



**University
of Victoria**

Graduate Studies

**Notice of the Final Oral Examination
for the Degree of Master of Science**

of

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BSc (Vancouver Island University, 2013)

**“Rapid Quantitative and Qualitative Screening of Naphthenic Acids in
Contaminated Waters Using Condensed Phase Membrane Introduction
Mass Spectrometry”**

Department of Chemistry

Thursday, May 5, 2016

1:30 A.M.

Engineering and Computer Science Building
Room 128

Supervisory Committee:

Dr. Tom Fyles, Department of Chemistry, University of Victoria (Co-Supervisor)

Dr. Erik Krogh, Department of Chemistry, UVic (Co-Supervisor)

Dr. Chris Gill, Department of Chemistry, UVic (Member)

External Examiner:

Dr. Chris Simpson, Environmental and Occupational Health Sciences, University of Washington

Chair of Oral Examination:

Dr. Michael Miller, Associate Vice-President Research, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies

Abstract

Naphthenic acids (NA) are a highly complex mixture of aliphatic carboxylic acids that may contain multiple rings and unsaturated double bonds, and are a subset of the naphthenic acid fraction components (NAFC), which can contain heteroatoms, unsaturations, and aromatic structures. Mono-carboxylated NAs can be classically represented by $C_nH_{2n+z}O_2$ where z is a negative integer representing the hydrogen deficiency. NAs and NAFCs are components of the acid extractable organics (AEO) frequently associated with increased toxicity and observed at elevated concentrations in oil sands process waters (OSPW). Numerous chromatographic and mass spectrometry techniques have recently emerged to probe the composition and concentrations of these components. This thesis reports the use of a capillary hollow fiber polydimethylsiloxane (PDMS) membrane mounted on a probe interface that can be immersed directly into an aqueous sample. A methanol acceptor phase passing through the lumen transports analyte to an electrospray ionization source and a triple quadrupole mass spectrometer. This technique, termed condensed phase membrane introduction mass spectrometry (CPMIMS), allows for rapid screening of m/z profiles and on-line quantification of NAs in complex samples within minutes. This thesis reports parametric studies of several model carboxylic acids and a standard naphthenic acid mixture (Merichem) involving the effect of sample pH on membrane transport and acceptor phase pH on ionization enhancement. Several quantitative strategies are explored including the use of an internal standard in the acceptor phase to correct for ionization suppression and variations in instrument sensitivity, and the use of selected ion monitoring (SIM) experiments to increase analytical sensitivity and potentially target specific NA isomer classes for quantitation. Analytical performance measures such as the linear dynamic range (1-2300 ppb [NA]T as Merichem), sensitivity (~ 1 ppb [NA]T as Merichem detection limit), precision (~ 20 %RSD for replicates of a single OSPW) and accuracy are reported. Quantitative results for various OSPW samples in the ppb to ppm range are reported as equivalents of several surrogates, including 1-pyrenebutyric acid (PyBA), Merichem, and a large volume extract of northern Alberta OSPWs. The variety of quantitation strategies allows results to be compared with several other published methods. Results for three OSPWs provided by Environment Canada are compared to data provided by the group, and on average are -21% different. Results for five OSPWs are compared to data from AXYS Analytical, and on average are -49% different. Applications of CP-MIMS as an *in-situ* monitor of removal efficiencies of NAs on adsorbents and real-time mass profile changes are also presented, along with some interpretation of the resulting high-resolution kinetic data to obtain decay constants. Using the targeted SIM method, adsorption decay can be followed in real-time for various isomer classes within the Merichem mixture, and kinetic data extracted to obtain decay constants for each. CP-MIMS is also used to characterize adsorption behavior for two activated biochars, including % removals for various loadings of each when added to stirred Merichem solutions. Preliminary multi-loading experiments are conducted with one biochar, and the ability of CP-MIMS to characterize adsorbent behavior by constructing adsorption isotherm plots is demonstrated.