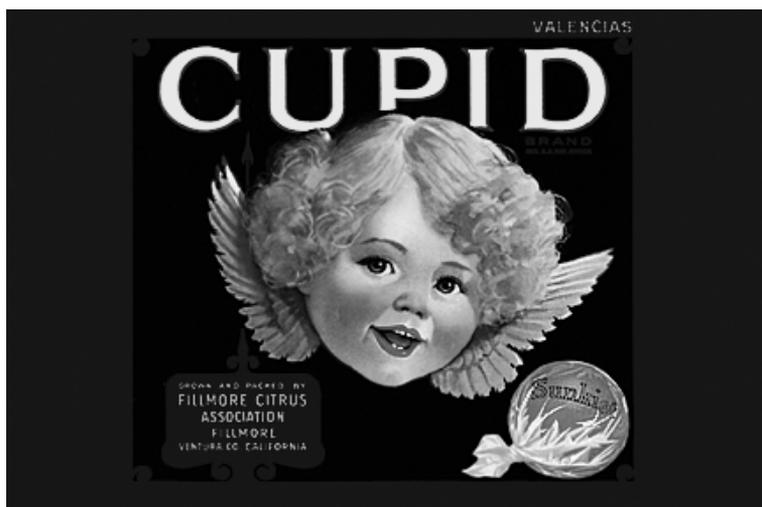


THE VORTEX

AMERICAN CHEMICAL SOCIETY
VOLUME LXXI NUMBER 2

CALIFORNIA SECTION
FEBRUARY 2010



Happy St. Valentine's Day

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Volume LXXI

February 2010

Number 2

Chair's Message

Paul Vartanian



Viva The VORTEX

The California Section's publication, *The VORTEX*, celebrated its 70th anniversary in January. *The VORTEX* began in January 1940, at a time when world conditions were in the be-

ginnings of the catastrophe of World War II. The United States would not be directly involved in the war for almost two more years. Ted Cleveland was the founding editor of *The VORTEX* and guided it for almost 30 years until June 1969. He established its high quality in both editorial content and usefulness to the Section members. During that time the Section underwent some spectacular changes.

Meetings of the Section in 1940 consisted of a main speaker and then four topical group gatherings of Analytical, Microchemical, Physical, Inorganic; Biochemical and Organic; Educational; and Industrial Chemistry. As an example, the March 1940 Industrial group heard a talk on the "California Sardine Industry" by A. H. Mendonca, after the main talk on "The Aging of Crystalline Precipitates" by I. M. Kolthoff. *The VORTEX* ran 28 pages

then and California Section dues were \$1.00/year. For perspective, the yearly dues in 1940 were equal to the cost of the dinner at a Section meeting, \$1.00. Now yearly dues are only \$15, compared to the cost of a dinner at a meeting of about \$25.

By the early 1970s, the Section had become less central to the chemical activities of its members. The topical group meetings were a thing of the past, the Santa Clara Valley Section had been established in 1954, and the San Joaquin Valley Sub-section was on its way to getting to that point. Robert Matteson became editor of *The VORTEX* in September 1969 and served until April 1972. Editor William Stanley succeeded him in May 1972. Bill guided *The VORTEX* until March 1976. Editor Robert Grinstead took over in April 1976. Bob was the first editor I got to know personally as I usually had to drive to his home in Walnut Creek at deadline time to give him my Chair's Message during my first term in 1987. *The VORTEX* was still publishing upwards of 20 pages per edition and carrying on with interesting columns and news under Bob's direction.

(continued on page 7)

*California Section
American Chemical Society
February Meeting*

"A Tour of Distillery No. 209" By Arne Hillesland, Ginerator

Date: Saturday, February 27, 2010

Time: 11:00 am (arrive by 10:45 am at site)

Place: Distillery No. 209, Pier 50, San Francisco (south of the Ferry Building, near AT&T Park)

Cost: no cost (Restaurants are in the area for an after tour lunch or snack)

Reservations: RSVP by Wednesday, February 24 to the Section office by e-mail at office@calacs.org or call (510) 351-9922. Tour limited to 30, no one under 21.

Abstract:

In 1870, William Scheffler bought a patent for a new design of a pot still in New York. He came west and set up a distillery at Krug winery in St. Helena, California. In 1880 he purchased his own winery in the Napa Valley called Edge Hill and the distillery erected there was given Federal license No. 209.

After he purchased the Edge Hill property, Leslie Rudd, a noted food and wine entrepreneur discovered "Registered Distillery No. 209" written on a hay barn on the property. He started his own winery and his daughter, Samantha Rudd, now continues her father's vision as the owner of Distillery No. 209.

The distillery was set up in San Francisco at Pier 50 to make high quality spirits, gin in particular. The Ginerator starts with a four times distilled neutral-grain spirit, with which he distills a fifth time to infuse a variety of botanicals. Traditional gin is based on juniper berry flavor, but Distillery No. 209 uses citrus, exotic fruits, and spices in its formula.

Speaker/Tour Guide:

Arne Hillesland is a complete stranger to distilling spirits, unless you consider that he learned the basics of chemistry from his father who was an aerospace engineer and chem-

ist, and he made beer, wine and hard cider in his spare time as a teenager.

A Bay Area native, a saxophonist, amateur chef, gardener and auto mechanic, Arne declined the offer to attend law school after his graduation from the University of California at Berkeley with a B.A. in history. It was the early 1980s and with the Silicon Valley as only a short commute, Arne was bound for a career in high technology management as a training, production and quality control specialist.

Twenty-plus years later, after moving from manufacturing and engineering into Artificial Intelligence software and internet start-ups, Arne began volunteering at Distillery 209 in the summer of 2003. He helped in the initial commissioning of the copper pot still from Forsyths in Scotland, and began working full-time as Distillery Supervisor in April of 2004. Working along side Two Scots - the former 209 Project Director and a Master Distiller from Scotland - Arne developed both the 209 Gin recipe and some of the unique distillation techniques that are used in making the gin today. In March of 2005, Arne Hillesland became Head Distiller at Registered Distillery No. 209 and, as a resident of San Francisco, is once again rewarded with a short commute.



The Nadjik Pheromone by Michael K. Hemp: A Book Review

L. Rigali

Michael Hemp has a Bay area connection, graduating as valedictorian from St. Mary's College High School in Berkeley and completing undergraduate work at UC Berkeley.

The guideline used for publishing articles in the *Vortex* is that the content be chemistry or science related. This article is a brief review of a thrilling, can-not-put-the-book-down spy novel with a little chemistry and science. In the *Nadjik Pheromone*, Michael Wolfson, (Wolf), the hero of the story, inspires the development of a special Gas Chromatograph/Mass Spectrometer (GC/MS) to detect biological molecules that are released when a person lies. Some of the ideas for the plot may have been generated during the time that Michael Hemp worked at Shell or later served as a Special Intelligence Officer to three Commanders-In-Chief of the Strategic Air Command, Offutt AFB, Omaha, Nebraska.

The story has all of the usual suspects as

bad guys and a few not so usual. There is the obligatory love scene very early in the story and then much later, near the end, there is a story-enhancing brief sexual encounter. The story line is contemporary with places and people we read about in the news every day.

Through the years as a Pulitzer Prize winning reporter, Wolf has gained inside information on some covert and secret projects, enough so that he is on the radar of many bad guys. And these bad guys have their way with him, almost. We soon discover that there may be one or more bad guys who want the development work on the *Nadjik Pheromone* project terminated along with Wolf and any history of this potentially powerful lie detecting system. The various scenes and dialogs with native warlords and secret agents from Afghanistan, Pakistan, Hawaii, Silicon Valley and Carmel all feel and sound authentic.

The story is told in slightly more than 300 pages and may demand completing in a single sitting.



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ELK-N-ACS Dyes and colors in art (part III).

Evaldo Kothny

In previous parts I and II, the most important earth colors of antiquity were presented, which can

be summarized as rust, charcoal and a few odd artificial reds. In most cases, the tones of these pigments are not pure and new substances were found with better characteristics.

Blue pigments were scarce and very expensive. As example, the material denominated Lazurite, consisted of natural ground-up and refined lapis lazuli (a sulfosilicate), which originally was worth its weight in gold. However, this substance was synthesized in 1928 and called ultramarine blue. This substance is a calcium aluminum silicate where the silica in the formula is partly replaced by sulfur of valence 4; and the oxygen is partly replaced by sulfur of valence 2. It is made by firing a mixture of clay, soda, sulfur, silica and rosin between 750 to 1380°C in a closed furnace. The heating and cooling ramp and the proportion of the ingredients are factors that determine the color and quality of the material. The product can be produced with a violet or a greenish hue. After its synthesis, it became popular as inexpensive house paint admixed with slaked lime or as bluing for white fabric.

Egyptian blue, also called Ancient blue or copper blue, is an artificial bright calcium-copper silicate ($\text{CaCuSi}_4\text{O}_{10}$) known earlier than 2000 years BC. It is made by mixing stoichiometric amounts of lime, copper oxide and silica with 10% soda, then heating for 6 to 16 hours at 700-900°C and leaching with dilute acid.

Zaffre, mentioned in some old writings, is a rare dark blue natural oxide containing cobalt and nickel.

The two first blue pigments discovered in AD that joined with all the blues and blue-greens known since ancient times (azurite, lazurite, Egyptian blue, malachite, turquoise,

indigo and zaffre) are smalt and Berlin blue. Smalt, also known as King's blue, which contains more Co or Azure blue, which is the darkest product was discovered in 1584. It consisted of a finely ground up silicate glass formulated with cobalt and potassium ($\text{K}_2\text{CoSi}_4\text{O}_{10}$), then leached with cold water as it may hydrolyze under other conditions, then dried. Impurities are alumina or zinc oxide.

The slaughtering operation furnishes large quantities of blood. Nowadays one known use is as a fertilizer, however, in antiquity it was beaten to remove the fibrinogen and then it was applied as a paint for preserving wood. But soon it was discovered that it could be transformed: dried blood incorporated into molten potassium carbonate and extracted into water produced a new material, the light yellow potassium hexacyanoferrate. The reaction of this salt with ferric sulfate produced a stable blue pigment that was discovered in Berlin in 1704. Thus it was named Berlin blue, although it was also known as Paris blue or Prussian blue. The ion hexacyanoferrate or the free ferrocyanide was also called prussic acid. Chinese blue has the same configuration as Berlin blue, but the molecular water normally retained is removed by heating to 250°C.

Ferric ferrocyanide was the ingredient of the most brilliant greens when mixed together with lead chromate. Industrially, the mixing occurred inside a vat by precipitating first the ferrocyanide, then adding a soluble lead compound and finally a solution of chromate under controlled pH conditions.

Thenard's blue (CoOAl_2O_3) of 1911 is obtained by impregnating alum and ZnO with a soluble Co salt, drying and calcinating this mix at 1300 to 1700 °C.

Sometimes one may find natural blue minerals which had not had the fortune of being used as a pigment. Such are the cases of certain iron silicates (Ferrous hydrous aluminosilicates, e.g., glaucophane, dumortierite). These are typically found in areas of strong tectonic pressures. Joining those silicates is vivianite, a dark blue ferrous phosphate $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. All these minerals have

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insufficient tinting power and would barely qualify as pigment.

Among the copper pigments, probably the oldest is malachite green which is an impure basic copper carbonate. It was first synthesized around 1800 and marketed as Bremen green. From it could be obtained a blue pigment by heating that was similar to the natural substance called Azurite. About at that same time, "Verdigris", was made. Verdigris of 1800 originally made by corroding copper sheets to moist air and acetic acid, can also be obtained by low temperature melting of Cu sulfate with lead acetate. The cooled melt is ground up and leached for removal of soluble lead compounds. A variety of names for this pigment exist depending on the ratio of acetate:hydroxide:water, which is 2:1:5 for the common verdigris.



February Chemical Anniversaries

Leopold May

February 6, 1860 One hundred and fifty years ago, Nikolai D. Zelinsky, was born on this date. He was a researcher on the catalysis of disproportionation reactions of hydrocarbons and the bromination of fatty acids (Heil-Volhard-Zelinsky reaction).

February 12, 1785 Two hundred and twenty-five years ago, Pierre L. DuLong was born on this date. He discovered nitrogen trichloride in 1813; and was a researcher on refractive indices and specific heats of gases. In 1819, he and Alexis Therese Petit discovered the Law of constancy of atomic heat and suggested that acids were compounds of hydrogen in 1815. He devised formula for heat value of fuels (DuLong Formula).

February 14, 1917 Twenty-five years ago in 1985, Herbert A. Hauptman and Jerome Karle shared the Nobel Prize in Chemistry for their outstanding achievements in the development of direct methods for the determination of crystal structures. Herbert A. Hauptman was born on this date.

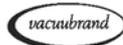


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Now, *The VORTEX* has entered a new phase as an electronic publication guided by its fifth editor, Lou Rigali, who took over the helm in April 1994. Lou has done a great job in carrying on the traditions of *The VORTEX* as costs rose and the Section members became more acquainted with modern ways of getting chemical information like using the Section's web site. With the conversion to electronic editions, we hope to add editorial content to *The VORTEX* and use the reduced printing and mailing expenses for other Section activities. Lou also has done well in leading the quick conversion of *The VORTEX* to the electronic format, while still providing paper copies for those members requiring them. For 70 years *The VORTEX* has been an integral part of the California Section and we hope it continues to meet the members expectations as a source of information on Section activities.





Moderation and Common Sense, XX

A. Pavlath

During the past two years I discussed in *The VORTEX* the pros and cons of increasing our energy supply using various alternate resources in addition to fossil fuels. It is evident that most of them can provide additional energy in form of electricity. The question discussed in the previous segment was the utilization of such electricity in everyday use. Through high voltage transmission lines the lighting, heating and cooling of the house can be helped. But at the same time, totally electric cars, not hybrids, still have technological and economical problems. Can we use electricity practically in transportation?

In the beginning, I mentioned that hydrogen is not an alternate energy source, but a carrier. By using hydrogen for transportation we do not gain additional amount of energy, we just use existing one in a different way. The argument in favor for hydrogen is that it is environmentally clean and it does not create carbon dioxide. However, we do not have natural hydrogen resources, therefore, we have to manufacture it. The question is, what processes are available for obtaining it?

Since hydrogen is essential for manufacturing artificial fertilizers through the Haber-Bosch synthesis, its production process is well established, but it uses almost exclusively fossil fuel as a starting material. Presently, about 50% of the hydrogen is produced from natural gas, about 30% from oil, and 15% by coal gasification. The rest is obtained by dissociating water through either high temperature (~1000°C) or electrolysis. The high temperature process in some nuclear power plants would help their efficiency by utilizing some of the heat which is not converted into useable energy.

There are various types of water electrolysis: low and high temperature and high pres-

sure. Each of them has various efficiencies from both energy and economy points of view. The bottom line is that the energy content of the hydrogen obtained is always less than the amount of energy invested in obtaining it. Depending on the reports, the energy efficiency is 50-80% of the electric energy used. To this we have to add the efficiency of obtaining electricity and the efficiency of using hydrogen in whatever propulsion system used in transportation to get the true picture of using hydrogen. The cost of hydrogen on site is \$0.32/lb, but off-site, requiring transportation in liquid form, is \$1.00-1.40/lb. On the plus side, the efficiency of a hydrogen fueled engine is 8% higher than its gasoline counterpart. Using fuel cells can provide 2-3 times more efficiency, but much more development is required to become an everyday economical transportation possibility.

Is hydrogen the answer to the solution of the environmental problems attributed to the use of fossil resources? Obviously the use of hydrogen instead of fossil fuels would help cut down carbon dioxide generation. There is no question that using hydrogen, wherever it is possible, could abate the environmental problems related to carbon dioxide. However, frequently, enthusiasm creates blind spots and we only see the advantages.

Hydrogen represents safety problems. The explosion of the Hindenburg air craft seventy years ago created an everlasting warning. Its household use could create more difficulties than natural gas. In addition there is an unknown environmental factor. Can we use hydrogen in every day life without any leakage to the atmosphere? Since it is the lightest gas, it tends to rise. Will it be completely destroyed before reaching the ozone layer? In case of the fluorocarbons, we were able to replace them easily with other aerosols. What happens if we find out a possible harmful effect of hydrogen spillage on the environment when our life will be already based on hydrogen? I might sound as a broken record but moderation and common sense must be common.





The Chemistry of Mineral and Bottled Water (Part 3)

Bill Motzer

Both bottled and tap water may be derived from surface sources (rivers and reservoirs) or

groundwater. Most of it (about 99.9%) consists of H₂O composed of the stable isotopes of oxygen: ¹⁶O (99.757%), ¹⁷O (0.038%), and ¹⁸O (0.205%), hydrogen including hydronium or ¹H (99.985%), deuterium or ²H (0.015%), and very small amounts of radiogenic tritium (³H), which is largely the residual effect of post WWII atmospheric nuclear weapons testing and emissions from nuclear power plants. The remainder, if it is "fresh" water, generally has a total dissolved solids (TDS) content of less than 1,000 mg/L (0.1%). TDS are defined as the total quantity of inorganic salts and small amounts of organic matter in mg/L remaining when a water sample is evaporated. By comparison, sea water has a TDS of about 34,650 mg/L (~3.47%).

Major Constituents

Metal (cation) and nonmetal (anion) analysis of water can involve a substantial number of constituents or it may involve only those considered to be the most important. Generally, the major cations and anions examined in a water analysis are sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺), chloride (Cl⁻), sulfate (SO₄²⁻), bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻). Minor anions include nitrate (NO₃⁻), nitrite (NO₂⁻), phosphate (PO₄³⁻), dissolved ammonia (NH₃) and nitrogen gas (N₂).

The major solutes in groundwater generally have the following relative abundances (from greatest to least):

HCO₃⁻ (± CO₃²⁻) > Ca²⁺ > SO₄²⁻ > Cl⁻ > Mg²⁺ > Na⁺ > K⁺ > N (as N₂, NH₃, NO₂⁻, NO₃⁻) > PO₄³⁻

Of the above listed constituents only Cl⁻, SO₄²⁻, NO₃⁻, and NO₂⁻ have regulatory requirements; these are secondary maximum concentration/contaminant levels (MCLs) of 250 mg/L for Cl⁻, and SO₄²⁻ and a primary

MCL for 500 mg/L for SO₄²⁻. The MCL for NO₃⁻, NO₂⁻ are 10 and 1.0 mg/L, respectively Other Minor or Trace Constituents

Important trace elements may include aluminum (Al³⁺), iron (Fe²⁺ and Fe³⁺), manganese (Mn²⁺ and Mn⁴⁺), arsenic [As(III) and As(V)] and lead (Pb²⁺). (I have written the arsenic as an oxidation state because it tends to form mostly anionic complexes.) The current arsenic primary MCL is 0.010 mg/L. Other trace elements of particular concern are chromium (Cr) which can occur as Cr(III) or Cr(VI) largely in the form of chromate [CrO₄²⁻] or dichromate (Cr₂O₇²⁻) ions. Cr(VI) is a known human carcinogen (see Valencing Oxidation States in the October 2007 *Vortex*).

Other Parameters

Hardness is a condition by which the calcium and magnesium ions form insoluble residues with soap. Hardness is determined by the range of calcium carbonate (CaCO₃) concentration in water in mg/L, which is known as calcium hardness or the range of magnesium expressed as CaCO₃ (magnesium hardness). Total hardness (H_T) can be calculated using the formula:

$$H_T = 2.5 \text{ Ca} + 4.1 \text{ Mg}$$

where Ca and Mg are concentrations measured in mg/L. Published hardness ranges vary:

Description of Water Hardness Ranges
Hardness Range in mg/L of CaCO₃

| Hem (1988)* | Todd (1980)** | |
|-------------|---------------|-----------|
| 0 - 60 | 0 - 75 | Soft |
| 61 - 120 | 75 - 150 | Mod. Hard |
| 121 - 180 | 150 - 300 | Hard |
| >180 | > 300 | Very Hard |

* Study and Interpretation of the Chemical Characteristics of Natural Water: U.S. Geol. Survey Water Supply Paper 2254, 263 p.

** Groundwater Hydrology, John Wiley & Sons, New York, NY., 535 p.

Most bottled and tap water derived from surface water sources generally are soft but groundwater sources can be moderately hard to hard.

Naturally Occurring Organic Constituents
Natural organic compounds may be found in

(Continued on page 10)

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surface water and to a minor extent in shallow groundwater but are most likely absent in deep groundwater. Runoff from organic soil may contain several thousand mg/L of various organic compounds that may include alkaloids, n-alkanes, organic cyanides, phthalates, porphyrins, and terpenes and humic and fulvic acids. Microorganisms (principally bacteria) degrade or decompose these soil hydrocarbons. Natural organic compounds generally are not toxic but do influence geochemical and biochemical processes in water bodies. Disinfection of water with chlorine and its subsequent reaction with organic substances may form trihalomethane (THM) compounds such as chloroform, which may pose problems because it is considered as a human carcinogen. For that reason, many water treatment works have changed to chloramine (NH_2Cl). Humic substances can also influence heavy metal speciation through compound complexation.

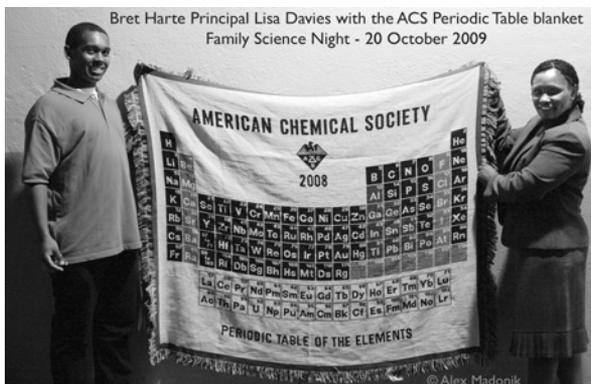
Synthetic organic compounds can include many thousands of commercially produced

compounds. These may occur in very trace amounts (measured in nanograms per liter or ng/L) and are either absent or virtually non-existent in treated water. Some of the “newer” contaminants of concern (COC) include pharmaceutical and personal care products (PPCPs) and n-nitroso-dimethylamine (NDMA). Many PPCPs rapidly degrade when released into the environment; others are persistent.

Micro-organisms

Bacteria and viruses are largely eliminated in drinking water by chlorination or the addition of chloramine. More modern methods include ultrafiltration, UV oxidation and/or ozonization.

Just 200 years ago, most Americans eschewed drinking any water, relying instead on consuming hard apple cider, beer, and wine because the alcohol generated by fermentation eliminated most harmful bacteria. The next time you turn on the tap or open a bottle of water, remember that for the most part, in the U.S., we have a reliable and safe drinking water supply.



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