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Operation of pneumatically-actuated membrane-based microdevices for *in situ* analysis of extraterrestrial organic molecules after prolonged storage and in multiple orientations with respect to Earth's gravitational field

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ABSTRACT

Pneumatically-actuated monolithic membrane microvalves are powerful microfluidic tools that can be integrated into programmable microfluidic architectures (PMAs) for multiple portable chemical analysis applications, including point-of-care (POC) diagnostics, environmental science, space exploration, etc…. However, these systems have not seen wide-scale deployment in industry or spaceflight due in part to (1) a concern that these systems may have a limited shelf-life and (2) a concern that performance depends on specific device orientation in a gravitational field. To address these concerns, we functionally tested a Mars Organic Analyzer microdevice fabricated in 2005 after 10 years of storage under ambient conditions. Using a square wave with a 500 millisecond (ms) actuation pulse width and a 1000 ms period and operating under vacuum at −980 millibar (mbar) from ambient pressure, all pneumatically-actuated valves opened in less than 1 h. The vacuum required to actuate an open valve ranged from −218 to −175 mbar from ambient pressure. The microvalves were then programmed to transfer fluid through the microdevice for flow rate characterization. Fluidic transfer occurred at a flow rate of 122 ± 8 microliters/minute (μL/min) right-side up in Earth's gravitational field and 114 ± 14 μL/min upside down in Earth's gravitational field, indicating likely successful implementation in an orbital microgravity environment. This demonstration that microdevices retain full functionality after over 10 years of storage combined with successful operation in multiple orientations in Earth's gravitational field further validates the value of microdevices based on these microvalves for fluidic manipulation and sample handling in outer planetary missions.

1. Introduction

The search for life beyond Earth has been an ongoing endeavor since the Viking missions' initial search for organic chemical signatures in the Martian regolith in 1976 [1–5]. The onboard thermal volatilization gas chromatography mass spectrometry (TV-GS-MS) system detected chlorinated hydrocarbons and other organic chemicals used to clean the spacecraft prior to launch [1–3]. With promising but ambiguous data from the biological suites [4,5], the results of these missions were interpreted as indicating the absence of life on Mars [1–3]. The only other organic analysis system sent to Mars was also a pyrolysis-based GC–MS system included on the Mars Science Laboratory Sample Analysis at Mars (MSL SAM) instrument suite, which detected only chlorinated hydrocarbons and contaminants resulting from leakage in the *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide (MTBSTFA) derivatization system [6]. The Phoenix lander Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) Wet Chemistry Laboratory (WCL) experiment measured parts-per-thousand (ppth) levels of

Abbreviations: POC, point of care; TV-GS-MS, thermal volatilization gas chromatography mass spectrometry; MSL, Mars Science Laboratory; SAM, sample analysis at Mars; MTBSTFA, *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide; MECA, microscopy electrochemistry and conductivity analyzer; WCL, Wet Chemistry Laboratory; ppth, parts-per-thousand; INMS, ion neutral mass spectrometer; μCE-LIF, microcapillary electrophoresis with laser-induced fluorescence; pptr, parts-per-trillion; MOA, Mars Organic Analyzer; PMA, programmable microfluidic architecture; PCR, polymerase chain reaction; ELISA, enzyme-linked immunosorbent assay; DNA, deoxyribonucleic acid; PDMS, polydimethylsiloxane; G, Earth-g; +G, right-side up directly in line with Earth's gravitational field; −G, upside down directly opposing Earth's gravitational field; aSi, amorphous polysilicon; RIE, reactive-ion etching; LDH, Lee's High Density Interface; LabVIEW, Laboratory Virtual Instrument Engineering Workbench; DO, digital output; cDAQ, compact data acquisition; M_c, size of the active chain between cross-linking points; EOA, enceladus organic analyzer; CAD, computer-aided design

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perchlorates [7,8], which upon heating to 300–600 °C oxidize *in situ* organic matter to chlorinated hydrocarbons and other species detected by both Viking and MSL SAM [9,10]. The combined data from these missions indicate that an alternate method using wet chemical extraction will be necessary for quantitative, compositional characterization of native *in situ* organic molecules on Mars [1,2,11].

Mars is not the only location in the Solar System with the potential to host life. The icy moons of Jupiter (Europa) and Saturn (Enceladus) have also been identified as high priority targets for future exploration missions [12]. Evidence has supported the presence of global subsurface oceans on both Enceladus [13] and Europa [14], and recent data has indicated ongoing hydrothermal activity on Enceladus [15]. Data has also suggested plume activity on Europa [16], which may also be tied to ongoing hydrothermal activity [17,18]. The Cassini Ion Neutral Mass Spectrometer (INMS) detected small organic molecules in a plume emitting from the South pole of Enceladus [19–21] but had neither the mass range nor sensitivity required to address the low level complex organics expected in outer planetary samples. Therefore, a more sensitive and higher resolution technique is required for future analysis of complex real samples. *In situ* quantitative and compositional analysis of organic molecules on the Martian surface or in the plumes or subsurface oceans of Enceladus or Europa would provide relevant, detailed information on formation, habitability, and on-going planetary processes of these celestial bodies and could provide the first evidence of the potential for extant life beyond Earth [22].

Microcapillary electrophoresis with laser-induced fluorescence (μCE-LIF) is a liquid-based technique capable of highly sensitive (sub-parts-per-trillion, pptr), automated, and quantitative compositional analysis of multiple organic compound classes, including amines, amino acids, aldehydes, ketones, carboxylic acids, thiols, and polycyclic aromatic hydrocarbons [23–29]. This lower temperature and liquid-based analysis avoids undesirable decomposition of organics in the presence of high salt and perchlorates [30]. Mars Organic Analyzer (MOA) portable μCE-LIF prototypes have been field tested in the Panoche Valley, CA [31], and in the Atacama Desert, Chile [32], and have conducted high resolution analyses of trace species in multiple relevant planetary analogue samples, including those from the Murchison meteorite [25], hydrothermal sites [24,27], the Saline Valley, and the Rio Tinto [30]. MicroCE-LIF systems based on these prototypes have been proposed for missions to Mars, Enceladus, and Europa [33–37].

The microdevices at the heart of μCE-LIF and MOA technology integrate a μCE separation channel with an automated microfluidic sample processor that uses pneumatically-actuated normally-closed microfabricated monolithic membrane microvalves first developed in 2003 (Fig. 1a) [38]. In order to minimize contamination between mixing cycles, the microdevice utilizes specially designed bus valves in addition to standard (stop) valves [31]. Bus valves, as opposed to standard valves, allow fluid flow through the primary input/output bus channel without actuation, an enabling feature for this application-specific device (Fig. 1b–c). Multiple valves in series operated sequentially form a peristaltic pump, and digital arrays of these microvalves form programmable microfluidic architectures (PMAs) for complex microfluidic processing, including metering, mixing, dilution, reaction, etc… [36].

Miniaturization of microfluidic processing architectures based on normally-closed monolithic membrane-based microvalves has made this technology useful in fields where portability and speed of analysis are imperative [23,36]. Membrane-microvalve processing architectures have been integrated with many chemical analysis techniques, including PCR (polymerase chain reaction) [39], ELISAs (enzyme-linked immunosorbent assays) [40], DNA (deoxyribonucleic acid) sequencing [41,42], and μCE [23,31,32,36]. These multipurpose architectures grew out of developments in single-purpose devices, like that shown in Fig. 2a. This single-purpose device was fabricated in 2005 for μCE-LIF detection of organic molecules in Mars-relevant environments using a portable MOA prototype. While the layout of this device is now outdated [23], the valve technology has not changed significantly, and the device itself presents a unique opportunity to study the longevity of the microvalve technology.

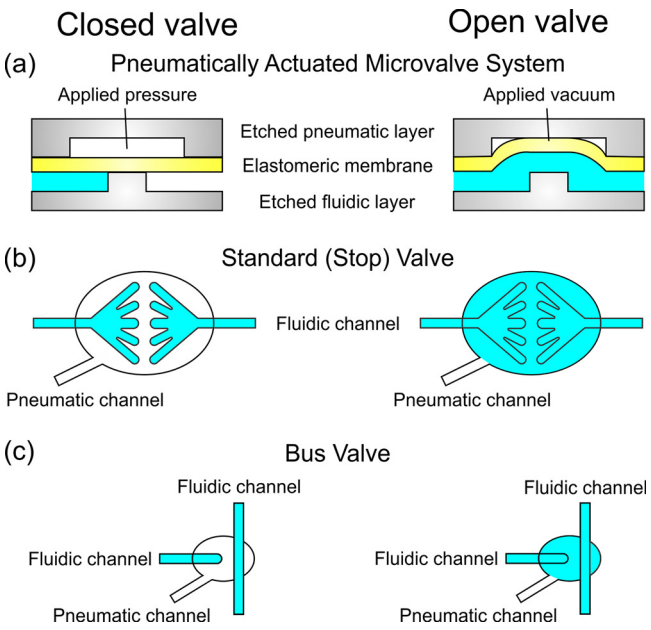

Fig. 1. (a) Cross-section of a pneumatically-actuated, normally closed monolithic membrane microvalve and depiction of (b) a standard (stop) valve and (c) bus valve. Application of a vacuum to the displacement chamber deflects the PDMS membrane layer, opening the valve and allowing fluid flow along the discontinuity. A mild pressure to the chamber deflects the membrane back, forcing the fluid out and to the nearest open fluidic connection.

Despite the power of microfluidic systems and the extensive studies done on the bonding behavior of PDMS to glass [43–45], the deployment of these systems for spaceflight has been limited by misconceptions that (1) microdevices have a limited shelf-life due to irreversible bonding of the PDMS (polydimethylsiloxane) elastomer to the glass substrate after an extended duration of non-operation and (2) fluidic manipulation within the device cannot occur in microgravity environments. These misconceptions persist despite no evidence in the literature to support them. Here, we are the first to assess PDMS microdevice extended shelf life by showing that microvalves in a Mars Organic Analyzer prototype microdevice function after 10 years of storage in ambient conditions. We open all valves on the prototype device after storage and determine the vacuum required to actuate valves. We functionally test the device by using the valves to transfer dye through the microdevice in multiple orientations relative to Earth's gravitational field (G). We define the microdevice orientations to be +G when right-side up and −G when upside down with respect to Earth's gravitational field. We then characterize flow rate at both +G and −G orientations to demonstrate the robustness of PMA-based microdevices for fluidic manipulation in outer planetary missions.

2. Materials and methods

2.1. Microfluidic device fabrication and treatment

The microfluidic device was fabricated in 2005 for automated on-chip fluidic manipulation and electrophoretic separations with the MOA prototype instrument; the fabrication process was previously described in detail [31]. Briefly, amorphous polysilicon (aSi, 1000 Å) was deposited on a 100 millimeter (mm) diameter, 700 micrometer (μm) thick D263 borofloat glass wafer (Precision Glass and Optics, Santa Ana, CA). Photoresist (S1818) was spin-coated and patterned using a chrome mask and MA-6 aligner. The photoresist was developed and the