Department of Chemistry



Research Symposium: Honoring the legacy of legendary chemist Izaak M. Kolthoff

> Saturday, Sept. 13, 2014

Symposium Schedule

| 8-8:30 a.m. | Registration |
|------------------|--|
| 8:30-8:40 a.m. | Welcome/Opening Remarks Professor William Tolman Chair of the Department of Chemistry University of Minnesota |
| 8:40-9:10 a.m. | Professor Richard Zare (abstract on page 4) Stanford University |
| 9:20-9:50 a.m. | Professor Laura Kiessling (abstract on page 5) University of Wisconsin-Madison |
| 10-10:30 a.m. | Professor Allen Bard (abstract on page 6) University of Texas at Austin |
| 10:40-11 a.m. | Break |
| 11-11:25 a.m. | Professor Peter Carr (see pages 7 & 10) University of Minnesota |
| 11:25-11:55 a.m. | Professor Judith Klinman (abstract on page 8) University of California, Berkeley |
| 12:05-12:35 p.m. | Professor Harry Gray (abstract on page 10) California Institute of Technology |
| 12:45-1:30 p.m. | Lunch |
| 1:15-3 p.m. | Tours |

The women's restroom is located just outside the doors of 100 Smith Hall and a short distance down the hallway. The men's restroom is located through the lobby and down the hallway on the other side. Restrooms are also located on the 2nd and 3rd floors.

Izaak Maurits Kolthoff

Professor Kolthoff was an active faculty member in the Department of Chemistry from 1927 to 1962, and continued to conduct research as a Professor Emeritus until his death, at age 99, in 1993.

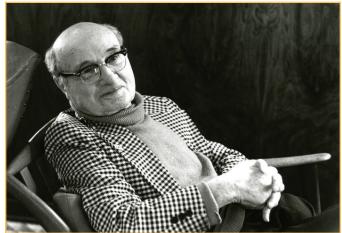
Kolthoff was a preeminent educator who authored nearly 1,000 scientific papers, numerous textbooks, and a definitive 30-volume treatise. At the University of Minnesota, Kolthoff advised more than 50 doctorate chemists, many of whom went on to major academic positions of their own. In all, more than 1,100 chemists can trace their scientific roots to Kolthoff.



Kolthoff's scientific achievements garnered many

accolades. He was inducted into the U.S. National Academy of Sciences and knighted by his native Netherlands as a Commander in the Order of Orange-Nassau. He received the William H. Nichols Medal, the Robert Boyle Medal from the Royal Society of Chemistry in England, the Fisher Award, and the first J. Calvin Giddings Award for Excellence in Teaching Analytical Chemistry, among many other awards and medals. In 1972, the University of Minnesota Board of Regents named a new chemistry research building Kolthoff Hall. In 2012, Kolthoff was posthumously inducted into the Minnesota Science and Technology Hall of Fame.

Today, the Department of Chemistry continues to honor Kolthoff's legacy with the Kolthoff Lectureship in Chemistry, annually inviting some of the most renowned scientists in the world, including Nobel laureates Jean-Marie Lehn and Harold Kroto as well as dozens of National Academy of Sciences members to present a series of lectures and meet with faculty members and students.



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Chemistry Tours 1:15 p.m. to 3 p.m.

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Professor Peter Carr

Peter Carr has been a professor and researcher in the Department of Chemistry since 1977. He earned his bachelor's degree in chemistry from the Polytechnic Institute of Brooklyn, and his doctorate in analytical chemistry from the Pennsylvania State University.

Carr's contributions to the field of chromatography are many. He also is known for his teaching, mentoring, publications, and patents. He has mentored more than 50 graduate students and post-doctoral researchers; published more than 400 papers on a variety of analytical chemistry areas such as electrochemistry, ion selective electrodes, thermochemistry, and chromatography; shared his research at numerous professional workshops and seminars; and holds more than 18 patents in chemical analysis and chromatography areas.



He has received numerous accolades throughout his distinguished career, including being honored with American Chemical Society awards in chromatography and in analytical chemistry as well as the 2013 LCGC Lifetime Achievement Award for his contributions to the field of liquid chromatography and surface chemistry.

Welcome

Professor William Tolman Chair of the Department of Chemistry University of Minnesota

Welcome you to this research symposium, honoring the legacy of legendary chemist Professor Izaak M. Kolthoff. He gave us the foundation for modern analytical chemistry. More than 1,100 descendants have carried on and continue to carry on his life-long commitment to research and educating the next generation of scientists.



We have a proud tradition of excellence at the University of Minnesota and in the Department of Chemistry, thanks to Professor Kolthoff and others like him. This tradition has set us on the course of providing a world-class education through our classroom and laboratory teaching. This tradition propels us forward to create new scientific knowledge through research that is aimed at solving some of society's most important human health, energy, and environmental problems.

Today, we have the privilege of hearing how some of the most renowned scientists in their field who are living out that tradition at their universities and in their work. Some can trace their scientific lineage back to Professor Kolthoff. Special thanks to one of our scientists and a Kolthoff descendant, Professor Peter Carr, who will share his story of friendship with Kolthoff.

Thank you for being with us at this wonderful time of celebration.

Bill Tolmon

Professor William Tolman has been chair of the Department of Chemistry since 2009. He joined the department faculty in 1990. He earned his doctorate in chemistry from the University of California, Berkeley, and did post-doctorate research at the Massachusetts Institute of Technology. He has received many awards for his research and his teaching. He is a fellow of the American Chemical Society and the American Association for the Advancement of Science, and is one of the university's Distinguished McKnight Professors. He is editor-in-chief of *Inorganic Chemistry*. His research encompasses synthetic bioinorganic and organometallic/polymer chemistry.

Richard N. Zare is the Marguerite Blake Wilbur Professor in Natural Science at Stanford University. He was born in Cleveland, and is a graduate of Harvard University, where he received his bachelor's degree in chemistry and physics, and his doctorate in chemical physics.

His career in academia includes professorships at the Massachusetts Institute of Technology, University of Colorado, and Columbia University, before moving to Stanford University in 1977. He was named chair of the Department of Chemistry in 2005, and in 2006, he was named a Howard Hughes Medical Institute Professor.



Professor Zare is renowned for his research in the area of laser chemistry, resulting in a greater understanding of chemical reactions at the molecular level. By experimental and theoretical studies, he has made seminal contributions to the knowledge of molecular collision processes and has contributed significantly to solving a variety of problems in chemical analysis. His development of laser induced fluorescence as a method for studying reaction dynamics has been widely adopted in other laboratories.

He has received numerous honors and awards, and is a member of the National Academy of Sciences and the American Academy of Arts and Sciences. He has given named lectures at numerous universities, is the author of more than 800 research papers and four books, and has more than 50 patents.

Chemical Modification of Plastic Blood Collection Tubes

Accuracy and reliability of clinical blood analysis depends on blood-material interaction within blood collection tubes, which are typically made of plastic. The hydrophobic surface is problematic because of analyte adsorption and adverse activation of blood components. We propose a simple reaction scheme for transforming the interior surface to become hydrophilic by introducing covalently bound hydroxyl groups. As opposed to conventional approaches, our method causes a fast, permanent, and contaminant-free conversion of the surface with no distortion of optical and mechanical property of the plastic container. We demonstrate its applicability to blood analysis by comparing the results from routinely performed assays. We expect the proposed approach will not only reduce the cost of manufacturing high-quality blood collection devices, but also can be generalized to other types of plastic materials.

Shown are two blood collection tubes made of polyethylene terephthalate (PET), each filled with water. The one on the right, marked a), has been untreated; the one on left, marked b), has been chemically modified. The shape of the water meniscus shows that the chemical treatment converts the interior surface of the blood collection tube from hydrophobic to hydrophilic.

Samuel Kim^a, Raffick A.R. Bowen^b, and Richard N. Zare^a ^aDepartment of Chemistry, Stanford University, Stanford, CA 94305 USA ^bDepartment of Pathology, Stanford University, Stanford, CA 94305 USA **Harry Barkus Gray** is the Arnold O. Beckman Professor of Chemistry and the founding director of the Beckman Institute at the California Institute of Technology. After graduate work in inorganic chemistry at Northwestern University and postdoctoral research at the University of Copenhagen, he joined the chemistry faculty at Columbia University. In the early 1960s, he developed ligand field theory to interpret the electronic structures and reactions of transition metal complexes. After moving to Caltech in 1966, he began working in biological inorganic chemistry and inorganic photochemistry, which led to the development of molecular systems for the storage of solar energy.



Professor Gray has published more than 850 research papers and 18 books. His awards include the National Medal of Science, the Wolf Prize in Chemistry, the Welch Award in Chemistry, and the Priestley Medal. He is a member of the National Academy of Sciences, the American Philosophical Society, and a foreign member of the Royal Society of Great Britain. He is a director of University Science Books and chair of the Board of Directors of the Arnold and Mabel Beckman Foundation.

The 21st Century Solar Army

The sun is a boundless source of clean energy, but it goes down every night. We and many others are trying to design solar-driven molecular machines that could be used on a global scale to store solar energy by splitting water into its elemental components, hydrogen and oxygen. Hydrogen is a clean fuel that could be used directly or combined with carbon dioxide to produce methanol, a liquid fuel. We are investigating the structures and mechanisms of hydrogen evolving catalysts made from Earth abundant elements such as cobalt, iron, nickel, and molybdenum. We also are employing pulsed laser ablation for synthesis of metal-oxide nanoparticles that will be deployed as catalysts on photoanodes such as tungsten oxide. To aid our research, we have recruited hundreds of students to join a Solar Army whose mission is the discovery of mixed- metal oxides for testing on the photoanodes of our solar water splitters.

Judith P. Klinman is a Chancellor's Professor, Guggenheim Fellow, and Miller Fellow at the University of California, Berkeley (UCB). She grew up in Philadelphia and received her Artium Baccalaureatus and doctorate degrees in chemistry from the University of Pennsylvania. She was a post-doctoral fellow at the Weizmann Institute of Science, Rehovot, Israel. She spent 10 years at the Institute for Cancer Research in Philadelphia, first as a post-doctoral fellow and later as a staff scientist. She has been on the Department of Chemistry faculty at the University of California, Berkeley, since 1978. She was its first female professor, not only in chemistry, but in all the physical sciences and engineering at UCB.



She has been elected to the National Academy of Sciences, the American Academy of Arts and Sciences, and the American Philosophical Society. She has received the Repligen Award and the Remsen Award from the American Chemical Society and the Merck Award and Mildred Cohn Award from the American Society of Biochemistry and Molecular Biology. She is currently a fellow of the American Association for the Advancement of Science and a member of the Royal Society of Chemistry.

Professor Klinman's research is focused on four areas: nuclear tunneling in enzyme-catalyzed reactions and the relationship of this phenomenon to the role of protein dynamics in catalysis; the development of a general theory for enzyme catalysis that utilizes protein motions to generate active site compression; the mechanism of dioxygen activation by enzymes; and the biogenesis and catalytic mechanism of quino-proteins and cofactors.

Tunneling and the Role of Barrier Width in Enzymatic C-H Activation Reactions

The ability to design highly active enzyme catalysts from first principles remains one of the outstanding challenges in biology. The physical principles that emerge from such an undertaking may also aid in the creation of biomimetics capable of approximating the rate accelerations achieved by enzymes. Although nuclear tunneling had been considered a low temperature phenomenon, it is now recognized as an important component of reactions at room temperature. This talk will focus on the tunneling properties of lipoxygenases to illustrate the emerging evidence for reduced barrier width and its link to protein dynamics in enzyme catalysis. **Laura Kiessling** is the Steenbock Professor of Chemistry and the Laurens Anderson Professor of Biochemistry at the University of Wisconsin-Madison. She is director of the Keck Center of Chemical Genomics and the National Institutes of Health Chemistry-Biology Interface Training Program.

A Wisconsin native, Professor Kiessling received her undergraduate training in chemistry at the Massachusetts Institute of Technology, conducting undergraduate research in organic synthesis. She received her doctorate in chemistry from Yale University, where she worked on the synthesis of anti-tumor natural products. Her post-doctoral training at the California Institute of Technology led her to explore the recognition of duplex DNA through triple helix formation. In 1991, she began her independent career at the University of Wisconsin-Madison.

She is a member of the American Academy of Arts & Sciences, the American Academy of Microbiology, and National Academy of Sciences. Her honors and awards include a Guggenheim Fellowship, an

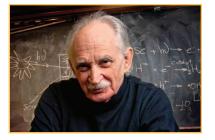


American Chemical Society (ACS) Frances P. Garvan-John M. Olin Medal, a Harrison-Howe Award, an Arthur C. Cope Scholar Award, the Hudson Award in Carbohydrate Chemistry, the Alfred Bader Award in Bioorganic or Bioinorganic Chemistry, and a MacArthur Foundation Fellowship. She is also the founding editor-in-chief of *ACS Chemical Biology*.

Her interdisciplinary research interests focus on elucidating and exploiting the mechanisms of cell surface recognition processes, especially those involving protein-glycan interactions. Another major research interest is multivalency and its role in recognition and signal transduction.

Us Versus Them: Distinguishing Human and Microbial Cells by Their Glycans

Humans not only encounter microbes in their environment, they harbor different bacteria and fungi within their microbiome. Means of distinguishing between host and microbial guests must therefore exist, but it is unclear how such distinctions are made. The surfaces of mammalian cells are decorated with glycans that differ markedly from those displayed on microbes. Lectins that selectively recognize microbial glycans could be useful detectors, but the human lectins described to date can bind human glycans. We used new high throughput analytical tools to identify a human lectin that fails to bind human glycan epitopes but interacts with selectively with epitopes presented on microbial glycans. To probe the molecular basis for this specificity, we used X-ray crystallography to determine the structure of this human lectin, which represents the first member of a new structural class of lectins. These investigations reveal the molecule basis for the lectin's unprecedented selectivity for microbial glycans. Homologs of this lectin are widespread throughout vertebrates, suggesting that lectins can be used by hosts to identify microbial guests. **Allen J. Bard** is the Hackerman-Welch Regents Chair at the University of Texas at Austin (UT), and is director of the Center for Electrochemistry. A native of New York City, he earned his bachelor's degree from the City College of New York, and his master and doctorate degrees from Harvard University.



He joined the faculty at UT in 1958. His research interests encompass the application of electrochemical methods to the study of chemical

problems. It encompasses investigations in scanning electrochemical microscopy, electrogenerated chemiluminescence, and photoelectrochemistry.

Professor Bard has worked as mentor and collaborator with 75 doctorate students, 17 master students, 150 post-doctoral researchers, and numerous visiting scientists. He has published more than 900 peer-reviewed research papers and 75 book chapters and other publications, has written three books, and has received more than 23 patents.

He has received many accolades and awards for his research and contributions to the scientific community. He is a member of the National Academy of Sciences, and an American Academy of Arts and Sciences Fellow. He also served as editor-in-chief of the *Journal of the American Chemical Society* from 1982-2001.

The Possibilities and Problems of Stochastic Analytical Chemistry: Can Single Molecule Detection Approaches Be Applied to Determinations at Ultralow Concentrations?

In recent years, a number of approaches (microscopic, spectroscopic, and electrochemical) have been demonstrated for the detection of single molecules, single nanoparticles (NPs) and even atoms. Could such techniques be used for analytical purposes, i.e., in qualitative and quantitative analyses? In this case, determinations simply by counting molecules i.e., stochastic analytical chemistry) would be a possibility for studying very low (e.g., sub picomolar) concentrations.

Recently, we and others have been working on the electrochemical detection of single molecules and NPs. Currently a lot of research deals with a variety of nanoparticles of widely varying composition (e.g., metals, semiconductors, organics, and emulsion droplets) and structure (spheres, cubes, and wires) has been reported. While microscopic and spectroscopic methods are widely used to characterize NPs, all suffer from limitations. However, over the past years, electrochemical methods, based on observation of single NP collisions with an ultramicroelectrode have been developed. These are based on using the electrochemical response and the frequency of collisions to extract information about the nature, size, and concentration. An overview of this field will be given, especially as it applies to analytical possibilities.

Piet and Pete Remembrances of a special friendship by Professor Peter Carr University of Minnesota Department of Chemistry

I first became aware of Professor Kolthoff when I took a sophomore course in analytical chemistry. One of the textbooks was the third edition of Kolthoff and Sandell's "a textbook of quantitative inorganic analysis." In addition, both of my analytical chemistry teachers were descendants of Professor Kolthoff. A bit later, I chose Professor Louis Meites as my bachelor's thesis research adviser. My research was squarely in the field of electro analytical chemistry, which at that time, was totally dominated by Professor Kolthoff.

Subsequently, I went to Penn State University to study with Professor Joseph Jordan who did post-doctoral research with Professor Kolthoff. During my first year in graduate school, Kolthoff was Penn State's Priestly Lecturer. My adviser threw a cocktail party in Kolthoff's honor, and invited all of the analytical graduate students and faculty. This was an awesome event and an opportunity to meet someone who had such a brilliant career. My wife said it was the first time she saw me in a white shirt. Amazingly, I met Professor Kolthoff in the very year that he retired from active teaching.

Many years later, I was hired as an associate professor of chemistry by Professor Paul Gassman who was chairperson of the University of Minnesota's Department of Chemistry. Paul made it very clear to me that one of my major duties, in addition to helping to rebuild the analytical chemistry group, was simply to "keep Kolthoff happy." I shortly called Professor Kolthoff to see if he would be available for lunch and he graciously accepted. Lunch turned into a long conversation in his sitting area on the fifth floor of Coffman Union where he had a small office. We soon became Piet and Pete to one another.

Over some six years, there were many lunches and afternoon chats with Piet. These often included Piet's visitors, such as former students Johannes Coetzee and Herb Laitinen. Both visited Piet almost annually. After his death, Herb's wife Marge sent me Ostwald's book on analytical chemistry (now on display in the lobby of Smith Hall), which Piet had given Herb many years earlier.

Initially, my lunches with Piet ran from noon to about 4 p.m., when he had an inviolable appointment to watch reruns of Hogan's Heroes. Sometimes these lunches, which were often proffered in the morning, were inconvenient. However, I soon learned that I could tell Piet that I already had a lunch commitment with a visitor or a committee meeting, and offer to come over a little later in the afternoon. I was able to "keep Kolthoff happy" and not disrupt my work schedule. I learned a lot about and from Piet during these frequent, impromptu symposia, and I met many of his old friends and former students.

> Read about Professor Peter Carr's outstanding scientific career on page 10.