Chemistry

Even 'purest' silvers get the blues

Hang a sheet of "purest" silver over fermenting grapes and keep it warm with fermenting horse dung. From the technical literature of the 9th to 16th century period comes this medieval craftsman recipe for making a blue pigment from sheets of silver. That recipe recently puzzled Mary Virginia Orna of the College of New Rochelle in New York and others who noted that metallurgical techniques of that period were sufficiently refined to produce high-quality silver—and that high-quality, pure silver used in the recipe tarnishes but produces no blue compounds. (Orna even tried the procedure, using vinegar instead of fermenting grapes and heaters instead of dung.) Now, after having delved more deeply into the literature of the Middle Ages, Orna reported at the recent American Chemical Society meeting in Seattle, she and colleagues may have solved the medieval blue mystery.

Fine silver is a relatively soft metal that can be worn away. So although medieval silversmiths could produce pure silver, they often alloyed it with small quantities of copper to strengthen it. From ancient times, when silver became a universal currency, laws regulated the amount of such debasement allowed in coinage. Later on, this regulation would extend to silver wares.

The first recorded attempt at silver wares regulation appears in 1238 when England's Henry III "issued an order stating that the standard of fineness for silver used for artifacts was to be no worse than [that for] the coinage — that is, 925 parts per thousand of silver," Orna reported. "It seems safe to surmise," she said, that the "purest silver" called for in the blue pigment recipes probably was the grade purest in the eyes of the law, which allowed for some copper impurity. Consequently, the medieval "silver blues" probably were copper corrosion products, such as copper (II) acetate monohydrate.

Electrified carbon dioxide makes fuel

Developing a system that can efficiently use sunlight energy to split water to generate the fuel source hydrogen is still the bull's eye sought by photochemists. However, an increasing amount of attention is being paid to the possibility of using solar energy to perform other chemistry — processes that may prove more useful than water-splitting. This is why photochemists at the recent meeting in San Francisco of the Electrochemical Society noted with interest a report that carbon dioxide (CO_2) — a waste-product of fossil fuel combustion — can be efficiently converted to the fuel methanol (CH_3OH) in an experimental process that ultimately may be able to utilize solar energy.

The process, developed by Karl W. Frese and colleagues of SRI International in Menlo Park, Calif., includes a gallium arsenide semiconductor electrode in sodium sulfate solution to which carbon dioxide is dissolved; a source of electricity; and a platinum electrode to complete the circuit. When current flows between the electrodes, the following reaction takes place at the semiconductor surface: $CO_2 + 6\text{ electrons} + 6H^+ \rightleftharpoons CH_3OH + H_2O$.

Methanol is produced in this setup with nearly 100 percent "Faradaic efficiency." In other words, nearly all the electrical energy passing through the system is utilized to make methanol (rather than methanol plus unwanted byproducts). And while the system now depends on electrical input, it ultimately may be possible to connect it to a photovoltaic cell that converts sunlight into the needed flow of electrons.

But several major problems have to be solved before such a system could be developed. For example, successful conversion of CO_2 to CH_3OH, Frese and colleagues inadvertently discovered, now depends on some unknown impurity—perhaps acting as a catalyst — in the sodium sulfate solution. In addition, the conversion can only be achieved now at low current density (number of coulombs passing through the circuit per unit time), so the yield of methanol remains low.

Biology

Cellulose digestion by lab bacteria

With genetic engineering techniques, scientists have made a standard laboratory bacterium produce an enzyme that converts cellulose into sugar. About 900 million metric tons of cellulose waste — including discarded paper, corn stalks and sawdust — are produced in the United States each year. The sugar produced by enzyme action on cellulose can be converted into ethanol for liquid fuel, plastics, synthetic rubber and drugs.

Cornell University biochemist David B. Wilson reported at the recent meeting of the American Society of Microbiology that he had isolated from high-temperature bacteria, *Thermomonospora,* the gene for the enzyme cellulase. He implanted this gene in the laboratory bacterium *Escherichia coli,* and the *E. coli* made stable and active cellulase. Wilson next hopes to modify the bacterium to produce larger amounts of the enzyme.

What is DNA?

It's a poison, say 2 percent of American people. "Don't know," say another 63 percent. Twenty-seven percent answer: genes, molecules, chemicals in the body, the essence of life, genetic engineering, biology or human cells. Two percent of adult men and women in the 48 contiguous states surveyed by Cambridge Reports, Cambridge, Mass., gave an accurate definition. According to the American Chemical Society, which submitted the question, the full-credit answer is that DNA is "large molecules—long paired chains of connected atoms—within human cells, and the cells of virtually all living things, that make copies of themselves to build, maintain, and pass on biological traits to succeeding generations."

Light-gathering limits beet energy

The mechanisms within a plant that convert solar energy into food may be so carefully balanced that attempts to increase plant productivity must consider several systems simultaneously. Most research has focused on improving a plant's use of chemical energy to produce sugar from carbon dioxide and water. But now work by Norman Terry at the University of California at Berkeley shifts attention to the initial light-collecting process. Terry reports in the April PLANT PHYSIOLOGY that in sugar beets a limiting factor is the capacity of plant leaves to convert sunlight into chemical energy, the initial step in the food-producing cycle. He finds that both in iron-deficient plants, with reduced chlorophyll content, and in plants varying over the normal range of chlorophyll amount, the rate of photosynthesis is proportional to the amount of the light-harvesting components. Thus plant breeders may well need to increase chlorophyll content in plants, as well as increasing the capacity of later reactions, in order to increase crop yields. Terry concludes, "The photosynthetic apparatus has apparently developed in such a way as to achieve a remarkable balance in the capacities of each part of the total system so that no one part dominates in the control of photosynthetic rate."

Money from industry to basic research

Nine young investigators are being sponsored by an innovative fellowship. A group of biological scientists last year established the Life Sciences Research Foundation as a means to attract industry support for nontargeted research instead of for specific projects. The foundation chooses the grant recipients, and the sponsors have no say in directing the research project and receive no patent rights. The seven companies funding fellows are Hoffmann-La Roche Inc., Monsanto Co., Pioneer Hi-Bred International, Inc., Schering-Plough Foundation, Burroughs Wellcome Fund, Merck, Sharp & Dohme Research Laboratories and Hoechst-Roussel Pharmaceuticals.