

MICROFRACTIONATION OF GASES SEPARATED BY GAS CHROMATOGRAPHY

G.K. Kurup¹ and Amar S. Basu^{1,2*}

¹Electrical and Computer Engineering Department, ²Biomedical Engineering Department,
Wayne State University, USA

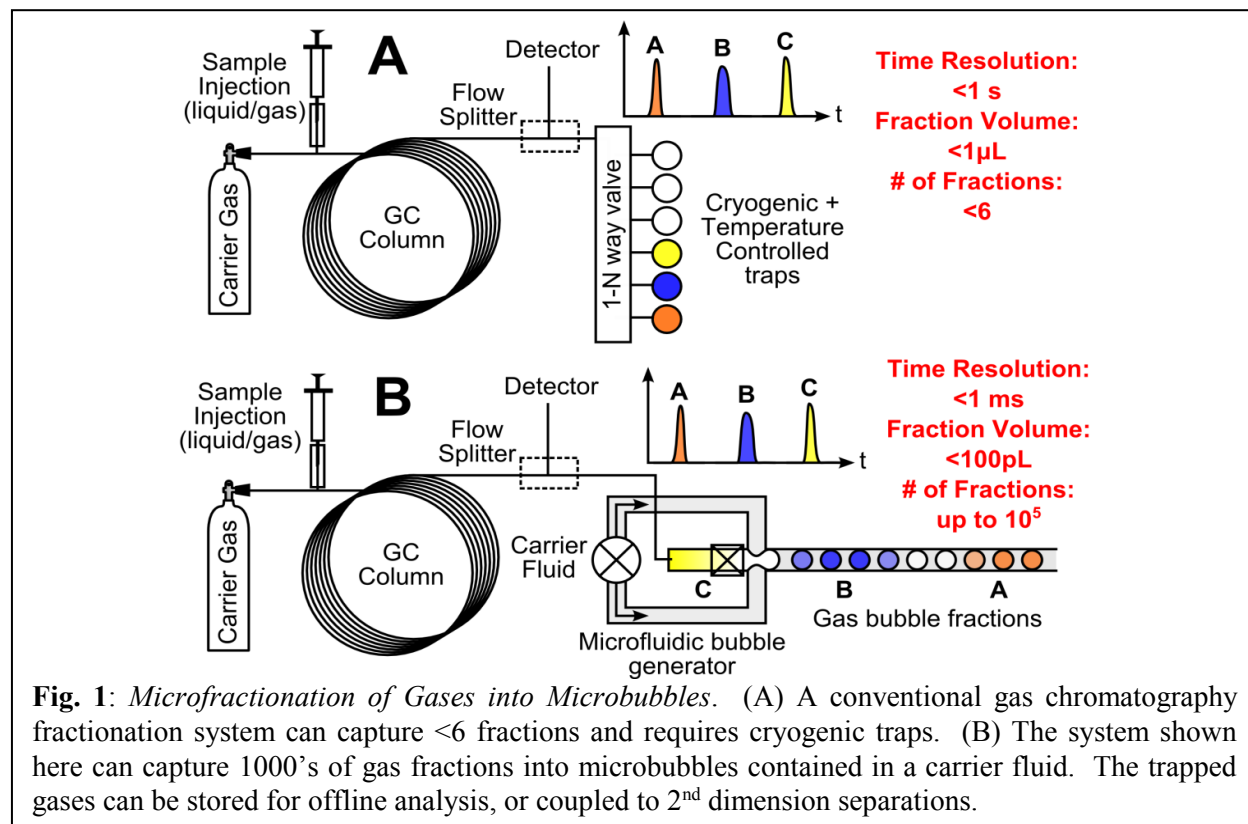
ABSTRACT

Fraction collection is an important step in the analysis of complex samples. While it is commonly used in liquid separations, fraction collection is challenging with gases. This paper demonstrates that samples separated by gas chromatography (GC) can be encapsulated into microbubbles, by coupling a microfluidic bubble generator to a conventional GC. We present 3 results: 1) the encapsulation of the carrier gas (N₂) eluting from the GC into microbubbles, 2) the change in bubble characteristics as different gases elute from the GC, and 3) the condensation of gases in the bubbles, forming 3 phase flow.

KEYWORDS: Gas chromatography, droplet microfluidics, fraction collection, encapsulation

INTRODUCTION

Fraction collection, a critical step in complex sample analysis, refers to the process of separating a complex mixture followed by the collection of the separated components into isolated containers. In liquid chromatography, fraction collection robots are used to pipette each separated peak into distinct vials as they elute from the column. At the microscale, fraction collection can also be accomplished by coupling a microfluidic droplet generator at the outlet of a chromatography column. These devices capture the separated components into a stream of droplets formed at a microscale flow-focusing junction [1]. The technique, referred to as microfractionation in droplets, was demonstrated by our group [2] and DeMello's group [3] in 2009, and by Huck's group [4] in 2010.



Despite its frequent use in liquid separations, fraction collection with gases is much more challenging because gases cannot easily be contained. In gas chromatography (GC), commercial fractionation systems utilize cryogenic traps [5] which rapidly condense separated gases onto a solid support (**Fig. 1A**). Due to the complexity of the traps, these systems can only be scaled to accommodate <6 fractions. Furthermore, the slow time response of the cryogenic valves limits the time resolution to >1s and fraction volumes to >1mL. The limited resolution is a disadvantage in multidimensional and heart-cutting GC.

In this paper, we demonstrate that gases separated by a commercial GC can be captured in bubbles, by coupling a microfluidic bubble generator to the outlet of the GC (**Fig. 1B**). This encapsulation technique can collect thousands of gas fractions at time intervals of <10ms and fraction volumes <1nL, roughly 1000X better than commercial systems. These ‘gas bubble’ fractions can then be stored and analyzed offline.

EXPERIMENTAL

The system (**Fig. 1**) consists of a microfluidic flow-focusing bubble generator [1] coupled to the outlet of a commercial GC (Trimetrics) with a fused silica capillary. Carrier fluid (Oleic acid or Fluorinert FC-40) enter from the two side inlets while the GC eluent enters from the middle inlet. The bubble generator is fabricated in polydimethylsiloxane (PDMS) using soft lithography, and the channels have a 100x100 μm^2 cross section. The GC is operated with an inert stainless steel column (Restek 0.25mm ID), placed in an oven set at 250°C. The chip is placed in a heated platform to provide temperature control in the microchannel. The bubble generator operates at 10s of $\mu\text{L}/\text{min}$, while the GC is operated at 1 mL/min. To accommodate the mismatch, a 100:1 flow splitter is used.

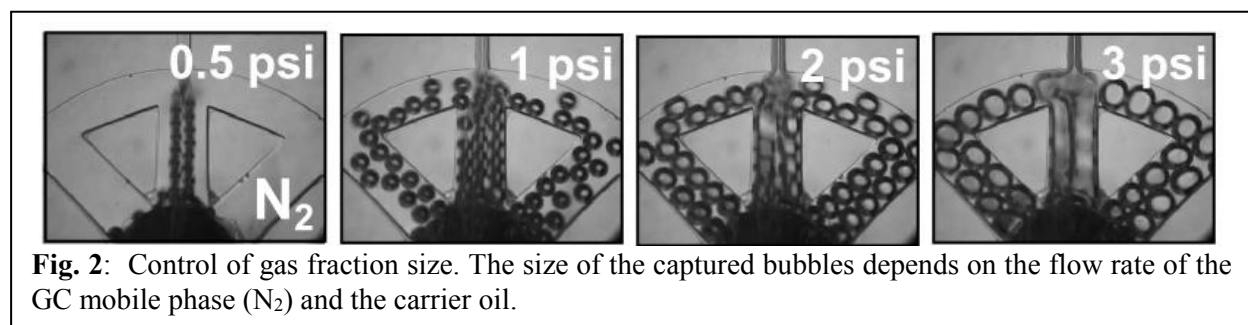


Fig. 2: Control of gas fraction size. The size of the captured bubbles depends on the flow rate of the GC mobile phase (N₂) and the carrier oil.

RESULTS AND DISCUSSION

The experiments demonstrate three findings. The first establishes the feasibility of encapsulating GC eluents into bubbles using the bubble generator. Figure 2 shows the collection of N₂ carrier gas eluting from the GC. The size of the bubble fractions can be proportionally controlled by adjusting the carrier gas pressure between 0.5 and 3 psi, while keeping the carrier liquid constant at 0.5 psi. When the carrier gas pressure is <0.5 psi, bubbles do not form, and if greater than 3 psi, jetting occurs and the bubbles are no longer monodisperse.

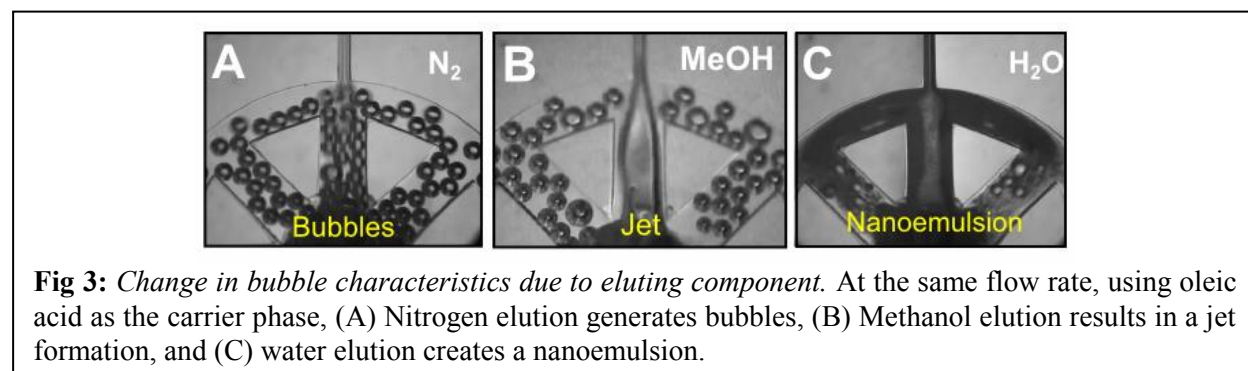


Fig 3: Change in bubble characteristics due to eluting component. At the same flow rate, using oleic acid as the carrier phase, (A) Nitrogen elution generates bubbles, (B) Methanol elution results in a jet formation, and (C) water elution creates a nanoemulsion.

The second experiment (**Fig. 3**) shows how the bubble characteristics changes depending on the sample component eluting. Three gases, nitrogen, methanol vapor, and water vapor, were passed through the heated column and combined with oleic acid in the bubble generator, which remained at room temperature. Nitrogen remains in the gas state and forms monodisperse bubbles. By contrast, methanol vapor condenses to a liquid which is miscible with the carrier fluid, and forms liquid jets. The water vapor, which is immiscible with oleic acid in its liquid state, forms a droplet nanoemulsion. These differences in bubble/drop characteristics can potentially enable label free quantification of eluting gases.

The third experiment shows that separated gases may be maintained in the gas state by holding the chip temperature above the boiling point, or recondensed to liquid droplet form by reducing the chip temperature below the boiling point (**Fig. 4**). Water was vaporized in the GC column, eluted with N₂ carrier gas, and combined with oleic acid in a temperature-controlled bubble generator. The water and oil flow rates were kept low so that plugs form at the junction. When the chip temperature is maintained at 150°C, the water vapor remains in the gas state, forming gas plugs composed of N₂ and H₂O. Conversely, when the chip is held at room temperature, the water vapor condenses into droplets, while the carrier gas forms bubbles. In some cases, the bubbles and droplets combine to form three phase plugs. The condensed droplets can be used for quantification since the drop size is a direct visual measurement of the gas concentration. In addition, gases can be selectively condensed by controlling the chip temperature.

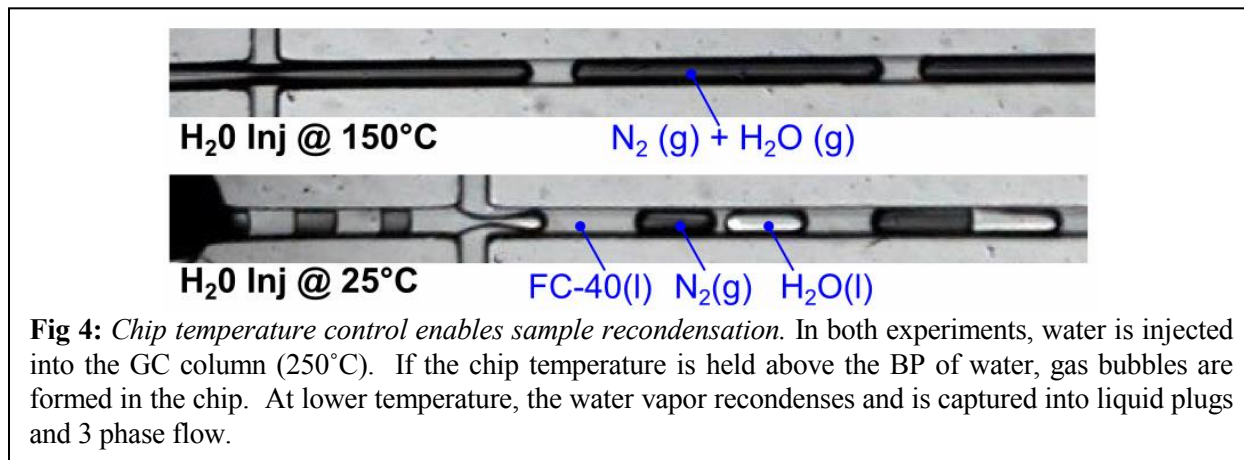


Fig 4: Chip temperature control enables sample recondensation. In both experiments, water is injected into the GC column (250°C). If the chip temperature is held above the BP of water, gas bubbles are formed in the chip. At lower temperature, the water vapor recondenses and is captured into liquid plugs and 3 phase flow.

CONCLUSION

This study has shown the ability to capture chemically separated gases into microbubbles. Looking ahead, the fractionated gases could potentially be coupled to 2D separations or other analyses. The ability to recondense gas components samples is particularly interesting because the recollected samples can be quantified or assayed using conventional liquid phase methods.

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CONTACT: *A.S. Basu; phone: +1-313-577-3990; abasu@eng.wayne.edu