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Developing Polymer Microchips for CE-ESI-MS

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Overview

- Polymer microchips for use with CE-ESI-MS were fabricated
- Relative electroosmotic flow (EOF) of glass vs. thermoplastics (bare and covalently modified) was measured using the current monitoring method
- Porous polymer monoliths (PPMs) were fabricated in glass and polymer capillaries and tested for their ability to maintain stable electrospray at low flow rates

Introduction

Microfluidic devices are increasingly of interest for high-throughput assay development due to low sample consumption, high sensitivity, high speed, instrument integration capabilities, and the potential for multiplexing several processes on one chip. Mass spectrometry is a powerful analytical tool as it can indiscriminately determine the molecular mass of a wide range of samples. Molecular mass is a key component of identifying any chemical species. The integration of microchips with electrospray ionization mass spectrometry (ESI-MS) has several advantages over conventional chemical assays for the above-mentioned reasons. To integrate microchips with ESI-MS, electroosmotic flow (EOF) in the channel of the microfluidic device must be high enough to provide a flow rate that will generate a stable Taylor cone. Plastic is an ideal candidate as a substrate for microfluidic devices as it is inexpensive and suitable for mass production. However, due to its hydrophobic nature, plastic microchips have low EOF rates. Surface modification of poly(methyl methacrylate), PMMA, is one approach to modify the EOF properties of a plastic. Another strategy that can be used to facilitate the integration of polymer microchips with mass spectrometry is the use of an emitter that will support the lower flow rate.

Summary of Approach

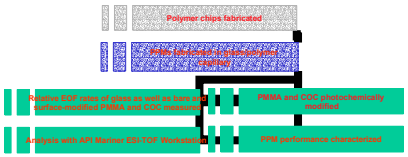
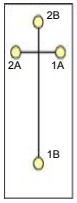


Figure 1. Overall research strategy.

Experimental

Current Monitoring Method [1]:

- Fill chip with buffer1 by applying vacuum
- Empty reservoirs
- Fill 2B, 2A, & 1A with buffer 1 and 1B with buffer 2
- Apply potential
- Monitor current change over time as buffer 1 is replaced with buffer 2



Reservoir	Potential, kV	Solution
1A	Float	2
1B	Ground	1
2A	Float	2
2B	3.00	2
Time	600 sec	

Figure 2. Current monitoring method schematic

PPM Fabrication [2,3]:

- Fused silica capillaries (UV-transparent 360 µm o.d. 75 µm i.d.) were from Polymicro Technologies (Phoenix, AZ) and polymer capillaries PMMA and COC (360 µm o.d. 50 µm i.d. and 360 µm o.d. 180 µm i.d., respectively) were from Paradigm Optics (Vancouver, WA)

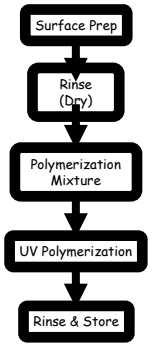


Figure 3. PPM Fabrication schematic

ESI Mass Spectrometry:

- ESI buffers were prepared
  - 50% MeOH, 49% H2O, 1% HOAc
- Standard mixture of equimolar bradykinin and angiotensin (Sigma-Aldrich) prepared in ESI buffer
- Mass spectra of the standard mixture acquired using a pulled-tip ESI emitter and PPM emitter in positive ion mode

Results and Discussion

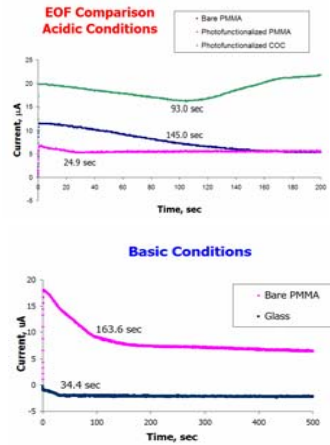


Figure 4. Plots of current vs. time for glass, bare PMMA and surface-modified PMMA and COC in both acidic and basic conditions. The location of the point of inflection indicates the time required to completely exchange buffer in the channel and gives a relative measure of the EOF rate.

Surface (pH)	Flow Rate, nL/min
PMMA (high)	90
Glass (high)	150
Surface (pH)	**Flow Rate, nL/min**
PMMA (low)	90
Photofunctionalized PMMA (low)	280
Photofunctionalized COC (low)	270

Table 1. Results of the current monitoring studies performed on glass, bare PMMA, modified PMMA and modified COC

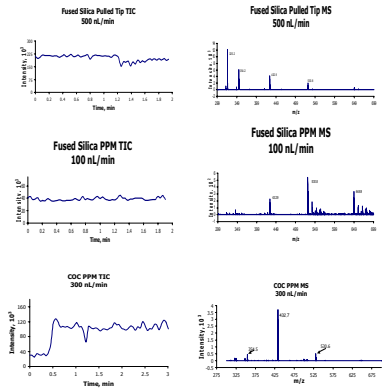


Figure 5. (Left) Total ion chromatograms and (right) ESI mass spectra of standard peptide mixture using fused silica emitter (top) fused silica PPM (middle) and COC PPM (bottom). Flow rates included on spectra.

Summary

- Photofunctionalized PMMA and COC microchips exhibit sufficient EOF rates for chip-MS integration
- PPMs maintain stable electrospray at flow rates lower than that of fused silica pulled tip emitters
- Future work includes fabricating PPMs in PMMA capillary, as well as COC, PMMA, and PDMS microchips and establishing stable spray at electrokinetic flow rates in each device

References

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[3]. Bedair, MF and Oleschuk, RD. **2006** *Anal. Chem.* 78, 4, 1130

Acknowledgements

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