ION-SELECTIVE OPTICAL SENSORS FOR THE CHARACTERIZATION OF EUROPA'S OCEANS. P. Sobron[1], M. Bamsey[1], C. Thompson[2], A. Berinstain[1], S. Caron[3], A. Scott[4]. [1]Space Science and Technology, Canadian Space Agency (pablo.sobron@asc-csa.gc.ca). [2]University of Guelph, School of Environmental Science. [3]INO – Institut National d'Optique. [4]COM DEV International Inc.

Introduction: The discovery of satellites in our solar system that generate enough internal energy to support liquid oceans below their icy crusts has started a series of questions related to the search for extraterrestrial life. The young surface age of Europa [1] suggests recent replenishment of the surface with material originating from the potentially habitable oceans underneath [2], thus making Europa's ocean "the highest priority in the outer solar system to explore as a potential habitat for life. Characterization of its internal ocean and ice shell, searching for plumes and evidence of organics are key goals for [the 2010-2020] decade."[3].

Here we describe a novel method for characterizing the subsurface ocean of Europa. Our method uses optical sensors equipped with ion-selective membranes which exhibit a change in an optical property that can be correlated with the concentration of a specific ion [4,5]. We have implemented a system for multi-ion sensing that includes the use of a single spectrometer in tandem with a fiber optic multiplexer that is capable of reading a suite of attached optrodes, each of them dedicated to a unique ion. In this abstract we report the experimental characterization of a potassium optrode as a template for ion-selective optrodes and their application to the characterization of Europa's oceans. Additional details about the prototype multi-ion instrument will be discussed at the conference.

Optrode technology for measuring the abundance of ionic species in aqueous solutions: Conceptually, optrodes are devices incorporating a light source and an optical transducer often placed on the end of an optical fiber and positioned in the environment of interest. The optical fiber carries light from a light source to the optical transducer where it interacts and is then carried to a spectrometer for analysis. For our particular application, highly plasticized polymer membranes incorporating an ionophore, chromoionophore and ionic sites form the basis of a 'bulk' optrode type instrument. Upon immersion into an aqueous solution, ions of the analyte of interest enter the membrane while hydrogen ions are concurrently extracted which result in a change to the ratio of complexed versus uncomplexed chromoionophores and thus an optical change to the film (e.g. change in absorption). With knowledge of solution pH, the absorbance of the membrane can be directly related to the ionic activity of the analyte (Figure 1).

It can be argued that optrodes can provide the following benefits over other proposed ion-specific monitoring methods (e.g., ion-selective electrodes and ion-selective field effect transistors):

- Decreased mass and ease in miniaturization
- Robustness (solid-state, no-moving parts)
- Immunity to electromagnetic interference
- Decreased/no analyte consumption and potential for greater sensitivity
- No requirement for an additional reference element
- Reduced degradation in aggressive analytes
- The optical signal can provide multi-wavelength/ratiometric information
- Improved detection limit
- Reduced cost

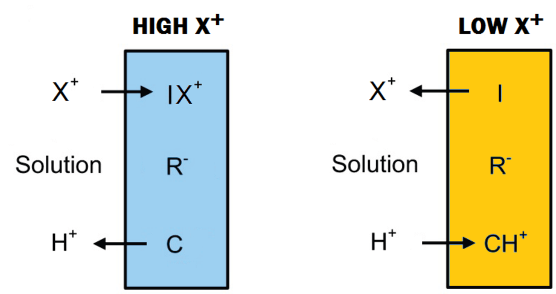

Figure 1. Simplified schematic of functioning of a bulk optrode membrane for analyte X^+, incorporating an ionophore (I) for X^+, chromoionophore (C) for H+ and anionic sites (R^-).

Key specifications for our instrument are:

- Measuring range: measuring ranges for our application typically cover 2-4 orders of magnitude depending on the particular optrode (membrane composition, ionophore-ion stoichiometries, ion charges etc.). This measuring range can be tailored by modification of the ion-selective membrane recipe to provide higher response near the expected analyte activity.
- Lifetime: all ion-selective sensors have a finite lifetime. Bulk optrode lifetime is generally related to either component leaching from the membrane or photobleaching of the chromoionophore. Optrodes developed as part of this work have demonstrated lifetimes on the order of tens of hours when continuously immersed [6]. These lifetimes can potentially be extended by removing the optrode from the solution of interest when measurements are not being conducted.

- Response time: the relatively thin nature of bulk optrode films implies that they respond quite rapidly to changing sample solution conditions. For a typical optrode film thickness of 4 μm a 95% response time of approximately 20 seconds is predicted and response times on the order of 1-2 minutes demonstrated experimentally.

Instrument layout: The developed multi-ion, ion-selective optrode system used in this work (Figure 2) is made up of several individual components including: light source, filter, the optrode itself which is made up of a bifurcated optical fibre, the ion-selective film and support/holder, optical multiplexer, spectrometer and a data acquisition and control system.

Case-study: Experimental results of a potassium optrode: Figure 3 presents measured absorption spectra of a potassium optrode in pH buffer at pH 6.0 at various potassium concentrations. The potassium selective film is blue when exposed to low potassium activity (fully complexed chromoionophore) and is purple in high potassium activity (fully uncomplexed chromoionophore). The two colors, or absorption spectra, represented the two extremes in optical response of the dynamic range of the sensor. All the measureable potassium activities fall between these two extremes and are represented by the other spectra presented in Figure 3. Changes to the active ion-selective membrane concentrations (ionophore, chromoionophore, ionic sites) would result in a film that would produce similar absorption spectra but for a different range of potassium activities/concentrations. Further, ion-selective optrode membranes can be developed utilizing a similar bulk optrode design methodology for different ions of interest including those of primary interest in an initial characterization of Europa's oceans.

Future developments and implications for solar system exploration:

It has been suggested that life may be present in Europa's subsurface liquid reservoirs which may be depleted in redox-pairs [7]. The presence of sodium chloride, sodium bicarbonate, potassium-bearing salts, and salt-rich ice in Enceladus' plume materials indicate the presence of liquid water as a means to producing these salty plume particles [8]. This hypothesis is also consistent with the discovery of ammonia in the plume. Titan's surface is populated with lakes filled with liquid hydrocarbons, including methane and ethane [9]; Titan's lakes could host prebiotic-like chemistry.

We are currently developing instrumental and analytic approaches to demonstrate the feasibility of measurements of the abundance of multiple ions in solutions analogue to Europa, Enceladus, and Titan and at environmental conditions relevant to these moons.

Future landed missions to these moons may benefit from our ion-selective sensing technology in that it will enable characterizing the ionic composition of the liquid reservoirs and the organic content in these moons; our sensors may thus help shed light on outstanding questions related to the presence of life elsewhere in our solar system.

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References: [1] J. R. Spencer et al., in Saturn from Cassini-Huygens, (2009. [2] M. Y. Zolotov et al., JGR. 106, 32815 (2001). [3] Planetary Science Decadal Survey, (2011). [4] M. Bamsey et al., Sensors 12, 13349-13392 (2012). [5] Bakker, E. et al., Chem. Rev. 97, 3083-3132 (1997) [6] M. Bamsey et al., Anal. Chim. Acta, 737, 72-82. (2012). [7] E. J. Gaidos et al., Science 284, 1631 (1999). [8] F. Postberg et al., Nature 474, 620 (2011). [9] D. Cordier, et al., PSS 61, 99–107.

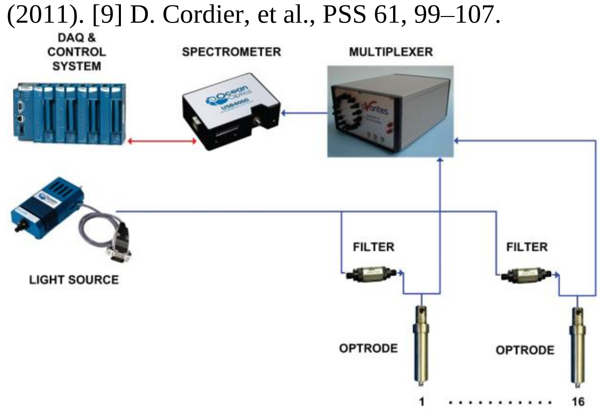

Figure 2. Schematic of a potential architecture of a multi-ion selective optrode sensing system.

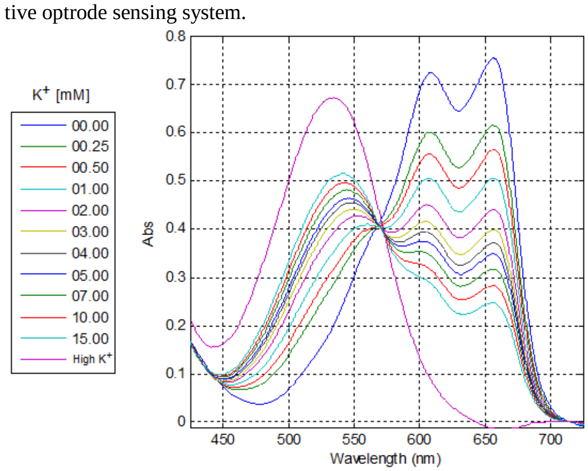

Figure 3. Sample absorption spectra of a potassium optrode in pH 6.00 buffer at various potassium concentration.