

Vapochromic Detection and Identification of Important Analytes

Principal Investigators:

Kent Mann Prof. of Chemistry (UM) (612) 625.3563 krmann@umn.edu
Brian Marquardt Senior Principal Engineer (UW) (206) 543.6054 marquardt@apl.washington.edu

Research Personnel:

Executive Summary: This proposal involves a collaborative effort between analytical chemist Dr. Brian Marquardt at the Applied Physics Laboratory (APL) of the University of Washington and physical inorganic chemist Professor Kent Mann at the University of Minnesota to engineer novel and robust optical vapochromic sensor systems. The vapochromic compounds of interest are highly porous crystalline metal complexes with strong absorption and emission i.e. high quantum efficiency. In these sensing compounds, analyte molecules perturb the chromophore and induce reversible shifts and/or intensity changes in the emission/absorption spectrum of the chromophore. Thus, these vapochromic sensors are attractive as sensing elements for reversible, small, low power, fast, robust, and inexpensive optical sensors. This proposed work will continue to: 1) investigate the spectral of known and new compounds to specific analytes; 2) test the efficacy of mathematical modeling and calibration of sensors made from these various vapochromic compounds for qualitative sensing of desired chemical species in gas and dissolved phases; and 3) investigate how the vapochromic compounds can best be formed into chemically sensitive layers and optimized for reliable use in process environments. In addition a focused research effort will be started to design, develop, and evaluate a process ready oxygen sensor for monitoring the oxygen concentration at volcanic sites at the bottom of Pacific Ocean.

Goals/Objectives: Our primary goal is the development and evaluation of vapochromic compounds for the detection and quantification of process gas and vapor systems. We will continue to design, synthesize and study new compounds with high quantum efficiency, that exhibit shifts in visible absorption or emission spectra upon exposure to analytes of environmental or industrial relevance.

Additional research will be undertaken to:

- Develop novel membrane chemistry for deposition of vapochromic sensing compounds
- Improve sensor bonding to probe interfaces
- Increase robustness from chemically incompatible solvents.

Furthermore during the 2015-16 budget cycle, we will continue our development and design of vapochromic sensors for dissolved and gas phase oxygen and will pursue routes for the detection of carbon dioxide and hydrogen sulfide. As a final goal, we will develop a process ready oxygen sensor with the ultimate objective of deploying it to measure oxygen concentrations at deep ocean volcanic sites in the Pacific Ocean later this year.

Budget for 2015-2016: \$28,800 - Funds would support a graduate student and research staff to support the analytical work and supplies/travel needs for the research.

Background: Vapochromic compounds undergo a reversible color change when exposed to analyte gases or vapors. This effect makes such compounds attractive candidates for sensing a variety of low molecular weight analytes due to their insolubility, chemical stability, sensitivity, selectivity, reversibility, broad dynamic range and rapid response characteristics. Vapochromic compounds can form suitable sensing elements for fiber optic-based devices with applications in process control, air quality monitoring, alkane detection and ground water monitoring.

We have designed strongly absorbing transition metal-complex dyes, with nano-porous crystalline structures, which allow easy diffusion of analyte molecules to chromophores in the crystalline lattice. Thus, exposure to specific analytes results in fast, reversible changes in the color or intensity of luminescence and leads to fast response times. The changes in color and intensity can be effectively modeled using multivariate techniques to produce calibration curves for quantification of a desired analyte.

We have previously demonstrated the applicability of these vapochromic compounds as chemical sensing elements in a three channel “vapochromic nose” to qualitatively identify simple organic solvent molecules in the gas phase. A similar array was also used to accurately determine relative humidity in air in the range 5-95%. More recently, ammonia and moisture were simultaneously measured with a prototype single-channel vapochromic sensing system.

Significant Progress to Date:

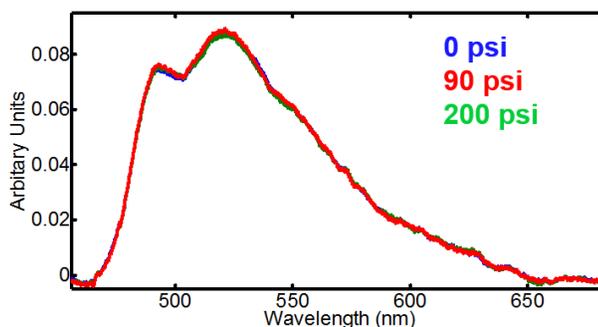
Fiber optic oxygen sensor update. During the last few years, substantial effort has been put forth to design and optimize a fiber optic oxygen sensor. Sensors were fabricated and calibrated using partial least squares analysis, allowing the detection of dissolved oxygen from 2 – 1240 $\mu\text{mol/L}$ in liquids, as well as 0 – 100% in the gas phase. The 95% equilibrium response time was on average 4 seconds in the liquid phase and 150 msec in the gas phase. Tests were conducted to evaluate the photostability of the sensing compound, finding a 0.12% / day reduction in emission intensity over 12 weeks of continuous illumination at 405nm, an extremely low rate of photo-decomposition (lower than that of the LED used for illumination). These sensors have successfully sensed dissolved oxygen in complex mixtures such as blood, seawater and fermenter media. Recently the use of these oxygen sensors has been extended to common organic solvents. This was achieved by encapsulating the delicate sensing material in a gas permeable matrix that freely pass gasses and excluded organic solvent molecules. Because of the success of our preliminary protection methods, further effort is being put forth to optimize current protection capabilities and develop improved ones.

Development of a Process Ready Oxygen Sensor. Monitoring dissolved oxygen concentrations in high-pressure process environments remains a significant hurdle for current oxygen sensing technology. To assess the efficacy our oxygen sensor in high pressure systems, a collaboration with Dr Giora Proskurowski from Department of Oceanography at the University of Washington was initiated to package and deploy our oxygen sensor on a deep ocean ROV to study the unique environment surrounding volcanic sites in the Pacific Ocean (>3000m depth and >4000 psi). An important component of the work will be to design and develop a small and low power high-pressure deep ocean deployable oxygen sensor that will fit in a 2in ID x 5in titanium housing. This is a non-trivial task because the optical source, filters, DAQ, and small spectrometer will all need to fit into this small housing. Obtaining a small spectrometer with the specifications required to measure the response of the oxygen sensor with sufficient

sensitivity and accuracy will be the most challenging part of packaging the sensor into the high-pressure housing. Over the last year we have evaluated the performance of

numerous small spectrometers and determined that a custom-built Qmini spectrometer meets the demanding specification of this application. Table 1 shows the nearly identical models produced by an oxygen sensor calibrated in the gas phase using the gold standard spectrometer and the custom-built Qmini spectrometer.

Establishing a high-pressure optical interface on the probe head is another challenge. To provide a high-pressure optical seal, the oxygen sensor will use the Raman ballprobe technology. This Raman ballprobe has already been used as an optical interface for a deep ocean Raman instrument that was capable of monitoring turbulent and opaque samples at high temperature and pressures. Thus, the ballprobe will provide a high-pressure barrier to protect the electronics and optics in the housing and a standardized optical interface between the oxygen sensing membrane and optics. A prototype of the high-pressure process ready oxygen sensor has been built (Photo 1) and the tests to evaluate its performance in high-pressure environments have been completed. Figure 1 shows that the oxygen sensor is unaffected by changes in water pressure from 0 to 200 psi.



In the next year, we will continue to refine our current prototype with the goal of deploying it this summer to monitor the environment surrounding hydrothermal vents. A description of this project and our preliminary results will be presented at the upcoming CPAC meeting.

Synthesis of new oxygen sensing compounds.

We have recently discovered that solutions of very emissive platinum compounds that contain the $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_8)^{4-}$ anion are also very sensitive to oxygen with a K_{sv} in excess of 200! This is more than a factor of 2 larger than our best previous sensor compound. We will conduct research to incorporate this anion into the usual type of porous vapochromic crystal lattice to fully utilize its high response and sensitivity. We believe that sensors based on this compound could be very useful for extremely low oxygen level sensing.

Synthesis of new vapochromic carbon dioxide sensors. We will continue to investigate two different carbon dioxide sensing mechanisms. In the first system, the luminescent core of $[\text{Ir}(\text{ppy})_2\text{L}_2]^n$ ($\text{ppy} = 2\text{-phenylpyridine}$) is paired with hydrazino ancillary ligands ($\text{L} = \text{N}_2\text{H}_4$). Bubbling CO_2 through a sample of $[\text{Ir}(\text{ppy})_2(\text{N}_2\text{H}_4)_2]\text{OTf}$ in DMSO results in a red shift of the $[\text{Ir}(\text{ppy})_2(\text{N}_2\text{H}_4)_2]\text{OTf}$ emission λ_{max} accompanied by a change in peak shape during exposure to CO_2 to produce $\text{Ir}(\text{ppy})_2(\text{H}_2\text{NNHCOO})$, due to carbamate formation. This work demonstrates the

utility of coordinated hydrazine as a suitable receptor site for optical CO₂ detection schemes. In the second system, the inclusion of CO₂ in the crystal lattice of Ru(diphenylphen)₃(B(C₆F₅)₄)₂ causes a reversible shift in the emission spectrum of the complex, even in the presence of oxygen.

Proposed Research:

1. Gas phase oxygen detection, quantification and validation of oxygen sensing with a NeSSI Gas/Vapor System. New oxygen sensing compounds and newly developed sensor interfaces for gas phase oxygen sensing applications are currently under evaluation. NeSSI based experiments with mixed gas calibrations standards are being employed to determine sensor stability, sensitivity and reproducibility. Recent improvements to this system include added capabilities to analyze solid and powder samples reproducibly.

2. Extending the chemical stability of the oxygen sensor in common organic solvent. Efforts to evaluate the fiber optic oxygen sensor for detection of dissolved oxygen in common solvents will continue. We will further refine the vapochromic/optical interface to improve the chemical and physical stability in common solvents of industrial relevance.

3. Development of a Process Ready Oxygen Sensor. In the coming months, the prototype high-pressure process ready oxygen sensor will be evaluated in the lab and in simulated high-pressure environments. A description of this project and our preliminary results will be presented at the upcoming CPAC meeting.

4. Synthesis and evaluation of new vapochromic sensing compounds for oxygen and carbon dioxide. New [Ru(phen)₃] salts, as well as salts using a variety of cations (including various metal centers) and anions (including tfpb) are being developed. 19 historic vapochromic compounds in total, including compounds with sensitivity to multiple gases have been acquired / synthesized and are currently under investigation for their potential in sensor applications. The new platinum anion will also be included in these synthetic chemistry investigations. Compounds are also being synthesized specifically for the detection and quantification of carbon dioxide. A number of potential new carbon dioxide sensors will be evaluated via an improved gas mixing system (aforementioned).

Sponsor Collaborators:

Dr. Nelson Lytle-UOP, Patrick Killough-Shell, Paul Weider-Shell

P. I. CVs:**Kent R. Mann – Department of Chemistry – 612-625-3563**Education and Training

University of Illinois, Champaign-Urbana	Chemistry	B. A. 1973
California Institute of Technology	Inorganic Chemistry	Ph. D. 1976
California Institute of Technology	NSF Energy Fellow	1976 - 1977

Research and Professional Experience:

Professor of Chemistry, University of Minnesota, 1990-present

Associate Professor of Chemistry, University of Minnesota, 1984-1988

Assistant Professor of Chemistry, University of Minnesota, 1978-1984

Ten Related Publications:

1. Kyle R. Schwartz, Kent R. Mann, “Optical Response of a Cyclometalated Iridium(III) Hydrazino Complex to Carbon Dioxide: Generation of a Strongly Luminescent Iridium(III) Carbazate” *Inorganic Chemistry* 50, 12477-12485 (2011).
2. Conor S. Smith, Charles W. Branham, Brian J. Marquardt, Kent R. Mann, “Oxygen Gas Sensing by Luminescence Quenching in Crystals of Cu(xantphos)(phen)⁺ Complexes.” *Journal of the American Chemical Society*, 132, 14079-14085 (2010).
3. Julia E. Rossini, Adam S. Huss, Jon N. Bohnsack, David A. Blank, Kent R. Mann, Wayne L. Gladfelter, “Binding and static quenching behavior of a terthiophene carboxylate on monodispersed zinc oxide nanocrystals.” *Journal of Physical Chemistry C*, 115, 11-17 (2011).
4. Adam S. Huss, Julia E. Rossini, Darren J. Ceckanowicz, Jon N. Bohnsack, Kent R. Mann, Wayne L. Gladfelter, David A. Blank, “Photoinitiated electron transfer dynamics of a terthiophene carboxylate on monodispersed zinc oxide nanocrystals.” *Journal of Physical Chemistry C*, 115, 2-10 (2011).
5. McGee, Kari A.; Veltkamp, David J.; Marquardt, Brian J.; Mann, Kent R. “Porous Crystalline Ruthenium Complexes Are Oxygen Sensors.” *Journal of the American Chemical Society* (2007), 129(49), 15092-15093.
6. Kari A. McGee and Kent R. Mann, “Inefficient crystal packing in chiral [Ru(phen)₃](PF₆)₂ enables oxygen molecule quenching of the solid-state MLCT emission.” *Journal of the American Chemical Society*, 131, 1896-1902 (2009).
7. Void Space Containing Crystalline Cu(I) Phenanthroline Complexes As Molecular Oxygen Sensors. Smith, Conor S.; Mann, Kent R., *Chemistry of Materials* (2009), 21(21), 5042-5049.
8. A Platinum(II) Extended Linear Chain Material That Selectively Uptakes Benzene. Drew, Steven M. , Smith, Lisa I., McGee, K. A., Mann, Kent R., *Chemistry of Materials* (2009), 21, 3117-3124.

9. Concurrent sensing of benzene and oxygen by a crystalline salt of tris(5,6-dimethyl-1,10-phenanthroline)ruthenium(II). McGee, Kari A.; Marquardt, Brian J.; Mann, Kent R. *Inorganic Chemistry* (Washington, DC, United States) (2008), 47(20), 9143-9145.
10. Carbon nanotube-coated surface acoustic wave sensor for carbon dioxide sensing. Sivaramakrishnan, S.; Rajamani, R.; Smith, C. S.; McGee, K. A.; Mann, K. R.; Yamashita, N. *Sensors and Actuators, B: Chemical* (2008), B132(1), 296-304.

Synergistic Activities

Review Panels: Program reviewer of the Chemistry Department at Occidental College (2004), Department of Energy "Review of the Brookhaven National Laboratory Chemistry Department" (1996), Department of Energy "Peer Review Panel for Solar Photochemistry" (1993).

Collaborators (past 4 years):

David Blank (University of Minnesota), Wayne Gladfelter (University of Minnesota), Steven Drew (Carleton College), Daniel Freedman (State University of New York, New Paltz), C. Daniel Frisbie (University of Minnesota), Larry Miller (retired), William Smyrl (University of Minnesota), Brian Marquardt (University of Washington), Ted Pappenfus (University of Minnesota), Daron Janzen (Saint Catherine University).

Graduate and Postdoctoral Advisors:

Harry B. Gray and George S. Hammond (Ph.D. thesis advisors) California Institute of Technology and Harry B. Gray (postdoctoral advisor) California Institute of Technology

Publications, Seminars, Dissertations Directed: 150 publications, 41 since 2001 (not including In Press and submitted); 65 Invited seminars; 21 Contributed papers; 20 Ph. D. 's; 4 M. S.

Former Graduate and Post-Graduate Advisees during the last five years (Current Location):

Ted Pappenfus (University of Minnesota), Lisa Smith (North Hennepin Community College), Daron Janzen, (Saint Catherine University), Jason Burney (Nalco), Xiaoli Wang (industry), Michael Burand (Carleton College), Kari McGee (3M company), Conor Smith (United Science Corp.), Raghu Chitta (University of Houston).

Overall: 40 graduate students; 9 postdoctoral associates

Current: 4 Ph.D candidates and 1 postdoctoral associate

Biographical Sketch

NAME Brian J. Marquardt, Ph.D. Applied Physics Laboratory University of Washington Seattle, WA 98105	POSITION TITLE Senior Research Engineer Research Professor, Electrical Engineering
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Education/Training

INSTITUTION AND LOCATION	FIELD OF STUDY	DEGREE	YEARS
Ripon College	Chemistry	A.B.	1993
University of South Carolina	Analytical Chemistry	Ph.D.	1997
University of Washington	Analytical Chemistry	POST-DOC	1998-1999

Appointments

2011-present Interim Director CPAC
 2009-present Research Prof., Univ. of WA, Electrical Engineering
 2007-present Senior Res. Engineer, University of Washington, Applied Physics Lab
 2000-2006 Senior Research Scientist, University of Washington, CPAC
 1998-1999 Post-doc, University of Washington, CPAC
 1993-1997 Research Assistant, University of South Carolina

Publications – 10 Most Recent

1. T. Dearing, W. Thompson, C. Rechsteiner and B.J. Marquardt, "Characterization of Crude Oil Products Using the Data Fusion of Process Raman, IR and NMR Spectra," *Appl. Spectrosc.*, 65(2), 181-186, **2011**.
2. E. Gunn, L. Wong, C.W. Branham, B. Marquardt and B. Kahr, "Extinction mapping of polycrystalline patterns," *CrystEngComm*, 13(4), 1123-1126, **2011**.
3. C. Smith, C. Branham, B. Marquardt, K. Mann, "Oxygen Gas Sensing by Luminescence Quenching with Crystals of Cu(xantphos)(phen)+ Complexes", *JACS*, 132(40), 14079-14085, **2010**.
4. K.A. McGee, B.J. Marquardt and K.R. Mann, "Concurrent Sensing of Benzene and Oxygen by a Crystalline Salt of Tris(5,6-dimethyl-1,10 phenanthroline) ruthenium(II)", *Inorg. Chem.*, **47**, 9143, **2008**.
5. N. K. Afseth, B.J. Marquardt, and J.P. Wold, "A Chromatographic Approach for Fluorescence Rejection in Raman Analysis," *Appl. Spectrosc.*, **61(12)**, 1283, **2007**.
6. K. R. Mann, J. R. Burney, K. A. McGee, B. J. Marquardt, "Crystalline Oxygen Sensors that Contain Ruthenium Complexes," *JACS*, **129(49)**, 15092, **2007**.
7. B. J. Marquardt, "Application of On-Line Raman Spectroscopy to Characterize and Optimize a Continuous Microreactor," (Eds) Koch, M.V.; VandenBussche, K.M.; and Chrisman, R.W., *Micro Instrumentation for High Throughput Experimentation and Process Intensification – a Tool for PAT*, Wiley-VCH, Chapter 9.2, **2007**.
8. B. K. Dable, B. J. Marquardt,* "Characterization and Quantitation of a Tertiary Mixture of Salts by Raman Spectroscopy in Simulated Hydrothermal Vent Fluid," *Appl. Spectrosc.*, **60(7)**, 773, **2006**.
9. N. K. Afseth, V.H. Segtnan, B.J. Marquardt, and J.P. Wold, "Raman and Near Infrared Spectroscopy for Quantification of Fat Composition in a Complex Food Model System," *Appl. Spectrosc.*, **59(11)**, 1324, **2005**.

10. B. K. Dable, K. S. Booksh, B. J. Marquardt*, "Rapid Multivariate Curve Resolution Applied to Near Real-Time Process Monitoring with HPLC/Raman Data," *Anal. Chimica Acta*, 544(1-2), 71, **2005**.

Synergistic Activities

- Currently funded by FDA to demonstrate the concept of Quality by Design (QbD) using inline PAT to fully optimize and control the continuous synthesis of a drug substance
- Developed a research program aimed at designing, optimizing and implementing optical sensors for on-line/*in-situ* analysis of industrial, biological and environmental processes and applications
 - the program includes training of undergrads, grads and post-docs to develop skills in optics, lasers, various spectroscopic techniques and general measurement science
 - the program emphasis of on-line measurement science has had an impact on how and where optical sensors are implemented in the laboratory, in the field and in industry
- Instructor, developer and advisor for FDA Process Analytical Technology (PAT) training course and certification program for reviewers and inspectors
- Organizer and chair for technical sessions at various national technical meetings (IFPAC, FACSS, ACS)

Collaborators & Other Affiliations

Rick Gustafson, Professor Forest Resources, Univ. of Washington

Renata Bura, Assoc. Professor Forest Resources, Univ. of Washington

Marvin Lilley, Professor, Oceanography, Univ. of Washington

Deborah Kelly, Professor, Oceanography, Univ. of Washington

Tyler McQuaide, Assoc. Professor, Chemistry, Fla. St. Univ.

Frank Gupton, Professor, Chem. Engineering, VCU

Karl Booksh, Professor, Chemistry, University of Delaware

Deirdre Meldrum, Professor, Electrical Engineering, Arizona State Univ.

S. Michael Angel, Professor Chemistry, University of South Carolina

Kent Mann, Professor, Chemistry University of Minnesota

Larry Ricker, Professor, Chemical Engineering, Univ. of Washington

Melvin Koch, CPAC, Univ. Of Washington

Viola Vogel, Professor, Swiss Federal Institute of Technology

Jens Petter Wold, Research Scientist, Food Research Institute of Norway

Olav Kvalheim, Professor, Chemistry, University of Bergen

Thesis Advisor and Postgraduate-Scholar Sponsor

Graduate Student's = 3

Post doc's = 5

Graduate and Post Doctoral Advisors

a) S. Michael Angel, Professor, University of South Carolina, Ph.D. Advisor

b) Lloyd W. Burgess, Research Professor, University of Washington, Post Doctoral Advisor