Production of expendable microfluidic systems by 3D-printing for petroleum processing

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Abstract: *This study introduces a simple protocol to manufacture disposable, 3D-printed microfluidic systems for sample preparation of petroleum. Successful incorporation of solid-phase extraction (SPE) to the microchip was ensured by facile 3D element integration using a 3D-printer. This device was applied to challenging matrices in O&G industry, such as crude oil and oil-brine emulsions. Case studies investigated important limitations of nonsilicon and nonglass microchips, namely, resistance to nonpolar solvents and conservation of sample integrity. 3D-printed µSPE devices enabled fast emulsion breaking and solvent deasphalting of petroleum. Analysis results demonstrated that accurate characterization may be accomplished for most classes of polar compounds, except for asphaltenes. Our approach pioneered the use of nonsilicon and nonglass microfluidic systems to process petrochemical matrices.*

Key-Words: *3D-printing; chromatography; energy & fuel; high-resolution mass spectrometry, sample preparation.*

Introduction: Application of microfluidic systems to oil and gas industry (O&G) are limited to silicon and glass-based devices. Microfluidic devices probed chemical composition, properties of water-oil interface, phase behavior, pressure, volume, and temperature of reservoir fluids. However, prospection of microfluidic platforms for sample preparation of petrochemical is still inexistent. In this context, plain uptake of microfluidic devices in molecular characterization of petroleum, that is, petroleomics, is defied by two constraints: the limited prospection of materials that can withstand extended exposure to nonpolar solvents, like n-heptane and toluene; and arduous integration of functional 3D elements to microfluidic platforms which restrains implementation of successful macroscale methods, including solid-phase extraction (SPE) (ref). In an effort to overcome current restrictions of fabrication approaches for microfluidic devices, we present a simple protocol to manufacture expendable 3D-printed microchip for SPE (µSPE), which was produced with an inexpensive and readily accessible 3D printer and a commercially available substrate. These microchips are easy to fabricate and assemble, even by untrained personnel in resource-limited laboratories. We further demonstrate the potential of 3D-printing as an alternative method for the fabrication of microfluidic systems. The performance of µSPE devices was investigated using two demanding sample preparation applications for petroleomics, namely, demulsification of trace-amounts of synthetic oil-brine emulsion and solvent deasphalting. For the first application, samples were characterized by comprehensive two-dimensional gas chromatography with flame ionization detection (GC×GC-FID) for fingerprinting of maltenes. The second application comprised one of the most important sample processing methods used in all GC-based petroleomics studies, namely, solvent deasphalting. Prospection and characterization of biomarkers are fundamental to organic geochemical investigations, therefore highly sensitive selected ion monitoring (SIM) by gas chromatography/mass spectrometry (GC/MS) was employed for screening analysis of the most common classes of biological markers. Additionally, in untargeted analysis, conservation of sample integrity during sample preparation is fundamental. Hence, unwanted analyte sorption by substrate or coextraction of interfering compounds from device must be avoided. Careful investigation of this parameter was performed by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).

Experimental: Micro devices were produced via 3D-printing using fusing deposition modeling (FDM). Devices were printed in poly(lactic acid) (PLA) by Graber i3 3D printer. The microchip for µSPE was produced by a simple procedure that consists of three steps: 3D-printing of device, dry packing of stationary phase, and irreversible sealing of system. Celite 545, a flux-calcined diatomaceous earth, was used as stationary phase. SPE experiments were performed with a syringe pump and solvents were injected to the microfluidic system at a constant flow rate of 1 mL min^{-1}. For oil-brine emulsion breaking, 60 mg of oil-brine emulsion was weighted to µSPE device; emulsion breaking and elution of maltenes were achieved with 5 mL of *n*-heptane. Phase separation by centrifugation was adopted as reference procedure in accordance to Petrobras internal protocol. Oil phase attained

by emulsion breaking was characterized by GC×GC-FID. For solvent deasphalting, 30 mg of crude oil was weighted into µSPE device; asphaltenes were removed by precipitation in *n*-heptane and the insoluble fraction was retained by sorbent material, during maltene elution with *n*-heptane. Reference procedure consisted of crude oil dissolution in *n*-heptane, followed by phase separation using centrifugation. Maltenes attained by solvent deasphalting were characterized by GC/MS. To perform petroleum analysis using FT-ICR-MS**,** 30 mg of crude oil was weighted to µSPE device; sample was eluted using a mixture of 10:25 (v/v) methanol/toluene. Dissolution of crude oil into the same solvent mixture was adopted as reference method. High-resolution analysis of polar constituents of petroleum was performed by FT-ICR-MS.

Results and discussion: Simple fabrication using 3D-printing and PLA as thermoplastic substrate enabled production of microchips (**Figure 1A**) less expensive than devices produced with glass and silicon. Overall dimensions of microfluidic device are 25 mm × 50 mm of base and 10 mm of height, comprising a cylindrical sample compartment, a rectangular stationary phase container, and two stainless-steel connection ports. Such 3D elements are interlocked by circular channels. The first millifluidic channel connected the sample compartment to sorbent recipient. This channel reduced pneumatic resistance to flow of highly viscous samples, like oil-brine emulsions. Next, microfluidic channel (**Figure 1B**) was positioned between stationary phase compartment and µSPE outlet. The surface of microfluidic elements were profiled. Digital stereoscope images showed microchannels approximately circular in cross section (**Figure 1C**), with an average diameter of 475 ± 20 µm (n = 10). Profilometry data, as shown in **Figure 1E**, also highlighted increased average surface roughness (R_a = 112 µm). Instruments with varying selectivity and sensitivity were used to perform a careful investigation about conservation of sample integrity. Comparison of GC×GC chromatographic profiles and peak integration results of samples attained by centrifugation (reference method) and 3D-printed µSPE device, (**Figure 2**), indicated that both sample preparation approaches are equivalent, as hydrocarbon compositions were not significantly different from each other (*n = 4, p = 0.05)*. Another sample processing method consisted of solvent deasphalting prior to GC/MS analysis. Comparative analysis (**Figure 3**) was attained by evaluating extracted ion chromatograms of important biomarkers-related *m/z* channels. Integration results ascertained that both methods are equivalent, as biomarker compositions were not significantly different from each other (*n = 4, p = 0.05)*. Although investigations using GC-based techniques mitigated hypothesis of alteration of hydrocarbon composition during sample preparation, analysis of traces of polar components of crude oil (~10 wt %, including oxygen-, nitrogen-, and sulfur- containing compounds) by ESI (±) FT-ICR-MS was also necessary to confirm broad applicability of our device for petroleomics and related applications in O&G. The most accurate characterization of crude oil was obtained by combining µSPE method and ESI (–) (**Figure 4**), as a 2-fold increase on signal intensity of petroleum related peaks was observed. Conversely, minor coextraction of heavy oligomers of PLA was only detected by ESI (+) FT-ICR-MS, resulting in a 4-fold reduction on peak intensities.

Conclusions: Successful proof-of-concept studies illustrated the potential of 3D-printed microsystems for sample preparation of petroleum. Tailored µSPE devices enabled reliable processing of trace-amounts of petroleum, yielding a 10-fold reduction in sample preparation time, compared to the reference method. Besides increasing sample throughput, microfluidic processing using such devices bypassed the use of sophisticated instruments for sample processing. Developed 3D-printing method is a compelling alternative to existing fabrication methods of microfluidic devices.

Reference:

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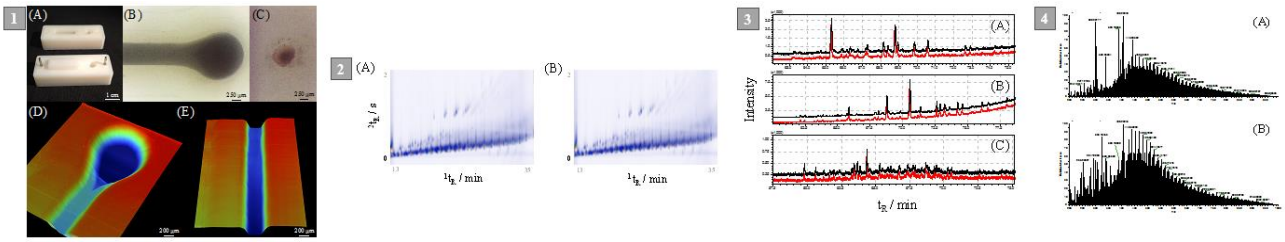

Figure 1. Micro analysis system in shown in (A) showcasing base component (top) and totally assembled device (bottom). Photos by digital stereoscope of microchannels, highlighting half-printed microchannel (B) and cross section view of approximately circular channels (C). Dyes were used to enhance visualization. Profilometry of half-printed base component near µSPE output (D) and microfluidic pathway (E). **Figure 2.** Comparative analysis of volatile and semi-volatile fraction of maltenes by GC×GC-FID. Samples of oil phase were attained by emulsion breaking using centrifugation (A) and 3D-printed micro analysis system (B). **Figure 3.** GC/MS chromatograms of nonpolar fraction sample were obtained by reference protocol (black) and 3D-printed µSPE device (red). Important biomarker-related channels were monitored, including *m/z* 177 (C_{10} demethylated terpanes) (A), *m/z* 191 (tri-, tetra-, and pentacyclic terpanes) (B), and *m/z* 217 (ααα-steranes) (C). Baseline of reference analysis was offset to facilitate chromatogram visualization. **Figure 4.** Negative-ion ESI 7.2 T FT-ICR MS of crude oil extracts. Samples were prepared by dilution of crude oil in 1:1 (v/v) methanol:toluene (A) and using 3D-printed µSPE-based method (B). Average mass resolving power ($m/\Delta m_{50\%}$) of 400,000 at *m/z* 400.