Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy
of

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BSc (Vancouver Island University, 2010)

“Condensed Phase Membrane Introduction Mass Spectrometry”

Department of Chemistry

Monday, December 7, 2015
1:30 P.M.
Elliott Building
Room 161

Supervisory Committee:
Dr. Chris Gill, Department of Chemistry, University of Victoria (Co-Supervisor)
Dr. Tom Fyles, Department of Chemistry, UVic (Co-Supervisor)
Dr. Erik Krogh, Department of Chemistry, UVic (Member)
Dr. Dennis Hore, Department of Chemistry, UVic (Member)
Dr. Roberta Hamme, School of Earth and Ocean Sciences, UVic (Outside Member)

External Examiner:
Dr. Lars Konermann, Department of Chemistry, Western Ontario University

Chair of Oral Examination:
Dr. Pamela Moss, Studies in Policy and Practice, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies
Abstract

Over the last few decades, membrane introduction mass spectrometry (MIMS) has been established as a robust tool for the on-line continuous monitoring of trace gases and volatile organic compounds. However, the range of amenable analytes has been limited by the need for molecules to pervaporate into a gaseous acceptor phase, or high vacuum environment of a mass spectrometer. This thesis expands the range of amenable analytes for MIMS to include larger, less volatile molecules (e.g., 200 to 500 Da), such as pharmaceuticals, persistent organic pollutants, and small biomolecules. This was achieved through the use of a liquid membrane liquid interface. We distinguish the technique from conventional MIMS, which uses a gaseous acceptor phase, by inserting the prefix condensed phase to emphasize the use of a solvent acceptor phase - thus yielding CP-MIMS. An initial flow-cell interface with a methanol acceptor phase was characterized, yielding detection limits for model analytes in ppt to ppb, and analyte response times from 1-10 minutes. The flow cell interface was miniaturized into an immersion style CP-MIMS probe (~2 cm), which allowed for analysis of smaller volume samples and improved membrane washing capabilities. Comparable detection limits were observed for the immersion probe, however, it was noticed that significant analyte depletion was observed for samples under 2 mL. In addition, each of the developed membrane interfaces were observed to suffer from ionization suppression effects from complex samples when paired with ESI. Several strategies for mitigating ionization suppression using CP-MIMS are presented, including the use of a continuously infused internal standard present within the acceptor solvent. The developed CP-MIMS system was challenged with the analysis of naphthenic acids (a complex mixture of aliphatic carboxylic acids) directly in contaminated real-world samples. The method used negative ESI to rapidly screen and mass profile aqueous samples for naphthenic acids (as [M-H]⁻), with sample duty cycles ~ 20 min. However, it was found that Negative ESI did not differentiate hydroxylated and carboxylated analytes, and both species contributed signal to the total naphthenic acid concentration. To increase method specificity for carboxylic acids, barium ion chemistry was used in conjunction with positive ion tandem mass spectrometry. Common product ions were used to quantify carboxylated analytes, while a qualifier ion was used to confirm the functionality. The increased selectivity afforded by the barium ion chemistry was at the cost of a modest increase in detection limits. CP-MIMS has been established as a technique capable of the direct analysis of real-world samples, and shows promise as a rapid screening method for amenable environmental contaminants and/or biomolecules.