chip.

III. Measurements and Results

The first phase of the project targeted breadborad development (Figure 1) to demonstrate proof-of-concept for miniaturization of an ion chromatography system. The phase II goal was to continue breadborad separations, fabricate and pack microfluidic ion chromatography chips, and demonstrate end-to-end system functionality.

A. Cation Chromatography

The breadboard system was assembled using commercial off the shelf products. These components included a microfluidic syringe pumps (2x), a high-pressure sample injection valve, in-house custom ion exchange resin packed fused silica capillary columns, and a COTS contactless conductivity detector. Cation separation experiments began

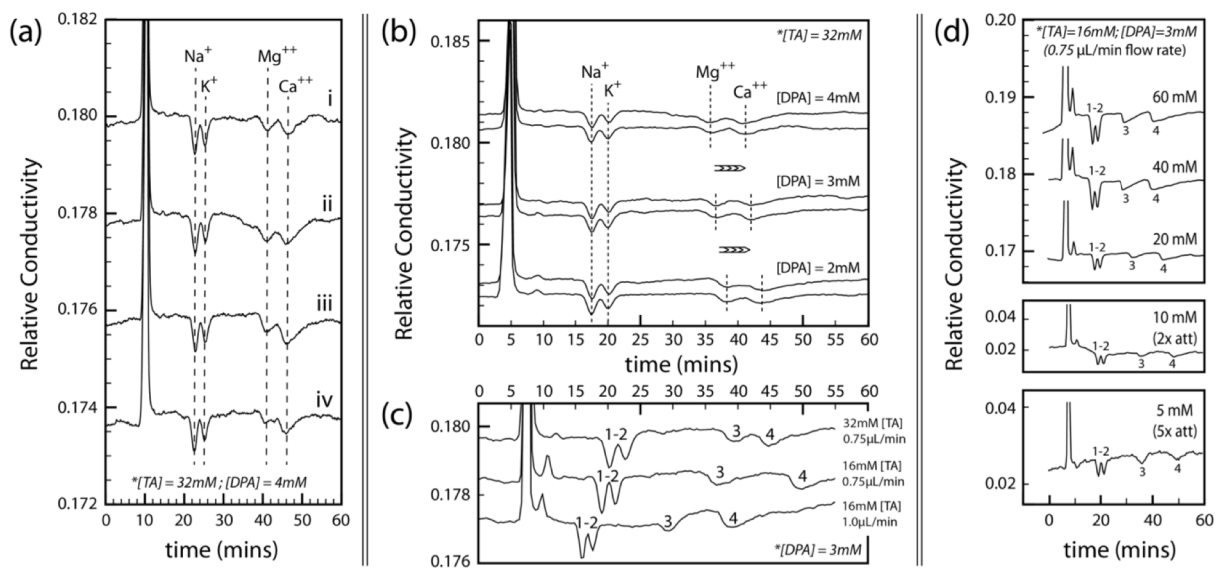

Figure 3. Test runs conducted to optimize separation conditions. *All experiments used tartaric acid (TA) as the eluting agent and dipicolinic acid (DPA) as a divalent complexing agent; 4-species mixtures were used for these experiments (Na^+, K^+, Ca^{2+}, Mg^{2+}). Capillary columns were packed with 30 µm diameter Phenomenex weak cation exchange resin, and pressures were between 0.7-1 MPa. Note that all runs include a system peak before any of the target cations appear – this feature is consistent with the literature. (a) Reproducibility tests (i – iv): four species resolved at 10 mM concentration – excellent reproducibility between runs (0.5 µL/min). (b) Effect of [DPA] variability – increased concentrations of DPA reduce divalent retention times (0.5 µL/min). (c) Effect of [TA] variability – shorter retention times are observed for divalent cations at higher [TA] at flow rates of 0.75 µL/min; a similar effect can be achieved using faster flow rates at lower [TA] (in this case 1.0 µL/min). While the run at 1.0 µL/min is shorter than the 0.75 µL/min run by ~10 minutes, the benefits are minimal with respect to peak resolution. (d) Serial dilution from 5 mM to 60 mM demonstrating detection thresholds in the micromolar range based on the signal-to-noise ratio of the 5 mM run. The sensitivity of the system is not as high as expected.*

once the system was assembled. Fused silica column packing was demonstrated to be robust through packing with a helium-driven commercial column packer operating at <13.8 MPa. Separations of cations demonstrated using the breadboard system using a commercial microcolumn for separation. The breadboard allowed for testing/verification of the solvent delivery system, injection valve, and CCD. Separations using custom fused silica ion exchange resin packed columns were tested at lengths of 5 cm, 10 cm, and 20 cm to examine the relative pressure drop as a function of flow rate, size of the packing material, and solvent type.

Separations were demonstrated using a 4-species cation mixture and provided baseline separation in runs up to 60 minutes duration (Figure 3). The sensitivity of the testbed has been determined to be in the high micromolar range. This sensitivity is still 1-2 orders of magnitude distant from that desired for Mars surface science, as sensitivity in the low micromolar range is required to be competitive with previous flight technologies (e.g. MECA-WCL [8]). IC sensitivity can be improved by: (i) providing greater sample injection volumes, (ii) implementation of a more sensitive CCD method, or (iii) implementation of post-column suppression to reduce conductivity associated with the buffer (e.g. TA/DPA). Future directions for this project include investigations into all three of these factors.

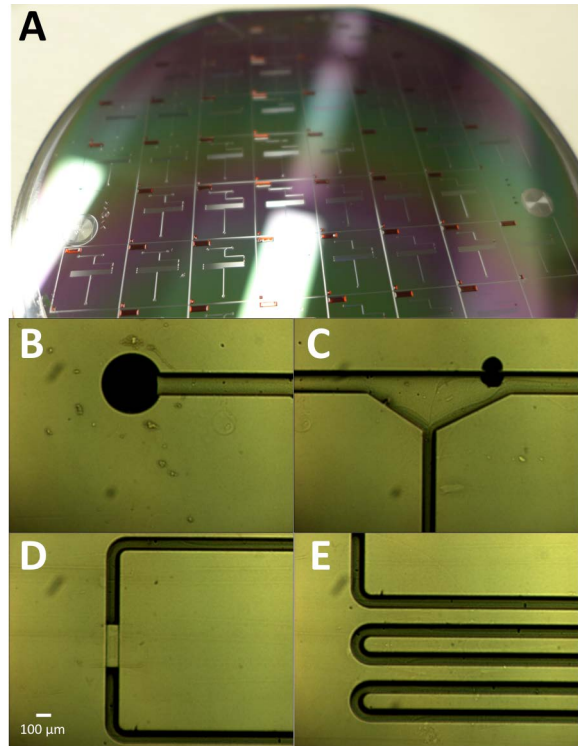

Figure 4. Photograph of the chip. *(A) Post hard bake of 2nd mask. (B) Images of a through-hole chip interconnect, (C) on-chip evaporative tee union, (D) bead filter, and (E) chromatography column channel.*

B. Ion Chromatograph Chip Fabrication and Functional Testing

Figure 4A shows a chip wafer after a hard bake of 2nd mask. Close-up images of some of the chips elements include a through-hole chip interconnect, an on-chip evaporative tee union, a bead filter, and the chromatography column microchannel (Figure 4, panels B-D).

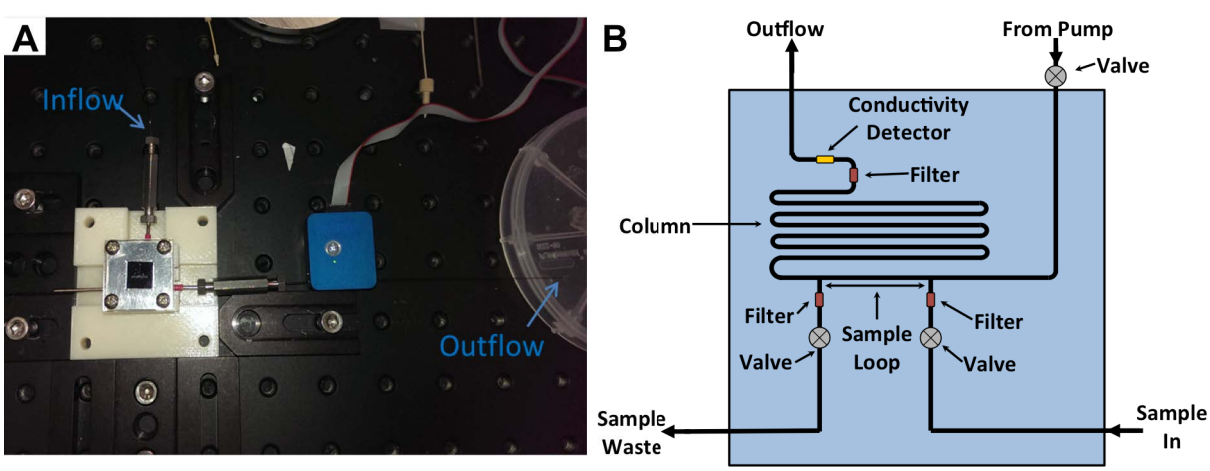

Figure 5: Chip test setup. *(A)Photograqph of the chip test setup (same as the breadboard in Figure 1). The capillary labeled Inflow is the output of the VICI Cheminert 50 nL Injector. It enters the chip through the chip holder. The output (on the right hand side) is converted into a fused silica capillary and passed through the eDAQ ET120 C^4D dectector (blue box) before going out to waste, labeled Outflow. (B) Schematic of the IC chip. The on-chip electrolysis pumps are on the back side of the chip (not shown).*

The current test setup (shown in Figure 5A) has a MEMS 80 µm x 50 µm microchannel packed with Hamilton PRP-X110 7 µm bulk media. A schematic of the chip is shown in Figure 5B. Packing occurs at high pressures, and as observed in Figure 6C, a dense packing is achieved; increasing the surface area to volume. The packed length is about 25 mm. The filter shown in Figures 4D and 6A prevents the chromatography media from escaping. These chips sit in an aluminum chip holder wth VICI 1/16" O.D. x 0.005" I.D tubing pressfit. Standard Valco unions are used to convert to 360 µm O.D. fused silica capillary tubing, as shown in Figure 5. This is then connected to a 20 nL VICI Cheminert Nanoliter Injector on the input side and a eDAQ C^4D ET120 capillary conductivity detector. The chip setup is the same as the breadboard in Figure 1. The injector is connected to a syringe pump containing a 100 µL Hamilton syringe filled with 2 mM of *p*-hydroxybenzoic acid (Sigma-Aldrich). Samples of sodium chloride, phosphate, and sulfate, and potassium bromate and nitrate are being tested. Flow rates between 2 µL/min and 0.5 µL/min are being used, which equate to pressures greater than 5 MPa.

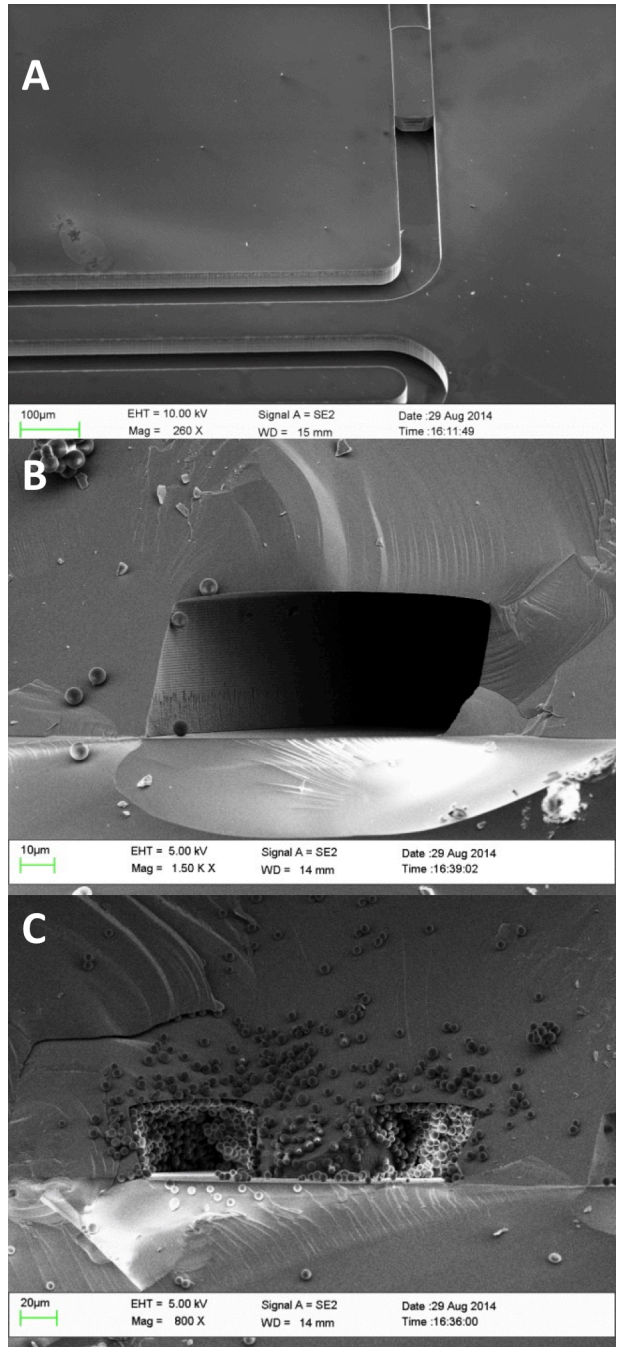

Figure 6. Cross-section of a packed channel. *Electron micrographs of (A) chromatography media filter (3 µm x 80 µm), (B) unpacked microschannel cross-section, and (C) PRP-C18 5 µm packed microchannel cross-section.*

IV. Conclusion

To our knowledge, there have been limited efforts to develop an *in situ* flight instrument focused on the complete integration of a microfluidic lab-on-a-chip IC pressure flow system. The central objective is to design and build a portable lab-on-a-chip IC flow system with nanomolar sensitivity for robotic and crewed missions to provide capability for separation and detection of small inorganic ions in aqueous samples. The project provides a natural evolution from compact microcolumn instruments to even smaller lab-on-a-chip systems with less consumable resource demands (e.g. solvent, buffer). For future deployable systems, the chip can be mounted in a different holder that utilized a 5-mm-thick Ultem cover (see Figure 3 of [2]). As described in [2], chambers, matched up with the pumps on the chip, can be machined into this cover piece to form reservoirs for the sample and solvent. A PDMS gasket provides the seal between the Ultem cover and the chip. Each of the solvent chambers are 10 mm^2 in area and 2 mm tall, creating a reservoir 20 µL in total volume. The sample chamber is only 3.9 mm^2 in area and 1.3 mm tall for a total volume of ~5 µL.

We note that eventual flight deployment will require the use of some form of sample acquisition system [e.g. the SASPAH on MSL, subsurface drill/corer (Honeybee), ultrasonic drill/corer and, perhaps, an inorganic extraction system [e.g. the Automated Sample Processing System [6], the Subcritical Water Extractor [13] both under development for liquid analytical instruments]. This instrument concept in this paper does not completely address the front-end sample handling system that would be required to "feed" the chip system on robotic missions. With human involvement, however, sample handling/ preparation/ introduction is far simpler - filter spin tubes, a

microcentrifuge, water and micropipets are all that would be needed. A human assisted chip-based system could be used for (a) monitoring drinking water quality on the *International Space Station* and during long-duration missions, (b) exploring for organic infall on the Moon or Mars in a pressurized field lab, or (c) organic analysis during far future human mission to asteroids/comets.

Development of the IC instrument will provide the capability to address multiple goals outlined by several NASA Directorates: (i) *in situ* experiment analytical capabilities for missions to Mars, Europa, or Enceladus (Science Mission Directorate, SMD); (ii) evaporitic salt detection can be used to trace past water activity for *in situ* resource utilization (ISRU) missions (Human Exploration and Operations Mission Directorate, HEOMD); (iii) detection of surface composition may identify harmful chemical species (HEOMD); (iv) implementation for water quality monitoring on manned missions (HEOMD).

Acknowledgments

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References

[1]Xie, J., Miao, Y., Shih, J., He, Q., Liu, J., Tai, Y.-C., and Lee, T. D. "An Electrochemical Pumping System for on-Chip Gradient Generation," *Anal. Chem.*, Vol. 76, 2004, No. 13, 2004, pp. 3756-3763.

[2]Xie, J., Miao, Y., Shih, J., Tai, Y.-C., and Lee, T. D., "Microfluidic Platform for Liquid Chromatography-Tandem Mass Spectrometry Analyses ff Complex Peptide Mixtures," *Anal. Chem.*, Vol. 77, No. 21, 2005, 6947-6953.

[3]Darrach, M. et al., "Results from the Vehicle Cabin Atmosphere Monitor: A Miniature Gas Chromatograph/Mass Spectrometer for Trace Contamination Monitoring on the ISS", *SAE Technical Paper Series*, 2008-01-2045, 2008.

[4]Madzunkov S. M. et al. "Recent Developments in Gas Chromatographs and Mass Spectrometers for Crewed and Robotic Space Missions," *43rd International Conference on Environmental Systems,* July 14-18, 2013, Vail, CO, AIAA 2013-3453.

[5]McKay, D. S., Gibson, E. K., Jr., Thomas-Keprta, K. L., Vali, H., Romanek, C. S., Clemett S. J., Chillier, X. D., Maechling, C. R., and Zare, R. N., "Search for Past Life on Mars: Possible Relic Biogenic Activity in Martian Meteorite ALH84001," *Science*, Vol. 273, 1996, pp. 924–930.

[6]Beegle, L., Kirby, J. P., Fisher, A., Hodyss, R., Saltzman, A., Soto, J., Lasnik, J., and Roark, S., "Sample Handling and Processing on Mars for Future Astrobiology Missions," *IEEEAC* paper #1602, 2011.

[7]Boynton, W. V. et al., "Evidence for Calcium Carbonate at the Mars Phoenix Landing Site," *Science*, Vol. 325, No. 5936, 2009, pp. 61-64.

[8]Hecht, M. H. et al., "Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site," *Science*, Vol. 325, 2009, pp. 64-67.

[9]Hecht, M. H., Kounaves, S. P., Quinn, R. C., and West, S. J., et al., "Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site," Science, Vol. 325, No. 5936, 2009, pp. 64-67.

[10]Glavin, D. P., Freissinet, C., Miller, K. E., Eigenbrode, et al., "Evidence for Perchlorates and the Origin of Chlorinated Hydrocarbons Detected by SAM at the Rocknest Aeolian Deposit in Gale Crater," *J. Geophys. Res.*, Vol. 118, 2013, pp. 1955-1973.

[11]Quinn, R. C., Martucci, H. F. H., Miller, S. R., Bryson, C. E., et al., "Perchlorate Radiolysis on Mars and the Origin of Martian Soil Reactivity," *Astrobiology*, Vol. 13, No. 6, 2013, pp. 515-520.

[12]Neagu, C., Jansen, H., Gardeniers, H., and Elwenspoek, M., "The Electrolysis of Water: an Actuation Principle for MEMS with a Big Opportunity." *Mechatronics*, Vol. 10, Issues 4–5, 2000, pp. 571-581.

[13]Aubrey, A. D. et al., "The Urey Instrument: an Advanced In Situ Organic and Oxidant Detector for Mars Exploration," *Astrobiology,* Vol. 8, No. 1, 2008, pp. 1-13.