**JUSTIN TOM**
**BSc (Chemistry), Dalhousie University, 2011**

**DEPARTMENT OF CHEMISTRY**

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| **TITLE OF THESIS:** | THE INFLUENCE OF CARBON-OXYGEN SURFACE GROUPS AND A WATER-MISCIBLE PRIMARY ALCOHOL ON THE VOLTAMMETRIC DETECTION OF BOVINE HEMOGLOBIN IN AQUEOUS ELECTROLYTE USING CARBON ELECTRODES |
| **TIME/DATE:** | 10:00 am, Monday, October 16, 2017 |
| **PLACE:** | Room 3107, The Mona Campbell Building, 1459 LeMarchant Street |

**EXAMINING COMMITTEE:**

Dr. Sasha Omanovic, Department of Chemical Engineering, McGill University (External Examiner)

Dr. Jan Rainey, Department of Chemistry and Biochemistry & Molecular Biology, Dalhousie University (Reader)

Dr. Mark Stradiotto, Department of Chemistry, Dalhousie University (Reader)

Dr. Peng Zhang, Department of Chemistry, Dalhousie University (Reader)

Dr. Heather Andreas, Department of Chemistry, Dalhousie University (Supervisor)

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| **DEPARTMENTAL REPRESENTATIVE:** | Dr. Erin Johnson, Department of Chemistry, Dalhousie University |
| **CHAIR:** | Dr. Julia M Wright, PhD Defence Panel, Faculty of Graduate Studies |

## ABSTRACT

This thesis focused on the electrochemical reduction of bovine hemoglobin (BHb) using carbon electrode materials. Carbon materials are abundant and affordable, but have variable carbon-oxygen surface functional groups and varying ability to electrochemically detect BHb. To better understand the role of carbon-oxygen surface groups in the electrochemical behavior of BHb, the surface groups were identified using attenuated total reflectance Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and temperature programmed desorption. The identified surface groups were then correlated with BHb electroactivity and key surface groups were further identified through selective carbon surface modifications. The results showed that carbonyl, quinone, and ether surface groups inhibit BHb electroreduction on carbon.

BHb has a slow electron transfer with bare electrodes, showing minimal electrochemical response in aqueous electrolyte. Nafion-bound BHb on carbon surfaces exhibits enhanced response, but until this work, the effects of a water-miscible primary alcohol solvent present in Nafion have been ignored. The presence of an alcohol solvent in Nafion was shown in this thesis to further increase the electrochemical response of BHb. Furthermore, adding a water-miscible primary alcohol to a BHb-containing electrolyte resulted in an increased BHb response.

The mechanisms by which the alcohol increased BHb electroactivity were examined. The water-miscible primary alcohols modified both BHb and the glassy carbon electrode. Ultraviolet-visible absorption and fluorescence data provided evidence of BHb denaturation, likely opening the heme cavity and facilitating the electron transport. Adding alcohol to a BHb-containing electrolyte formed more electroactive BHb films. Additionally, the alcohols changed the carbon-oxygen surface groups on the carbon material, showing a complex relationship where some alcohols removed inhibiting carbon-oxygen surface groups to increase BHb activity, while other alcohols had the opposite effect.

The work presented in this thesis contributed new understandings regarding the electrochemistry of BHb on carbon electrode surfaces and helps avoid spurious conclusions for alcohol-containing BHb films. Understanding carbon-oxygen surface functional groups can be used to intelligently modify carbon electrodes for improving BHb detection. BHb detection was further improved by adding alcohol to the electrolyte, a simple and inexpensive method. The mechanisms by which alcohol influences BHb reactivity was elucidated.

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