Monthly Meeting
Prof. Shana Kelley on Nanotechnological and Biomolecules

Arno Heyn
Dedicated NESACS Member

Organohalogenes
Gordon Gribble Writes

Philip Abelson
A National Figure in Science
The Eastern Analytical Symposium is the second largest meeting in the United States dedicated to the needs of analytical chemists and those in the allied sciences. Please help us to make the 2005 EAS the best ever—be a part of the program by contributing your own papers for inclusion in the oral or poster sessions.

To submit a contributed presentation for the 2005 EAS Technical Program, you should go to our web site, www.eas.org, after March 1, and follow the instructions for preliminary abstract submission. Invited speakers should not submit preliminary abstracts to EAS, although your session organizer may request one for his/her use. All preliminary abstracts must be submitted electronically via the EAS web site at www.eas.org. The abstract submission deadline is April 15, 2005. No faxed, e-mailed, or mailed preliminary abstracts will be accepted.

Please carefully review the following information:

1. All preliminary contributed abstracts will be submitted electronically in 2005. No faxed, e-mailed, or mailed preliminary abstracts will be accepted.

2. The title of the presentation and the list of authors that you submit are final, and may not be changed.

3. The preliminary abstract that you submit will be considered to be your final abstract for use in the abstract book for the 2005 Eastern Analytical Symposium.

4. All preliminary abstracts will be acknowledged via e-mail.

5. Presenting authors of contributed submissions will be notified in June 2005 of the status of their abstract and its session assignment.
Contents

Norris Award Nominations ............................................ 4
Call for Nominations 

Levins Award Nomination .............................................. 4
Call for Nominations 

Monthly Meeting .......................................................... 5
Prof. Shana Kelley 

Arno Heyn ....................................................................... 6
Obituary by M. Simon 

Philip Abelson ................................................................ 7
Obituary of a national figure in science 

Organohalogen Nature? Naturally! ................................. 8
by Gordon Gribble 

William H. Avery ............................................................. 12
Obituary by M. Simon 

Chemists and Chemical Engineers in Homeland Security ... 13
An Interview at Natick Soldier Center  by Martin Freier 

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Nominations

James Flack Norris Award For Outstanding Achievement In The Teaching Of Chemistry

Nominations are invited for the 2005 James Flack Norris Award for Outstanding Achievement in the Teaching of Chemistry. The Norris Award, one of the oldest awards given by a Section of the American Chemical Society, is presented annually by the Northeastern Section. The Award consists of a certificate and an honorarium of $3,000.

Nominees must have served with special distinction as teachers of chemistry at any level: secondary school, college, and/or graduate school. Since 1951, awardees have included eminent and less-widely-known but equally effective teachers at all levels.

The awardee for 2004 was Dr. Richard N. Zare of the Department of Chemistry at Stanford University, Stanford, California.

Nominations should focus on the candidate’s contributions to and effectiveness in teaching chemistry. The nominee’s curriculum vitae should be included. Seconding letters are also an important part of a nominating packet. These may show the impact of the nominee’s teaching in inspiring colleagues and students toward an active life in chemistry and/or related sciences, or may attest to the influence of the nominee’s other activities in chemical education, such as textbooks, journal articles, or other professional activity at the local or national level.

Materials should be of 8 1/2 by 11 inch size. The nomination packet should not exceed 30 pages and should not include books or reprints or software.

Please direct questions about the content of a nomination to Professor Howard R. Mayne at the University of New Hampshire, email: howard.mayne@unh.edu. For more information about the Norris Award, see www.nesacs.org.

Send nomination packets (as hard copy, or electronically in Adobe PDF format) to Ms. Marilou Cashman, NESACS, 23 Cottage St., Natick, MA 01760: e-mail, mcash0953@aol.com.

The deadline for nominations is April 15, 2005.

Nominations

Philip L. Levins Memorial Prize

Nominations for the Philip L. Levins Memorial Prize for outstanding performance by a graduate student on the way to a career in chemical science should be sent to the Executive Secretary, NESACS, 23 Cottage St. Natick, MA 01760 by March 1, 2005.

The graduate student’s research should be in the area of organic analytical chemistry and may include other areas of organic analytical chemistry such as environmental analysis, biochemical analysis, or polymer analysis.

Nominations may be made by a faculty member, or the student may submit an application. A biographical sketch, transcripts of graduate and undergraduate grades, a description of present research activity and three references must be included. The nomination should be specific concerning the contribution the student has made to the research and publications (if any) with multiple authors.

The award will be presented at the May 2005 Section Meeting.
The Nucleus February 2005 5

Monthly Meeting

*The 858th Meeting of the Northeastern Section of the American Chemical Society*

*Jointly with the Northeastern University Student Chapter of the Materials Research Society*

**Thursday, February 10th, 2005**

The Social Hour and Dinner will be at the Raytheon Amphitheater in the Egan Science Research Center at Northeastern University, Boston, MA.

The Evening Meeting will be in the Raytheon Amphitheater in the Egan Science Research Center.

5:30 pm  Social Hour and Graduate Student Poster Session

6:30 pm  Dinner

7:45 pm  Evening Meeting, Dr. Amy Tapper, Chair, presiding

Professor Shana Kelley, Boston College

*Nanotechnological Approaches to Detecting Disease-related Biomolecules*

Dinner reservations should be made no later than noon, Thursday, February 3, 2005. Please call or fax Marilou Cashman at 800-872-2054 or e-mail at Mcash0953@aol.com. Please specify vegetarian. Reservations not cancelled at least 24 hours in advance must be paid. Members, $28.00; Non-members, $30.00; Retirees, $15.00; Students, $10.00

THE PUBLIC IS INVITED

Anyone who needs special services or transportation, please call Marilou Cashman a few days in advance so that suitable arrangements can be made. Public transportation is strongly encouraged. Egan Science Center is immediately adjacent to the Ruggles T-stop on the Orange MBTA subway line and is a short walk across campus from the Northeastern University stop on the Green “E” MBTA subway line. A map of the Northeastern University campus and detailed directions for those individuals driving to the campus is available at URL:  http://www.campusmap.neu.edu/map_page_4.html

Biography

**Prof. Shana Kelley** directs a highly interdisciplinary research program at Boston College that involves aspects of biological, organic, physical, analytical, and materials chemistry. One aim of the research efforts in the Kelley laboratories is the development of electrical sensors for biomolecules that will lead to new clinical diagnostics. Her laboratory uses nanomaterials to develop different platforms for the detection of medically relevant proteins and DNA molecules, and focuses on creating technologies that will have the high sensitivity and accuracy required to diagnose disease or to study biological processes at the level of a single cell.

Shana Kelley holds a Ph.D. from California Institute of Technology, and was an NIH Postdoctoral Fellow at Scripps Research Institute. She obtained her B.A. degree from Seton Hall University.

Since joining the Boston College Chemistry Department in 2000, Kelley has received a Research Corporation Innovation Award, a Dreyfus New Faculty Award, a National Science Foundation CAREER Award, an Alfred P. Sloan Fellowship, and was named to Technology Review’s list of

Abstract

Technologies enabling low cost, high-throughput DNA analysis will provide powerful tools for the diagnosis of infectious and genetic disease. Approaches based on electrical and electrochemical readout of biomolecular targets are particularly attractive for this application given that electrical currents can be measured using simple instrumentation. Electroactive nanomaterials constitute new platforms for the detection of DNA and other biomolecules that may provide increased sensitivity and amenability to miniaturization. However, the use of nanoarchitectures for electrochemical biomolecular detection represents an undeveloped area. Several types of arrayed nanostructures composed of electroactive materials are available, and show great, but unrealized promise for ultrasensitive biosensing. Our laboratory recently developed methods to functionalize different nanoscale scaffolds with synthetic DNA molecules to produce new types of hybrid bionanomaterials. Subsequent efforts to use these materials for biomolecular detection showed that markedly improved sensitivity could be achieved. This presentation will summarize a number of discoveries made about the unique chemical and electrical properties of nanoscale objects relative to bulk materials, and will highlight the promise of nanomaterials for bioanalytical applications.

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**Biography**

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Kelley is currently a member of the National Academies/Keck Futures Initiative Nanoscience and Nanotechnology Planning Committee, has served as an NIH Study Section Member and NSF Panel Member, and has chaired the German American Frontiers of Chemistry Symposium. She also is a founding scientist and consultant at GeneOhm Sciences, a biotechnology company in La Jolla, California founded to develop a new platform for DNA-based clinical diagnostic devices.

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The news that Arno had died on December 5 was not unexpected. He had penned the information for his obituary just about a year ago, thinking he would not see the new year. The source of his immediate toxin was eliminated at that time, but the longer term problems could not be solved.

I’ve known Arno since the 1950s, first through our mutual interest in outdoor activities and our membership in the SubSig Outing Club, in which Arno took much the same role as in the Northeastern Section—jack-of-all-trades: long-time secretary, trip leader, cabin builder, electrician, and locksmith. Members of this Section knew him most, and most recently, as the editor and the man behind the revitalization of the NUCLEUS.

Arno was born in Breslau, Germany, now Wroclaw, Poland, in 1918. He was the son of Myron Heyn and Margarete Cierpinski Heyn. His father was a chemist who worked in the Detroit area for much of his career, so that after Arno completed his highschule education in Germany, America became his permanent home.

Arno received his Bachelor of Science and Doctorate degrees at the University of Michigan. He was fortunate to perform graduate work in Analytical Chemistry under the guidance of Hobart H. Willard who had received his degrees at Harvard under T. W. Richards, well known and much celebrated by members of this Section. Arno’s Ph. D. in Analytical Chemistry was awarded in 1944. In Ann Arbor he had met Helen Pielemeier, also a U of M graduate, and they were married in 1942. Arno is survived by his wife and their three children: Evan (1947), Margaret (1949), and Robert (1954).

Arno joined the faculty at Boston University as Instructor in 1947 and advanced through the ranks to full Professor, retiring in 1984 as Professor Emeritus. Summers and sabbaticals were spent as a visiting scientist in Brookhaven (summers 1954-1956), Eidgenössische Technische Hochschule Zurich (1965), Kernforschungzentrum Karlsruhe (1973, 1980, and summers of 1981, 1982, 1986). His European sojourns included walking trips and reunions with high school comrades.


Arno’s contributions to the Northeastern Section were equally varied and numerous. He was Chairman of the Section in 1968, Treasurer from 1959 to 1962, Chairman of numerous committees. In recent times he served on and chaired the Esselen Award Committee, the Awards Committee, the Nominating Committee, the Constitution and Bylaws Committee.

The crowning success of Arno’s Section activities was transforming the Section’s publication, the NUCLEUS, from an ordinary newsletter into the best publication among those of all the Sections of ACS. The proof of this pudding occurred a few years ago, when we learned that the NUCLEUS was being shown to chemists in ACS seminars on communications as the model for other Sections. Arno had become Editor in the summer of 1989. He asked me to join him as Associate Editor a year later, and this arrangement lasted until his decision to retire at the end of last year.

Arno was very precise in everything he did. He could be counted on to complete any task he undertook. His strong analytical mind governed his approach to any problem. It was a pleasure and an education to work with him. During recent months he encouraged new members of the editorial staff to meet with him at his home to learn details of the editorial process. The last such meeting took place in late November, when Arno gave words of advice to our new editor, Mike Filosa.

Arno used his scientific background in many ordinary life situations. Sometimes this could backfire, as it did some years ago when he led a canoeing trip to Turtle Island on Lake George. To solve the dinner problem that night, he had bought an uncooked ham and carefully wrapped it in dry ice so that it would not spoil on the trip from Boston. My wife and I paddled over to visit and found the group in a quandary. The ham was frozen solidly, the fire was hot, and neither a hunting knife nor an axe had been able to pry loose slices for cooking. Arno’s solution? - the bow saw he found in my canoe. The “sawdust” was highly edible.

The Northeastern Section was privileged to have this remarkable man as a member. We have missed Arno much of this past year, but we will miss him even more, now that he is more than a telephone call or e-mail away. May he rest in peace.
Scientist Philip Abelson Dies; Broke Ground in 4 Disciplines

By Matt Schudel
Washington Post Staff Writer

Philip H. Abelson, whose early research helped lead to the development of the atomic bomb and the nuclear submarine, and who later influenced scientific thinking during 23 years as the opinionated editor of Science magazine, died Aug. 1 of pneumonia at Suburban Hospital. He was 91 and lived in Washington.

Dr. Abelson was a force in science for more than 60 years, beginning in the 1930s, when he was one of the nation’s first nuclear physicists. He was the co-discoverer of the chemical element neptunium and during World War II worked on the Manhattan Project to develop the atomic bomb. For his work, he received the Navy Distinguished Civilian Service Medal in 1945, the first of many honors.

In 1944, barely past his 30th birthday, Dr. Abelson was put in charge of the Naval Research Laboratory in Philadelphia. Among other things, he devised a way to apply nuclear energy to locomotion. By March 1946, he had written a paper detailing how a nuclear reactor could be installed in a submarine, in effect designing the blueprint for the USS Nautilus, which was launched in 1955 as the Navy’s first nuclear-powered submarine.

After World War II, Dr. Abelson turned his attention to biology and geology. His 1955 book on E. coli, which was then little known, was the standard study for decades and pointed out the bacteria’s importance in the emerging field of genetic engineering.

Continued on page 16
DDT, PCBs, dioxin, CFCs, and other man-made organohalogen chemicals are familiar to the chemist and non-chemist alike. Less well known are the thousands of naturally produced organohalogen that pervade our environment, some of which are identical to their anthropogenic counterparts and others of which have extraordinary and unprecedented chemical structures often with fantastic biological activity.

The handful of natural organohalogen known to chemists in the 1950’s (griseofulvin, chloramphenicol, aureomycin, Tyrian Purple, vancomycin) were considered abnormalities of nature or isolation artifacts and not representative of an enormous class of natural products yet to be discovered. Naturally occurring organohalogen are ubiquitous in both marine and terrestrial environments. Produced by marine plants and animals, fungi, bacteria, lichen, terrestrial plants, insects, some higher animals, including humans, and geothermal processes, the number of known natural organohalogen is over 4100. This breakdown to 2300 organochlorines, 2100 organobromines, 110 organoiodines, and 30 organofluorines.

Several hundred marine metabolites contain both chlorine and bromine. This phenomenal increase in the discovery of natural organohalogen over the past 50 years parallels the revitalization of natural products research in general, facilitated by improved sample collection (SCUBA and remote submersibles), isolation methods (counter-current and HPLC), 2D NMR spectroscopy, advances in mass spectrometry, new and more selective bioassays, and an awareness of ethobotany and folk medicine.

Volcanologists have identified dozens of organohalogen in volcanic emissions (Mt. Etna, Vulcano, Kujju, Kamchatka, Satsuma Iwojima, and Santiaguuito), including simple haloalkanes, haloalkenes, some CFCs (CFCl3, CF2Cl2), and even tetrafluoroethylene, the Teflon precursor! Such organohalogen are also entombed in rocks, minerals, and shales. When crushed, silvinite ore yields small amounts of chloroform, chloromethane, carbon tetrachloride, dichloromethane, chlorobenzene, and related organohalogen. Organochlorines are found in several meteorites. Natural biomass burning, such as lightning-induced forest and brush fires, produces large amounts of chloromethane and bromomethane. Dioxins also form to some extent during forest fires but the amounts are difficult to quantify.

Marine life presents a treasure trove of organohalogen to the chemist. Seventeen percent of the 4100 new marine metabolites reported during 1998-2002 contain halogen. Utilizing the presence of halides in the world’s oceans, marine organisms have incorporated chlorine and bromine into their metabolites, which apparently are employed as repellents, antifeedants, and pesticides. Anchored to the reef, sponges, tunicates, soft corals, bryozoans, and marine algae employ chemical warfare for defense and survival. Likewise, nudibranchs (sea slugs), sea hares, marine worms, and other shell-less molluscs need chemicals to repel the ocean’s predators. The sea hare Aplysia brasiliana secretes the bromine-containing panacene (1), which is repellent to sharks, and the Floridian marine worm Ptychodera bahamensis produces ten different brominated phenols, presumably as antibacterial or other defensive substances. The polybrominated heptanones from the red alga Bonnemaisonia hamifera resemble the structure of riot control agents such as “Mace” (PhCOCH2Cl) and induced skin rashes and allergic reactions in the students.
Organohalogenes

Continued from page 8

who first isolated these compounds. Likewise, aplysiatoxin (2) from the cyanobacterium *Lyngbya majuscula* is the cause of “swimmer’s itch” in Hawaii. Many of these marine halogenated compounds have unique and powerful biological activity. Punaglandin 1 (3), which is one of 30 chlorinated, brominated, and iodinated prostaglandin-like compounds produced by octocorals and algae, has anticancer activity comparable to that of the anticancer drug vincristine. The structurally complex vinyl chloride-containing spongistatins are among the most potent compounds ever screened by the U.S. National Cancer Institute, and eudistomin K sulfoxide (4) from the New Zealand ascidian *Ritterella signillinoideis* is antiviral towards *Polio* and *Herpes* simplex. The monoterpenic plocamene B (5) from the red alga *Plocamium* violaceum is three times more potent than the commercial insecticide lindane (6) against mosquito larvae. The structural similarity of these two organochlorines is striking. Equally remarkable is the resemblance of the red alga (*Rhodomela confervoides*) antibacterial phenol 7 to the hospital antiseptic hexachlorophene (8). Many other brominated phenols are marine natural products. Many marine metabolites, halogenated and non-halogenated, have powerful anti-fouling activity to prevent otherwise lethal overgrowth by bacteria, fungi, and barnacles. For example, indole 9 from the bryozoan *Zoobotryon pellucidum* is a potent inhibitor of larval settlement by the notorious ship-fouling barnacle *Balanus amphitrite*.

Terrestrial organisms are equally adept at synthesizing highly complex and biologically active organohalogenes, most usually chlorine-containing compounds. More than 50 *Streptomyces* bacteria species have yielded biologically active organochlorines, many of which possess incredibly complex structures (simocyclinone D8, isocomplestatin, chloropeptin I, pyrroindomycin B, and C-1027). A simple example is streptopyrrrole (10), one of seven related metabolites from *Streptomyces rimosus*. Akashin A (11) is one of three related chlorinated indigo glycosides isolated from cultures of a *Streptomyces* sp. that have significant antitumor activity. The life-saving antibiotic vancomycin, which is produced by *Amycolatopsis orientalis*, has been used for 50 years to treat penicillin-resistant life-threatening infections, and the two chlorine atoms in this glycopeptide are essential for optimal activity. The design of the commercial pesticide “Pirate” (12) was based on dioxapyrrolomycin (13) a *Streptomyces* sp. metabolite.

Terrestrial fungi and lichen incorporate chlorine into some of their metabolites. The fungus *Mollisia venosa* produces several polychlorinated calmodulin inhibitors such as KS-504d (14), which is 70% chlorine by weight — comparable to the most heavily chlorinated PCB (polychlorinated biphenyl). The common white-rot fungus *Bjerkandera adusta* produces bjerkanderol B (15), and the wood-rotting forest fungus *Lepista nuda* has yielded 14 organohalogenes including several bromophenols (e.g., 16). A Venezuelan soil fungus *Emericella falconensis* contains several chlorinated azaphilones that are active against diazglycerol and acyl-CoA:cholesterol acyltransferases. The Japanese mushroom *Russula subnigricans* contains a number of novel chlorohydroquinones, and the fungi *Phoma* sp. and *Penicillium* sp. both have afforded topopyrone B (17), active against *Herpes simplex* virus. Another *Penicillium* sp. produces 2,4-dichlorophenol, the same chemical used to synthesize “2,4-D” (2,4-dichlorophenoxyacetic acid), which comprises 50% of the Vietnam warfare defoliant Agent Orange. The first naturally occurring chlorinated dibenzo-furan is AB0022A (18) from the slime mold *Dictyostelium purpureum*. Interestingly, several fungi produce chloromethane, chloroform, and other simple haloalkanes.

Both marine and terrestrial cyanobacteria (blue-green algae) produce astonishingly diverse halogen-containing metabolites (e.g., aplysiatoxin (2)), some of which have extraordinary biological activity. Several dozen cryptophycins (e.g., 19) are produced by a *Nostoc* sp. cyanobacterium and have powerful, possibly clinical anticancer activity. Removal of the chlorine results in a ten-fold decrease in activity. The blue-green alga *Lyngbya majuscula* is particularly synthetically prolific and various collections of this alga have yielded nordysidenin (20), barbamide (21), lyngbyaloside B (22), and many other organohalogenes. The terrestrial Kauai blue-green alga *Dichothrix baueriana* contains bauerines A-C (e.g., 23), which are active against *Herpes* simplex.

Continued on page 10
Organohalogen
Continued from page 9

plex virus. The terrestrial *Fischerella muscicola* has yielded more than 20 chlorinated indole isonitriles (e.g., hapalindole A (24)), and *Fischerella ambiguа* contains the HIV reverse transcriptase inhibitor ambigol A (25).

![Chemical Structure 1](image1)

Although relatively few organohalogens are found in terrestrial plants, those that are known are of great interest. The common vegetables cabbage, broccoli, radish, turnip, mustard, rapeseed, pak-choi, and others produce significant amounts of bromomethane from natural soil bromide. Both potato tubers and the ice plant produce chloromethane, and 4-chloroindole-3-acetic acid is a universal growth hormone biosynthesized in green peas, lentil, vetch, various beans, and other peas. Parsley and related plants contain the chlorinated psoralen saxalin, and several chlorine-containing iridoids are plant metabolites. The Thai plant *Arundo donax* is the source of the weevil repellent 26, one of very few natural terrestrial organobromines. The edible Japanese lily *Lilium maximowiczii* produces seven novel chlorophenolic fungicides (e.g., 27) in response to attack by the pathogenic plant fungus *Fusarium oxysporum* at the site of infection. The carrot truffle *Stephanospora caroticolor* contains 2-chloro-4-nitrophenol, which is also a commercial fungicide, and the related stephanosporin (28). Several liverworts have yielded polymeric chlorinated phenols including the bisbenzyl 29, one of the few natural compounds to contain a PCB ring system.

Although natural organofluorines are exceedingly rare, one notorious exception is fluoroacetic acid (30). This highly toxic compound, which was the widely used pesticide “1080”, is found in several plants (e.g., *Dichapetalum toxicarium*) indigenous to West Africa, Australia, and other countries, and has killed thousands of livestock over the years. These plants also contain the equally toxic 18-fluorooleic, 16-fluoropalmitic, and some other fluorne-containing fatty acids. Equally rare are terrestrial brominated fatty acids but two such compounds, e.g., 31, have been isolated from the seeds of *Eremostachys molucelloides*, and the fruit of the Asian shrub *Diospyros maritima* contains 3-bromoplumbagin (32).

It is well established that insects employ chemicals extensively for intraspecies communication (“pheromones”) and interspecies defense (“allomones”), but only a few of these are organohalogens. More than a dozen species of tick biosynthesize 2,6-dichlorophenol as a sex pheromone, and the German cockroach *Blattella germanica* utilizes two chlorinated stigmastane steroids as aggrega-
tion pheromones, e.g., blattellatanoside A (33). Termites produce large quantities of chloroform, a source that may account for as much as 15% (100,000 tons per year) of the global emissions. Several insects (e.g., locusts) contain halogenated tyrosine residues in cuticular proteins, apparently to strengthen the cuticle.

Only a few organohalogens have been identified to date in higher animals. The Ecuadorian poison tree frog *Epipedobates tricolor* secretes epibatidine (34), an extraordinarily potent (and toxic) analgesic, and superior to morphine. Bovine urine contains 3-chlorocarbazole, a monoamine oxidase inhibitor, and iodolactones 35 and 36 are found in the thyroid gland of dogs. The iodinated thyroxine hormones are well known in humans and other mammals. The unusual bromo ester 37, is present in mammalian cerebrospinal fluid (cat, rat, human). This compound is an effective inducer of rapid-eye-movement sleep and may play a role in the sleep phenomenon. Perhaps more surprising is that our white blood cells employ myeloperoxidase-catalyzed chlorination and bromination to fight infection by killing invading pathogens (bacteria, fungi, and perhaps tumor cells). Byproducts of this biochemistry are 3-chlorotyrosine, 3-bromotyrosine, 5-bromouracil, chlorinated cholesterol, and others. Humans deficient in myeloperoxidase are very susceptible to fatal fungal pneumonias from *Aspergillus fumigatus* and *Candida albicans*. It has been suggested that free chlorine gas is involved in this biochlorination process! Equally remarkable is the discovery that seven chlorinated benzodiazepines, including diazepam (Valium), are present in mammalian brains, including human brains that were preserved years before these compounds were synthesized in the laboratory! These naturally occurring organochlorines are biosynthesized in plants (corn, potatoes, lentil, rice, wheat, mushrooms, soybeans) and thus enter the food chain. There is evidence that the in vivo formation of these chlorinated benzodiazepines can occur in the mammalian brain. Benzodiazepine biosynthesis in *Penicillium cyclopium* is well known.

![Scheme 1](image)

A relatively new area of natural products research is the study of marine bacteria and fungi. Several novel halogenated bipyrroles (e.g., 38), which are believed to have a marine bacterial origin, were isolated from ocean-feeding sea birds (albatross, puffin, gull, eagle). These PCB-like compounds represent the first scenario of bioaccumulative natural organohalogens. The related “Q1” (39) has been discovered in a multitude of marine and other organisms (fish, seal, walrus, porpoise, dolphin, birds, whale) and in the milk of Eskimo women who consume whale blubber.

In addition to natural combustion sources of organohalogens (*vide supra*), other abiogenic pathways to these compounds are well established, especially in the soil where both biogenic and abiogenic sources are known. The breakdown of soil humic and fulvic acids has a biogenic component (e.g., chloroperoxidase) and an abiogenic component (e.g., Fe(III) in a Fenton reaction). Both processes afford chlorophenols, chloroform, and chlorinated acetic acids as end products (Scheme 1). Vinyl chloride is a recent addition to this collection of natural soil metabolites. In addition, dioxins can form via the oxidative dimerization of chlorophenols. This unexpected result was observed both in Canadian peat bogs (Scheme 2) and in a pristine Douglas fir forest. These results match the earlier laboratory observations that chlorophenols give dioxins and chlorinated dibenzoofurans in the presence of horseradish peroxidase. Dioxin formation occurs in sewage sludge and fresh garden compost piles, perhaps under the guidance of ubiquitous peroxidase enzymes.

![Scheme 2](image)

Marine organisms have also developed the ability to biosynthesize dioxins. Given the large number of polybrominated diphenyl ethers in sponges and algae, it was inevitable that polybrominated dioxins would be discovered in the marine world. Indeed, three separate studies have found that sponges (e.g., *Dysidea dendyi*) contain such dioxins (e.g., 40).

![40](image)

Why halogen? Why chlorine? Nature and drug companies alike have...
William H. Avery

William Hinckley Avery died on June 26, 2004 in West Yarmouth, MA, a month short of his 92nd birthday. He was born in Fort Collins, CO (1912), graduated from Pomona College (Phi Beta Kappa, 1933), earned masters (1935) and doctorate (1937) degrees in physical chemistry at Harvard. After two years of post-doctoral research in molecular physics at Harvard he joined the Shell Development Laboratory. In 1941 he moved to the Alleghany Ballistic Laboratory in Cumberland, MD to develop solid fuel propellants. His work there led to later development of the large rockets used in Polaris and ICBM programs, and earned him the Hickman Medal of the American Rocket Society, a Naval Ordnance Development Award and the Presidential Certificate of Merit and the Sir Alfred C. Egerton Gold Medal. He was a member of the American Chemical Society.

In 1947 he joined the Applied Physics Laboratory of Johns Hopkins University, where he was to remain for the next 42 years, making his career in a variety of areas including ramjet and rocket propulsion and the search for alternative sources of energy. His role at APL went from group leader to Assistant Director for Research and Development to Director of Energy Research. In the latter position his work led him to the realization that Ocean Thermal Energy Conversion, i.e. sea temperature differentials used to generate electricity, was a preferred route to alternative energy to supplement the oil economy. His conclusion was warmly received by then President Jimmy Carter. On retirement from APL in 1989 the William H. Avery Propulsion Research Laboratory, now the William H. Avery Advanced Technical Development Laboratory, was named in his honor.

In retirement he and Chih Wu, Professor of Mechanical Engineering at the US Naval Academy, published Renewable Energy from the Ocean-A Guide to OTEC. This survey of over 2500 documents is the history of development of thermal energy from the sea and the establishment of OTEC plants worldwide.

Organohalogens

Continued from page 11

discovered that halogens, such as chlorine, exhibit two general properties. Halogens on a benzene ring, for example, block metabolism by deactivating the entire ring towards metabolic oxidation. Secondly, halogens increase lipophilicity and enhance bioavailability of a compound.

New natural organohalogens are discovered at a rate of 100-200 per year as natural products chemists continue to scour the world for new medicinal agents. Given that hundreds of thousands of terrestrial and marine organisms remain unexplored for their chemical content, it is certain that countless novel organohalogens will be uncovered in the decades ahead.

GENERAL REFERENCES:

Chemists and Chemical Engineers in Homeland Security
An Interview by Martin Freier

Since it came into existence in 2002, homeland security has become a serious enterprise - one that now employs quite a number of scientists, and chemists in particular, with some spectacular results. The basic mission of homeland security, as it was originally envisioned, was to secure the homeland from terrorists who wish to come into this country through various means and disrupt our economy and way of life. That mission was and still remains a daily challenge because there are so many points of entry to our homeland, and our detection systems are a long way from fool proof. The chemists and scientists play a vital role in that challenge provided that the centralized authority for homeland security and all supporting agencies continue to establish and refine the specific threat requirements and priorities, and provide the funds needed to drive the total effort.

Chemistry plays a major role in the implementation of the homeland security mission in many ways. The basic analytical tools of chemistry developed years ago are used effectively in threat detection not only in the private sector, but also in the military.

Today’s world is a dangerous one, where everything could be suspect from the food we eat, the water we drink, and the containers that are used for transport or storage, as well the means for transport, the trucks, railroads, ships and aircraft themselves. While existing chemical tools for detection are already available, the terrorists are able to build or acquire more sophistication in their threats thus making them virtually invisible to the detection systems in place. The chemists’ greatest challenge is to refine their existing tools to make them more sensitive and capable.

Unlike many of the government agencies that now support the homeland security effort, US Army National Soldier Center (NSC) in Natick, Massachusetts is unique in that it is more than a driver of the overall effort related to security. It is an innovator in the development of products for the soldiers, such as food rations and army uniforms, as well as personal armor. Particularly impressive is the scope of NSC’s accomplishments, for which it received in November of this year the coveted Army Lab of Year Award (having previously won this award in 2001 and 2003).

NSC has honed the skills of its personnel and developed products that are now in demand. While soldiers’ security is the primary concern, NSC’s expertise and products are increasingly becoming indispensable in the fight against terror. More and more of its experts are called upon to share their input in some of the major conferences.

At NSC, the soldier’s suit development project for the soldier’s universal suit of the future is a case in point, where homeland security is able to learn some important lessons and use some of the tools being developed in that project for other civilian applications. Heading the team of engineers and chemists that make up the Chemical Technology Team is Dr. Eugene Wilusz. On his team he has 20 team members either working directly under him or indirectly (on loan from other departments). In addition, he also relies on numerous outside partner companies who do their own development, in support of his project.

Not surprisingly, most of the team members are chemists and chemical engineers at all degree levels. That is because of the key role chemists play in threat detection and protection, but there are also some mechanical engineers and clothing designers who make some important contributions as well. Because of their unique specialties, some the effort is done by other scientists and engineers within other sections of NSC, including, for example, polymer scientists, textile scientists, and plastic engineers. In addition, outside partner companies are supporting the effort. They have their own team actively developing certain products in which they have the expertise. In effect, Wilusz’s team uses the typical “interdisciplinary” approach to solving problems, with the chemists and chemical engineers leading the effort.

As a naive observer, I consider the suit development project as nothing more than a tailor’s job, with a few innovations and embellishments. What I find particularly interesting is the fact that the project team is manned primarily by chemists and chemical engineers at all degree levels (from BS to PhD) as well as mechanical engineers and designers.

Therefore, my first question to Wilusz was, “Given that a similar suit has been developed so many times before, why are all those chemists and chemical engineers needed on your team?”

He responded, “Well, there is quite a bit more to this project than you think. Today’s suits are much more sophisticated in their protection capability from the outside chemical threats. This is where chemists and chemical engineers assume the leading roles”.

From his remarks, it became

Continued on page 14

Martin Freier is a consultant specializing in technical management, technical, and training strategies. He holds a BS in Chemistry from Brooklyn College and an MS degree in Engineering and Management Science from Worcester Polytechnic Institute. He is a member of the ACS, Northeastern Section.
Homeland Security
Continued from page 13

I was wondering why Wilusz did not include the helmet, the bullet-proof vest, nor the underwear in the basic suit configuration.

Wilusz explained that the helmet and the vest were tasks assigned to the mechanical engineers responsible for work on ballistics in general. “They have years of experience in that area,” he said. “In addition to what we mentioned before, there are some other peripherals that are critical, like the respirator or mask, for example. They also require special attention from some specialists who have that responsibility.”

At that point, I was after more details about the special suit development effort his team was involved in as compared to that of the previous teams.

“The real effort is in the materials and the design,” he explained. “There are so many different materials out there and so many characteristics to look at. Specifically, the majority of the effort is in the characterization of the physical, chemical, and transport properties of the materials selected.”

Characterization is typically the job of analytical chemists, while the chemical engineers study the processes involved in the development of the new materials, but in reality, all chemists and engineers share that responsibility on the team. In fact, so complex is this material selection effort that the actual materials were proposed by outside industrial partners based on the requirements developed in response to specific needs by soldiers – those that are based on specific combat situations. Initially, the industrial partners developed the actual textiles and send in their samples for evaluation in co-operation with Wilusz’s team.

Considering the added complexity of the suit configuration and the material, I wondered how much of an improvement he expects in terms of security.

“We expect significant improvement in terms of protection, comfort, and performance, and that is a key component of security. Some kind of indicator could be part of this configuration. Without that, we really cannot tell what the threat is or whether it even exists,” Wilusz said. “We are now developing membranes to serve as permeation barriers to the threat agents so as to make them withstand the outside threats and environmental elements. The material of the standard suit itself is composed of a multi-layered textile - the outer shell is treated with a liquid repellent to repel rain and other liquids, and the inner shell has an activated charcoal universal adsorbent to adsorb chemical and biological agents.”

I was surprised by the catalog of chemical threats that soldiers could be facing nowadays in the battlefield – such as the most common chemical nerve agents, sarin, blister/vesicant agents like mustard, blood agents, including cyanide, and pulmonary agents, including chlorine and phosphogenc.

The suits are also effective against biological agents, even against alpha and beta rays from radioactive agents. As for the gamma rays, that’s another story. Much more research needs to be done in that area. The key to the suit’s effectiveness is its inner layer made from activated charcoal universal adsorbent.

The mask completes the basic suit configuration. I asked him where the mask fits in, when it comes to security, Wilusz answered, “A mask has to be used wherever respiration could be affected by either biological or chemical agents. Even if that is not the case, masks must be readily at hand for all soldiers, just in case.”

And yet, Wilusz does not recommend that as part of the homeland security strategy, masks be procured for civilians. He defends his position by saying, “I have concerns with the masks that are available to civilians today. One basic concern is that by the time a mask is put in place by an untrained civilian it could be too late.”

Indeed, in the absence of any sophisticated detection system, the civilians would never know that there is a chemical/biological attack in progress until it is much too late.

The military has many years of experience dealing with chemical warfare, while the civilian sector in most
countries does not, with the exception of Israel. Sophisticated military detection systems in place in the battlefield provide immediate warning to identify the presence of any kind of chemical and biological attack. In addition, collective protection in the form of shelters is available to the war fighters.

"Then there is the matter of training," Wilusz explained. "Most individuals are not well trained in putting on a mask. To be of any use, masks must be fitted perfectly. If there are even the tiniest openings through which the agents could enter, those masks become totally useless. Wilusz continued, "In contrast, the military personnel are not only trained to put on their masks, but their masks are perfectly fitted by experts."

Another problem Wilusz identified was that the civilian user is not aware that the mask filter is only effective for a limited time (possibly, a few hours) and then the filter has to be replaced. So, unless there is a built-in indicator, the effectiveness of the mask at a given point in time is questionable.

At this point, Wilusz made me understand why designers were employed as part of the interdisciplinary team. It was their task to make sure that there was a good fit not only in the overall suit itself (the jacket and trousers), but the interfaces between the different components as well — such as, the interface between jacket and trousers, sleeves and gloves, and trousers and boots. In addition, the interface between mask, the jacket and hood must also be perfectly fitted. In no case can any openings be tolerated without jeopardizing the soldier’s security.

As for the chemists and chemical engineers themselves, one of their major tasks is their involvement in determining the permeation of the chemicals through the suit materials. Because the actual chemical agents are not allowed in the testing effort for safety reasons, compounds that simulate the properties of the real agents are used. These are called simulants or surrogates.

As for direct homeland security application for the army suit, there is a development effort for first responders, such as the police, firemen, EMT’s, and hospital workers. Wilusz said, "We have the technology and wherewithal to design and make them protective suits and are heavily involved in such developments."

In addition, NSC does produce some highly specialized suits for a lot of different applications. Because of the Gulf War experiences, there are even suits outfitted with micro-climate cooling systems for use by helicopter aircrews where the temperatures could reach uncomfortably hot levels. Similar types of suits have been considered for troops working in the extremely hot desert environment. However, from a practical point of view, the batteries alone that would be required weigh 2 to 3 pounds; and that is on top of the weight of soldier’s sophisticated gear.

Other suits that have been developed include fireproofed suits and suits that are used by first responders to deal with major industrial chemical or bio mishaps, bio-terror, or weather emergencies.

Since Wilusz stressed how important detectors are in identifying the presence of a threat as well as the effectiveness of the suit in general, I contacted Louis Stuhl, Vice President of ChemMotif, Inc. His company is one of the independent outside partners, responsible for the development of detectors used in the suits. Under a contract from NSC, ChemMotif has developed a badge that turns from a almost white to a deep blue when too much pollutant (such as diesel fuel or cigarette smoke) has collected in the carbon inner layer of a suit. That would signal to the soldier wearing the suit that the capacity of the suit for agents has been compromised and he must change into something else immediately.

The badge itself appears to be a simple device, but it required three to five Chemists and several years to develop. Three types of chemists participated in the badge’s development effort. Physical chemists were used to...
Philip Abelson
Continued from page 7

During the 1950s, Dr. Abelson also discovered that amino acids can survive in fossils, particularly at low temperatures, for hundreds of millions of years, a finding that would influence biochemists and the study of paleontology.

“He brought this extraordinarily astute mind to every problem he encountered,” said Brauman, “whether it was with Science magazine, scientific research or social concerns.”

In 1962, Dr. Abelson was named editor of Science magazine, a weekly publication of the American Association for the Advancement of Science that is read by virtually every scientist in the country. He accepted the position on the condition that he be allowed to continue his own outside research.

He made the magazine more timely and more responsive to the latest research by cultivating a network of “bird dogs” across the country to tip him off to new developments. To accommodate the latest breaking news in science, he held the section open until the day before it was shipped.

But he might have been best known for his editorials, in which he often attacked commonly accepted scientific notions and did battle with other scientists. During the 1960s, he had a running feud with NASA Administrator James E. Webb because of his implacable opposition to the manned space program, which he called a waste of time and money that did little to accommodate the latest breaking news in science, he held the section open until the day before it was shipped.

In 1966. “We must not risk our homeland secure.”

Dr. Abelson opposed government regulation of science but also warned against eggheaded plans for building a genetically enhanced super race.

“He was a very revered figure,” said Donald E. Koshland Jr., who succeeded Dr. Abelson as editor of Science. “People knew he had total integrity.”

When Dr. Abelson became editor of Science in 1962, it had a circulation of 75,000. By the time he retired at the end of 1984, the circulation was 155,000. Dr. Abelson held many advisory roles with science foundations and stayed on as a contributing editor for Science, writing occasional editorials until the late 1990s. A collection of 100 of his editorials was published in 1985 as “Enough of Pessimism.”

“I don’t mind people getting mad at Phil Abelson,” he once said about his strongly worded opinions, “but I don’t want them to get mad at Science or science.”

New Nucleus Editor

Beginning with the March issue, the Nucleus will be under the Editorship of Dr. Michael Filosa. He can be reached at 781 386 8479 or via e-mail at filosam@polaroid.com.

Homeland Security
Continued from page 15

study the contaminant absorption and molecular desorption properties involved. When the pollutants get into the carbon sensor layer, they displace the dye, which then migrates to another layer where it can be seen. Chemists with analytical skills quantified the response of the badge as a function of chemical type and concentration. Formulations chemists developed the actual compositions of the layers making up the sensor and the fluids that were used to coat the various layers.

As an Army Research Office Contractor, ChemMotif has also developed an end of service life indicator for the carbon filter cartridges in gas masks; its purpose is to identify to the mask user that a nerve agent or pollutant has penetrated his carbon canister and, therefore, it has to be replaced.

In the past two or so years since the Homeland Security initiatives have been undertaken, no major terrorists incidents have occurred in the United States. And that is a testament to the excellent work that has been done by our fellow chemists and chemical engineers, as part of their mission to keep our homeland secure.
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Index of Advertisers

Am. Instrument Exchange ..........18
Chemir Analytical Services ......17
Chemo Dynamics ...................15
Desert Analytics Laboratory ......18
DuPont Analytical Solutions ......17
Eastern Analytical Symposium ...2
Eastern Scientific Co...............12
Front Run Organx ..................18
Gateway Chemical Technology ..10
HT Laboratories, Inc. .............19
Huffman Laboratories, Inc. .......18
Impact Analytical, Div. of M.M.I. 18
J. S. T. ...........................................19
Kopella Analytical Services ......18
Mass-Vac, Inc. .......................4
Micron Inc. ............................17
NuMega Resonance Labs ..........19
Organix, Inc. ..........................18
Organomedi Corporation ..........19
Phillips Academy ....................19
PolyOrg Inc. ............................17
Prime Organics .....................18
PrimeSyn Lab Inc. .................19
Robertson Microlit Labs ..........8
SBH Sciences, Inc. .................18
Schwarzkopf Microanalytical .....19
Scientific Bindery ..................19
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Calendar

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Note also the Chemistry Department web pages for travel directions and updates. These include:
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http://www.bu.edu/chemistry/events/
http://www.chem.brandeis.edu/colloquium.shtml
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Feb 1
Prof. J. Stephen Clark (Univ. of Nottingham)
Organic Seminar
Boston College, Merkert 127, 4:00 pm

Feb 3
Dr. Julian Adams (Infinity Pharmaceuticals, Inc.)
Industrial Speaker
Dartmouth College, Steele Hall, Room 006, 10:30 am
Prof. Julio Fernandez (Columbia Univ.)
Woodward Lecture Series in the Chemical Sciences/Harvard-MIT Physical Chemistry
Harvard Univ., Pfizer Lecture Hall, 12 Oxford St., 5:00 pm

Feb 7
Prof. Russell Hughes (Dartmouth College)
“Selective Activation of Aliphatic Carbon-Fluorine Bonds Using Transition Metal Complexes”
Brandeis Univ., Edison Lecks Building, Gerstenzang 122, 3:30 pm
Dr. Edward J. J. Grabowski (Merck Co.)
Woodward Lecture Series in the Chemical Sciences/Organic Chemistry
Harvard Univ., Pfizer Lecture Hall, 12 Oxford St., 4:15 pm

Feb 8
Prof. Oleg Z. Ozerov (Brandeis Univ.)
“How Pincer Ligands Can Dictate Reactivity at the Metal Center”
UNH, Iddles Auditorium L103, 11:10 am

Feb 9
Prof. Peter Beal (Univ. of Utah)
“Recognition of Duplex RNA by Proteins and Small Molecules”
(Chemical Biology)
Boston College, Merkert 130, 4:00 pm

Feb 10
Prof. Eric Herbst (Ohio State Univ.)
“The Chemistry of Star Formation.” (Woodward Lecture Series in the Chemical Sciences/Physical Chemistry)
Harvard Univ., Pfizer Lecture Hall, 12 Oxford St., 4:00 pm
Dr. Ben Cravatt (Skaggs Institute for Chemical Biology)
Novartis Lecture in Organic Chemistry
MIT, Room 6-120, 4:00 pm

Feb 14
Prof. Robert Pascal, Jr. (Princeton Univ.)
Woodward Lecture Series, Chemical Sciences/Undergraduate Chemistry Club
Harvard Univ., Pfizer Lecture Hall, 12 Oxford St., 4:15 pm

Feb 15
Dr. Suzanne Walker (Harvard Medical School)
Chemical Biology Seminar
Boston College, Merkert 130, 4:00 pm
Prof. Francois Gabbaï (Texas A&M Univ.)
“Main Group Polyfunctional Lewis Acids”
Brandeis Univ., Edison Lecks Building, Gerstenzang 122, 3:30 pm

Feb 16
Prof. Francois Gabbaï (Texas A&M Univ)
“Polyfunctional Lewis Acidic Molecules.”
(Woodward Lecture Series in the Chemical Sciences/Harvard-MIT, Inorganic Seminar.)
Harvard Univ., Pfizer Lecture Hall, 12 Oxford St., 4:00 pm

Feb 17
Prof. Naomi Halas (Rice Univ.)
MIT, Room 6-120, 5:00 pm

Feb 22
Prof. Dennis Hall (Univ. of Alberta)
“Allylboronates in Carbonyl Allylation: from Catalysis to the Synthesis of Antibiotics”
Boston College, Merkert 127, 4:00 pm
Prof. Vijay Pande (Stanford Univ.)
Physical Chem.
MIT, Room 4-237, 4:00 pm

Feb 24
Prof. Wolfgang Jaeger (Univ. of Alberta)
“Spectroscopy of (Helium)N – Molecule Clusters: Tracing the Onset of Superfluidity.”
(Woodward Lecture Series, Chemical Sciences/Physical Chemistry)
Harvard Univ., Pfizer Lecture Hall, 12 Oxford St., 4:00 pm

Feb 28
Prof. Kurt Zilm (Yale Univ.)
Brandeis Univ., Edison Lecks Building, Gerstenzang 122, 3:30 pm
Prof. Wilfred van der Donk (Univ. of Illinois at Urbana-Champaign)
Harvard Univ., Pfizer Lecture Hall, 12 Oxford St., 4:15 pm

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