Chemistry

Janet Raloff reports from Miami at the 189th national meeting of the American Chemical Society

Unwanted formaldehyde 'breakthrough'

Few would challenge formaldehyde's toxic status today. Because the chemical is also a strong irritant, not only inhalation but also skin contact is to be avoided. That's why so many biologists, pathologists, embalmers and others whose work requires use of this common chemical must wear protective gloves whenever they handle solutions containing formal-dehyde. But how protective are those gloves? Not very, according to data developed under the National Toxicology Program by teams of chemists at Radian Corp. in Austin, Tex., the National Institute of Environmental Health Sciences (NIEHS) in Research Triangle Park, N.C., and A.D. Little Co. in Cambridge, Mass.

The researchers examined five popular brands of commercial protective gloves commonly used at NIEHS — three models made from natural rubber (known generically as "surgeons' gloves"), and one variety each made from polyvinyl chloride (PVC) and polyethylene. Ranging from 0.05 to 0.2 millimeter thick, the material from all gloves permitted formaldehyde concentrations of as little as 8.5 percent in water to break through in 1 to 10 minutes. (Solutions of 33 percent formaldehyde took a few extra minutes to break through.) Once breakthrough occurred, material from all the gloves permitted the chemical to continue seeping through at rates of between 0.1 and 0.3 microgram per square centimeter per minute.

A sixth glove made from 25-mm-thick neoprene latex was experimentally developed just for this test. Reports Meredith Conoley of Radian, as a barrier to formaldehyde, neoprene far surpassed the others, allowing breakthrough only after 50 to 150 minutes. (As with the other gloves, these results were based on three different types of tests, each having different sensitivities.) Once breakthrough occurred, formaldehyde permeated the neoprene at a rate matching that of the others.

That's the good news. The bad news is that not only is there no glove on the market comparable to the neoprene test model, Conoley says, but even if there were, it might not win widespread popularity. One reason surgeons' gloves are so popular, he explains, is that they flex well enough to pick up a pin, and allow clear tactile sensations — attributes the neoprene glove cannot claim.

CO₂ makes carbon monoxide more toxic

Eighty percent of the people who die in fires die from inhalation of smoke and toxic gases, not from flames, notes Barbara C. Levin, head of fire toxicology at the National Bureau of Standards' (NBS) Center For Fire Research in Gaithersburg, Md. NBS has launched a program to identify the most toxic combustion products and the possible synergistic effects that the hundreds of gases created in a fire might pose when allowed to interact. The goal is to build a computer model that can predict the probability of toxic-gas production and the risks those gases would pose to humans, in environments of specific room dimensions, furnishings and building materials.

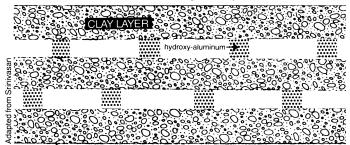
Many of the toxicity data for this model are coming from new tests. And Levin reports that some of these tests have already begun yielding surprising data. For example, carbon dioxide (CO₂) is normally considered nontoxic, she says. And though CO₂ levels in a fire usually do not exceed 21 percent, she says, experimental rats could survive up to 40 percent CO₂ in air before getting sick. Yet when CO₂ and carbon monoxide (CO) were delivered together for 30 minutes—a situation representative of fire conditions—concentrations of CO₂ as low as 5 percent in air were enough to double the toxicity of the CO, which became lethal at just 2,500 parts per million in air. Levin says the CO₂ appears to exert its damage by increasing the rats' uptake of CO and by producing an increased and prolonged respiratory acidosis (toxic acidification caused by a buildup of carbon dioxide in blood).

Dioxin and the clay that binds

By treating an inexpensive, naturally occurring clay with a solution of water-soluble aluminum hydroxide, researchers at the University of Michigan in Ann Arbor have been able to modify the clay so that it binds with toxic organic chemicals, most notably 2, 3, 7, 8-TCDD, the most toxic species of dioxin. This modified clay could be used as a filter to sieve out small quantities of dioxin and other toxic chemicals from industrial wastewater or drinking water. Alternatively, it could be substituted for those clays now lining hazardous waste landfills as an improved barrier against migration of toxic chemicals into soil.

The hydroxy-aluminum treatment expands certain structures of montmorillonite clay, creating a labyrinth of engineered pores inside the clay (see diagram) that are large enough to let water pass through but small enough to trap dioxins, dibenzofurans and PCBs (polychlorinated biphenyls), explains Keeran Srinivasan, one of the project scientists.

Not only is this clay less expensive than the best available alternative — activated carbon — for water treatment, but it's also more effective, Srinivasan says. It can extract 3 milligrams of dioxin from 20 million gallons of water, a separation capability equal to finding 2 molecules of contaminant out every 10^{15} molecules of water, he says. He adds that the clay sieve might even be recyclable once it's collected its fill of contaminant. Because hydroxy-aluminum is a good catalyst, Srinivasan says, there are indications it might foster relatively low-temperature dechlorination (degradation) of the toxic organics—perhaps at 100° C or lower—without affecting the clay.



Schematic of chemically modified clay

Where is your orange juice from?

An experimental procedure that quantitatively measures 22 trace metals is being developed to identify the geographical origin of orange juice that is sold in the United States. Because trace metal abundances in soil vary widely throughout the world, each citrus region imparts its own characteristic mineral fingerprint to fruit grown there. In fact, each region's trace-metal fingerprint is so distinct that misdiagnosing the origin of an unidentified sample should be next-to-impossible, according to the technique's developer, Seifollah Nikdel of the Florida Department of Citrus in Lake Alfred.

His process employs radio-frequency heating to ionize juice samples. The values for the characteristic spectra emitted by each sample are compared by a computer against 100 sets of reference values previously calculated for fresh juice from every major citrus region marketing orange juice in the United States.

Nikdel's research was prompted out of concern that some juice being sold as "all Florida orange juice" might in fact be adulterated with less expensive juice from other regions. While this form of adulteration does not threaten human health, it could jeopardize the economic health of Florida's more than \$2 billion orange juice industry. Moreover, Nikdel says, federal legislation is pending that will soon require country-of-origin labeling on all orange juice sold in the United States. When that occurs, this trace-metal mapping system could become a primary forensic tool for policing truth-in-labeling laws.

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