Paper spray mass spectrometry-based method for analysis of droplets in a gravity-driven microfluidic chip

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Analyst. 2014, 139, 1023

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08/03/2014
Introduction

- Droplet-based microfluidics has been emerging as a powerful platform for performing chemical and biological experiments, due to its advantages of low sample consumption, rapid mass/heat transfer, and high throughput.

- Detection methods such as fluorescence, electrochemistry, and Raman spectrometry, have been successfully applied to analyze the contents of droplets.

- Coupling a microdroplet system with MS detection, or the ‘Droplet-MS’ scheme, is a very attractive approach where the advantages of small droplets and MS can be combined together.

- Droplet-MS analysis depends on versatile ionization methods that can serve as the interface between droplet systems and MS.
DMF with MALDI and ESI

Christopher et al., Anal. Chem. 2012, 84, 2955−2960

Mais J. Jebrail et al., Lab Chip. 2011, 11, 3218–3224

Steve et al., Anal. Chem. 2012, 84, 3731−3738

Andrea et al., Lab Chip. 2013, 13, 2533–2540

Wyatt et al., Anal. Chem. 2010, 82, 9932–9937

Aaron et al., Anal. Chem. 2004, 76, 4833-4838
Coupling microfluidic chip with Paper spray

Experimental design

Geometrical Structure of Fabricated Chip
Results and discussion

Schematic illustration of the collection part (a) and images for the typical collection process of one droplet (b–e).
(a) Total ion current (TIC) for eight consecutive droplets. (b) Mass spectrum of the peak indicated by the dashed red line in (a) (c) Relative quantification analysis of droplets containing different concentrations of 4-chlorophenol (10^-5 to 10^-3 M) and 2,4-dichlorophenol (5 × 10^-4 M) internal standard. (d) Typical mass spectrum of a droplet containing 4-chlorophenol and
Flow injection analysis (FIA)-based generation of droplet concentration gradient sequence. (a) The FIA-based generation of concentration gradient system consists of a six-way valve to perform sample zone injection, a flow tube to generate the concentration gradient, and a microfluidic chip to produce the microdroplets. (b) A series of images for droplets with a concentration gradient generated by FIA-droplet systems. (c) The effect of the carrier phase flow rate on concentration profile. (d) The generation of the droplet sequence.
Microdroplet MS for kinetic analysis of on-chip alkaline acetylcholine hydrolysis. (a) Photograph of the microdroplet chip for on-chip reaction. (b) The concentration gradient profile of the droplet used in kinetic analysis. (c) Representative average mass spectra of reaction droplets under different concentrations of KOH. (d) Linear fitting curves obtained according to secondary reaction law. The second-order rate constant, $k$, is determined to be 14.71 M$^{-1}$ s$^{-1}$ from the slope of the fitting line.
Conclusions

This work reported a paper-based integration of absorption and ionization method for the analysis of discrete microfluidic droplets by mass spectrometry.

- This method turned to be a simple, low-cost, easy to implement interface for droplet-MS analysis.

- Microdroplet-MS scheme is a useful platform for the monitoring and analysis of organic-phase chemical/biological reactions.
Future plan

- Coupling microfluidic chip with nanotube spray and various studies at low voltage.

Thank you