

## Nancy McGuire in Noteworthy Chemistry (ACS) Winter 2013–2014

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March 3, 2014

**Ice shells stabilize methane hydrate particles in oil suspensions.** Gas hydrates are clathrate compounds that consist of hydrogen-bonded water molecule frameworks that trap gases or volatile liquids. Gas hydrates form naturally in the deep ocean; in cold climates, they can form plugs in oil and natural gas pipelines. Preventing gas hydrate formation during the production and transportation of natural gas and crude oil costs almost \$200 million annually in the United States.

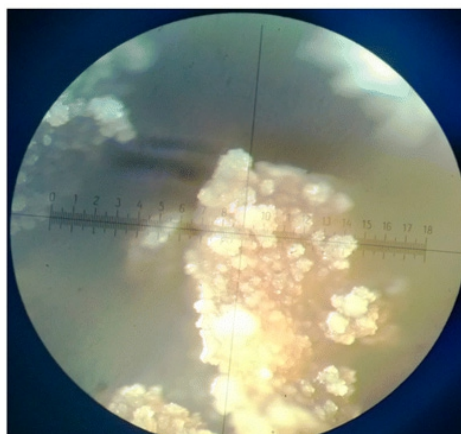
To better understand the mechanisms of gas hydrate particle formation and stabilization, A. Yu. Manakov and coauthors at the Nikolaev Institute of Inorganic Chemistry (Novosibirsk), Novosibirsk State University, and the Institute of Petroleum Chemistry (Tomsk, all in the Russian Federation) prepared water suspensions in four crude oils and an asphaltene–resin–wax suspension in decane, with and without a surfactant. Gas hydrates were formed by placing the emulsions in pressure cells and holding them under constant methane pressure for as long as 2 months. The entire apparatus was cooled to liquid nitrogen temperature before the samples were removed from the pressure cells.

The authors measured gas emission as a function of temperature, and they examined crushed samples by using low-temperature X-ray diffraction as the samples were gradually warmed.

All of the crushed hydrate suspensions in crude oil exhibited three stages of gas emission. During the first stage (–120 to –80 °C), an oversaturated solid solution of methane in oil decomposed. This was followed by partial decomposition of the hydrate particles in the suspension (–80 to –50 °C) and the completion of the decomposition process (0 °C).

The authors interpret the three-stage process as evidence of "self-preservation" of some of the hydrate particles between –80 and –50 °C. The second stage was observed only in samples of frozen suspensions that had been crushed. The suspended hydrate particles had characteristic sizes of <1 mm. This self-preservation effect was not observed for the particles suspended in decane.

The authors determined that decomposition of the hydrates occurs first on the particle surfaces. The water forms an ice shell that protects the particle interiors during the second decomposition stage. They attribute the greater stability of the smaller hydrate particles in oil to the formation of a layer of heavy hydrophobic–hydrophilic oil components (including asphaltenes, resins, and naphthenic acids) on the surfaces of the hydrate particles, which facilitates ice shell formation. (*Energy Fuels* **2014**, *27*, [794–802](#); Nancy McGuire)



Micrograph of a frozen (–150 to –100 °C) specimen of methane hydrate and ice agglomerates washed from crude oil media. The field of vision is  $\approx 250 \mu\text{m}$  wide.

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**February 24, 2014**

**A decision-support framework helps develop energy strategies.** Implementing the 2013 US Climate Action Plan requires a national strategy for energy generation and delivery that is based on scientifically sound evidence and stakeholder decisions. Research suggests that effective decision-support systems help decision-makers make more thoughtful tradeoffs among objectives and strike a better balance between intuitive and analytic reasoning.

D. L. Bessette\*, J. Arvai, and V. Campbell-Arvai at the University of Calgary (AB) and Decision Research (Eugene, OR) developed and tested a decision-support framework that draws on two established methods: structured decision-making (SDM) and portfolio analysis. SDM, a time- and resource-intensive approach, breaks complex decisions into components, allowing an attribute-by-attribute evaluation of a complex technical issue. Portfolio analysis is a rapid, intuitive holistic approach that ranks options on the basis of real-world constraints.

As their test case, the authors chose an initiative at Michigan State University (East Lansing) to generate a new long-term plan for the university's power-generating system. The study participants, 182 randomly selected college juniors and seniors, used an online dashboard to work with an interactive energy system model tailored to the MSU campus with the assistance of an onsite facilitator.

Two groups of participants built their own portfolios, whereas two other groups did not. All of the participants evaluated six energy portfolios on how effectively they achieved six objectives (for the first two groups, these strategies included portfolios that they had designed themselves). They then performed holistic ranking (portfolio analysis) and attribute-weighting (SDM) procedures. Two groups (one with self-designed portfolios and one without) performed the holistic analysis first; the other two groups started with the attribute weighting.

The order in which participants engaged with the holistic-ranking and attribute-weighting exercises had no significant effect on any of the self-reported responses with respect to adequacy of information provided and ease of use of the system. A review of the participants' decisions, however, indicated that the group that built its own portfolios and performed attribute weighting before holistic ranking produced the most internally consistent choices. The rankings more closely matched the preference orders implied by attribute weights.

Participants consistently gave the highest rankings to portfolios that contained nuclear power and the lowest rankings to portfolios that relied on coal and natural gas. The most expensive portfolios with the least greenhouse gas and particulate air emissions were consistently preferred over the least expensive higher-emitting portfolios. Emission reduction took precedence over cost, job creation, and land use.

The authors are conducting follow-up studies to investigate whether this ranking holds when a more diverse population is surveyed and when the entire survey is conducted online in the absence of a facilitator. (*Environ. Sci. Technol.* **2014**, *48*, [1401–1408](#), [Nancy McGuire](#))

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February 17, 2014

**Nanoparticles preserve medieval bones.** Although ancient bones decay more slowly than soft tissues, they eventually demineralize by a process similar to osteoporosis. Archaeologists and paleontologists use various methods for preserving fragile old bones for transport and study, many that involve filling the pores with vinyl or acrylic polymers. But this can lead to problems with compatibility, reversibility, and stability.

P. Baglioni, L. Dei, and co-workers at the University of Florence (Italy) devised a way to grow aragonite-polymorph  $\text{CaCO}_3$  crystals in situ in bone remains, thereby increasing bone strength by 50–70%. They used the collagen present in the remains, atmospheric  $\text{CO}_2$ , and  $\text{Ca}(\text{OH})_2$  nanoparticles. They note that although the aragonite polymorph is less stable than calcite, it has greater mechanical strength.

Bone fragments from the late Middle Ages were obtained from a parish church in Milan as part of a restoration project.

The authors confirmed that the bone samples contained enough collagen to promote the formation of the aragonite polymorph. The bones were conserved in a closed shrine, which limited their contact with external biological agents that could have degraded the collagen.

They treated the bones in a room of the church that had climatic conditions similar to the shrine in which the relics were kept, including a relative humidity of  $\approx 75\%$ . They immersed the bone fragments in a commercially produced suspension of  $\text{Ca}(\text{OH})_2$  nanoparticles in *i*-PrOH. When the solvent evaporated, a fresh batch of the suspension was applied. They repeated the process 10 times over 3 months.

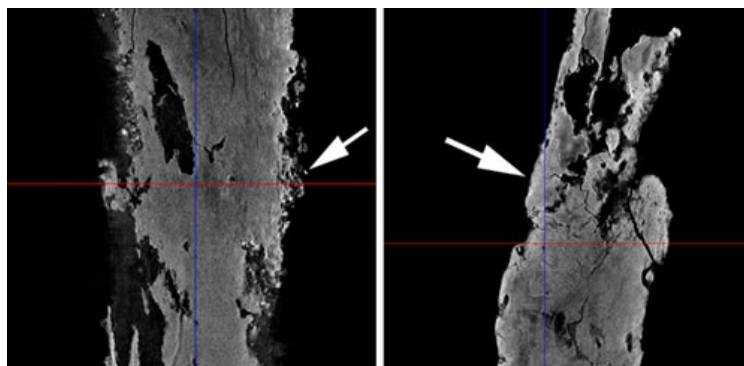
Ordinarily, the alkaline environment in the vicinity of the  $\text{Ca}(\text{OH})_2$  nanoparticles would have denatured the collagen during treatment, but with *i*-PrOH instead of water as the suspending liquid, the speed of the carbonation reaction reduced the extent of collagen hydrolysis.

The authors confirmed the complete carbonation of the nanoparticles by using scanning electron microscopy and Fourier transform IR spectroscopy. The samples were further characterized with a variety of chemical, mechanical, and structural analytical techniques. The authors verified that a new crystalline carbonate matrix had not only formed on the surface, but it acted as a binder and filler inside the original weakened porous substrate.

The carbonate crystals prevented the bone fragments from further flaking and powdering, and they were physically and chemically compatible with the bone substrate. The process is easy and cost-effective. An added benefit is the antimicrobial protection offered by the nanoparticle suspension.

(*Langmuir* 2014, 30, 660–668; [Nancy McGuire](#))

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Microtomography sections of untreated (left) and treated bone fragments. The arrows indicate the front surface of each fragment.

**February 3, 2014**

**What happens when crude oil is exposed to sunlight?** As the worldwide consumption of petroleum increases, producers are using lower quality petroleum to meet the demand. Heteroatomic species in low-quality petroleum (e.g., sulfur-, nitrogen-, and oxygen-containing compounds) can poison catalysts during refining, corrode containers and pipes, and damage the environment when they are released by petroleum fuel combustion or by spills and leakage during transport.

Exposing petroleum to sunlight produces changes that affect its solubility and toxicity. M. P. Barrow and co-workers at the University of Warwick (Coventry, UK) simulated the effects of exposing crude oil to sunlight and studied the results by using Fourier transform ion cyclotron resonance mass spectrometry coupled with atmospheric pressure photoionization (APPI). They found that this technique is well suited to analyzing complex mixtures such as crude oil, especially when they monitored the effects of a particular process on the entire mixture.

The authors used a light-sour crude oil standard reference material obtained from the National Institute of Standards and Technology. Solar radiation was simulated by using a 35-W SoLux halogen bulb, which closely mimics natural sunlight. They compared the results with those obtained with a 4-W UV light and a control sample that was shielded from light. The samples were analyzed after 938 h ( $\approx 5.5$  weeks) of exposure.

The postexposure analysis showed that the control sample changed very little, and the sample exposed to the UV source became more viscous. The sample exposed to the SoLux source resembled a solid more than a liquid, and it exhibited the greatest composition change. Compounds that contained heteroatoms underwent photo-oxidation more readily than did hydrocarbons. Oxygen-containing species increased, but nonoxygenated sulfur- and nitrogen-containing species decreased significantly, indicating photoinduced oxidation. The oxygen-containing species may be acidic, soluble, and bioavailable; and therefore it is potentially toxic in a marine environment.

Reactivity was more closely associated with compound class and the number of double-bond equivalents than with carbon number. Compounds with fewer double bonds were more reactive, with some exceptions. The hydrocarbon components were highly stable. The polyaromatic hydrocarbons were especially stable, making them good markers for the origins of spilled or leaked petroleum after prolonged exposure to the environment. (*Anal. Chem.* **2014**, *86*, [527–534](#); [Nancy McGuire](#))

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**January 27, 2014**

**Stormwater runoff gives chemical clues to its origin and history.** The concentration and characteristics of dissolved organic matter (DOM) in runoff water are determined by the original source of the organic material and biogeochemical processing that occurs during transport through watersheds. This information can serve as important indicators of the health of an ecosystem. Although the types and amounts of DOM from forests and agricultural land runoff have been studied extensively, recent studies indicate that these results are probably not applicable to runoff from urban areas.

S. P. McElmurry\*, D. T. Long, and T. C. Voice at Wayne State University (Detroit) and Michigan State University (MSU, East Lansing) evaluated the effects of land cover, solution chemistry, climate, and other factors on DOM characteristics in runoff water from urban and suburban areas. They collected 146 samples from 48 locations in central Michigan's Grand River watershed within 24 h of runoff events such as heavy rainstorms. Of these sites, 29 receive more than 95% of their runoff from ground sources with a single type of land cover.

The authors compared runoff from forested and agricultural lands with that from golf courses, parking lots, and storm sewers on MSU's main campus. The sewer water came primarily from parking lots, rooftops, and landscaped areas dominated by grass lawns. Environmental data, including precipitation and solar radiation, were collected from a weather station on the MSU campus. They used statistical analysis to identify correlations among the various examined factors and to determine which factors had the most influence on DOM concentrations and characteristics.

The authors conclude that urban landscapes produce DOM with lower molecular weights and higher aromaticity than more natural landscapes. Urban and suburban landscapes have significantly different hydrologic flow paths, which are likely to influence the characteristics of DOM in the respective runoff waters. Land cover and environmental factors combine to determine DOM characteristics, so studies of runoff from natural environments should not be extrapolated to draw conclusions about runoff from paved surfaces and storm sewers.

The authors note that significant changes to urban infrastructure and land use practices will be required if urban runoff water is to be restored to a state that more closely resembles natural runoff water. (*Environ. Sci. Technol.* **2014**, *48*, 45–53; [Nancy McGuire](#))

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January 20, 2014

**Reduce lubricating oil's carbon footprint by re-refining used oil.** Re-refining used oil reduces the need to produce base oil from crude oil sources, and it eliminates emissions associated with disposing used oil. Base oil, also known as mineral oil, is a finished petroleum stock that can be blended with additives to produce lubricants for internal combustion engines.

Re-refined base oil has properties that are almost identical to those of base oil produced from crude oil in a refinery. L. N. Grice, C. E. Nobel, and coauthors at ENVIRON International (Denver) and Safety-Kleen Systems (Plano, TX) found that the life-cycle carbon footprint for re-refined base oil is 81% lower than that for an equivalent product derived from virgin stock (*see figure*).

Previous studies evaluated the waste management aspects of re-refining used oil compared with burning it to produce heat or

electricity; but these studies did not factor in the upstream greenhouse gas emissions during the production and processing phases. Grice et al. evaluated greenhouse gas emissions in all phases: extraction, transport, base oil production and refinement, and end-of-life management.

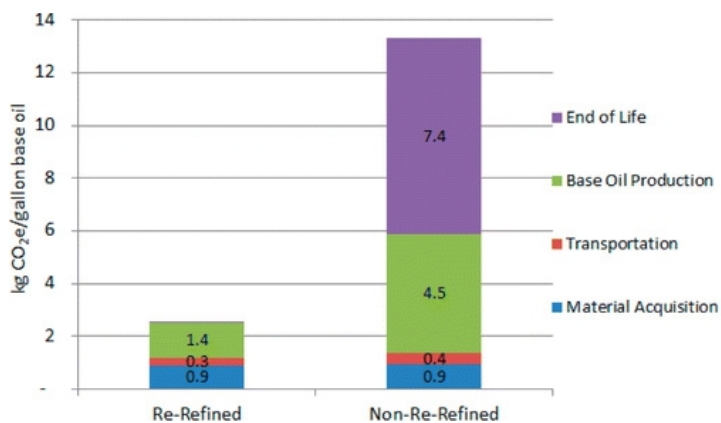
The authors did not address transport to the customer or customer use of the base oil because these factors are similar for re-refined and virgin-stock base oils. For the re-refinement scenario, they assumed that the oil would be reused and re-refined repeatedly until it was used up. This meant that 1 gal of re-refined oil would have the usage equivalent of 7.14 gal of one-use oil.

The study factored in operations information, including electricity used and miles traveled, based on primary data from Safety-Kleen operations records. Base case (first-use oil) process activity data and emission factors were obtained from academia and industry data.

The key differences in life cycle emissions between the base case and the re-refined oil are associated with production and waste management. Electricity, natural gas, and refinery fuel used during re-refinement account for 57% of the carbon footprint of re-refined base oil, whereas initial production of the base oil accounts for only 29%. For base oil that is not re-refined after the first use, the initial production accounts for 34% of the carbon footprint, and disposal (combustion or dumping) accounts for 56%.

The authors summarized the ranges of results that they obtained using various values for their model parameters. In all cases, the re-refined base oil produced less than half of the greenhouse gas emissions over the course of its life cycle than did non-re-refined base oil. (*ACS Sustainable Chem. Eng.* **2014**, *2*, [Article ASAP](#); [Nancy McGuire](#))

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**January 13, 2014**

**Milk digestion produces a complex series of organized nanostructures.** Dairy milk is a protein-stabilized emulsion of water- and oil-soluble vitamins, salts, proteins, carbohydrates, fat, and other hydrophobic components. Absorption of milk fat by the enterocytes (absorptive cells in the small intestine) relies on lipase-catalyzed hydrolysis into fatty acids and monoglyceride, but little is understood about this process.

B. J. Boyd and coauthors at Monash University (Parkville, Australia) and the Australian Synchrotron (Clayton) discovered that highly ordered geometric nanostructures form as milk undergoes an in vitro digestion process designed to mimic natural digestion. They used a high-intensity synchrotron source and time-resolved small-angle X-ray scattering to track the transition of milk from a normal oil-in-water unstructured emulsion through a series of ordered nanostructures. They displayed the results by using cryogenic transmission electron microscopy.

Adding pancreatin (a mixture of amylase, lipase, and protease) to the milk emulsion at pH 6.5 and 37 °C converts the milk triglycerides mainly to diglycerides and fatty acids. During digestion, the lipid cores of the milk particles gradually become more hydrophilic as water and hydrophilic molecules move into the lipid phase.

In the absence of bile salt, lipase-catalyzed digestion causes water-filled micelles to form within the oil droplets. As the digestion progresses and more water is incorporated into the system, these micelles self-organize into a cubic lattice and then form water-filled tubes that pack into a hexagonal array that evolves into a bicontinuous cubic array. The high internal surface area of these structures might facilitate lipid digestion in bile-compromised individuals.

Adding bile salt accelerates the digestion of the milk lipids. Within 1 min after adding pancreatin, milk is transformed into a microemulsion that contains multilamellar fragments as long as 400 nm, tubular structures, and unilamellar vesicles—but no higher-ordered liquid crystalline structures. After 30 min, vesicles are the dominant structures. The bile salt is incorporated into the self-assembled structures inside the emulsion particles, creating more hydrophilic interfaces and swelling the internal structures.

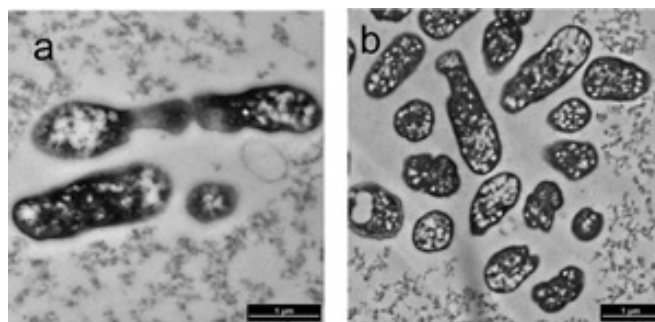
Decreasing the pH of the system "back-tunes" the morphological changes developed during digestion and shifts the balance toward the structures formed earlier in the digestive process. (*ACS Nano* **2014**, *8*, [10904–10911](#); [Nancy McGuire](#))

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January 6, 2014

**Bacteria set up housekeeping in silica cages.** For almost 20 years, scientists have known how to entrap living bacterial cells in silica matrices. Trapped cells have potential use in drug screening, biological sensing, and building bioreactors. They can remain viable for >1 year; the entrapment process does not cause the cells to express stress-response genes; and the cells remain metabolically active. The cells lose their ability to divide, however, and they are physiologically compromised by their entrapment.

J. D. Brennan and coauthors at McMaster University (Hamilton, ON), Lund University (Sweden), the University of California, Riverside, and the University of Guelph (ON) entrapped *Escherichia coli* cells in a sol-gel-derived mesoporous silica matrix in such a way that the cells can divide. The cellular pathway regulation is similar to that in solution, and promoters in the entrapped cells can be specifically induced with small molecules.



The researchers used mild conditions to form the mesoporous silica matrix. The bacteria cells were introduced in a biofriendly buffer solution (phosphate-buffered saline) that promoted rapid gelation. When the buffer was combined in a 1:1 v/v ratio with a sodium silicate precursor sol, a biologically inert silica matrix was formed, and only water was released upon gelation.

The authors used a strain of *E. coli* bacteria that contained transcriptional fusions of green fluorescent protein to promoters that report on cell growth, cell division, the cell envelope, heat shock, osmotic stress, and transition into the stationary (nondividing) phase. Additional promoters were selected for their response to antibiotics with known modes of action to compare the entrapped bacteria's response with bacteria in solution.

The researchers showed conclusively that the entrapped cells grow and divide, are not perturbed at the promoter level by the entrapping matrix, and respond in a concentration-dependent manner to small molecules that induce specific promoters. Transition electron microscopy showed that the entrapped bacterial cell clusters expanded into space that was formerly occupied by silica particles (*see figure*). The silica gel was formulated for a low degree of cross-linking, which allows the expanding cell clusters to rupture siloxane bonds and enlarge the pores in the matrix.

Screening several promoters against 25 antibiotics with known mechanisms of action showed that the upregulation of genes by small molecules was essentially identical for entrapped cells and cells in solution. The antibiotics could access the entrapped cells, whose promoter regulation remained intact after entrapment. These studies set the stage for developing new solid-phase bioassay formats based on entrapped live cells, including sol-gel-based living-cell microarray platforms. (*Chem. Mater.* **2014**, *26*, 4798–4805; [Nancy McGuire](#))

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**December 16, 2013**

**Polar solvents and oxygen functionalities increase coal-extraction yields.** HyperCoal (HPC) is an ashless product made by the thermal solvent extraction of a natural coal. It is free of mineral matter and inert organic compounds; and it has good softening properties, which reduce the tendency to form clinkers. HPC is expected to be useful as a fuel for low-temperature catalytic gasification or as coking coal for steel production.

N. Sakimoto, K. Koyano, and T. Takanohashi\* at the National Institute of Advanced Science and Technology (Tsukuba, Japan) investigated the influence of polar extraction solvents and oxygen functional groups in the coal on extraction yields. Hydrogen bonding in low-rank coals reduces the extraction yield, but these hydrogen bonds can be broken by the action of a polar solvent on the oxygen functional groups of the coal.

Previous studies showed that polar solvents increase extraction yields. As the solvent polarity increases, the extraction yield is influenced less by the oxygen content of the dry, ash-free coal (O% daf) than by the C/H atomic ratio, indicating a greater influence of aromaticity. This suggests that polar solvents could increase the extraction yield of coals rich in oxygen functional groups, such as hydroxyl and carboxyl, that contribute to hydrogen bonding.

When 1-methylnaphthalene is the extraction solvent, extraction yields decrease with increasing O% daf in the coal. Adding indole to 1-methylnaphthalene increases the polarity of the solvent and weakens the effect of oxygen content on extraction yield. Yields increase linearly with increasing indole content up to 20 mass% for all coals investigated.

One of the coal types had numerous metal carboxylate bonds. The ionic cross-links among these bonds could not be released by using 1-methylnaphthalene. When the ionic cross-links were removed by treating the coal with acid, the extraction yield increased from  $\approx 30\%$  to almost 50%.

Another coal type had a high C/H atomic ratio because of its high aromatic content, which increases  $\pi$ - $\pi$  interactions between aromatic rings. In this coal, the extraction yield is less than half of the value that the correlation between oxygen content and extraction yield would predict.

For coals with up to 13% oxygen content, solvent effectiveness (ratio of extraction yield to indole content) increases almost linearly with increasing oxygen content. Above 13% oxygen, solvent effectiveness remains constant at  $\approx 0.8$ . One reason for the increase in effectiveness may be the solvent's ability to break hydrogen bonds in the coal.

Previous studies showed that polar solvents work by releasing the hydrogen bonds formed by phenolic hydroxyl groups. In this study, the authors found an almost linear relationship between the phenolic content of the coal and the extraction efficiency, indicating that this is the dominant factor in extraction efficiency. (*Energy Fuels*, **2013**, *27*, [6594–6597](#); Nancy McGuire)

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**December 9, 2013**

**What makes wheat beer smell like wheat beer?** Wheat beer is made from a mixture of wheat malt and a smaller amount of barley malt. It has a characteristic clovelike, slightly phenolic aroma. Although more than 600 volatile compounds that contribute to beer aromas have been reported, research on the nonphenolic aroma compounds in wheat beers is lacking.

D. Langos, M. Granvogl, and P. Schieberle\* at the German Research Institute for Food Chemistry and Munich Technical University (both in Freising, Germany) used a sensomics method to characterize wheat-beer aroma compounds. They identified and quantified key odorants in two commercial wheat beers and then simulated their aromas by recombining the key odorants in the concentrations present in the beers. The beers that they studied had the most (beer A) and least (beer B) "typical wheat-beer aroma" of nine beers that had previously been evaluated by a consumer panel.

The authors fractionated vacuum-distilled wheat beer diethyl ether extracts into acidic and neutral-to-basic volatiles. Each group was separated into its components with high-resolution GC-olfactometry and high-resolution GC-MS. The samples were also analyzed by stable isotope dilution assays.

The authors used tap water solutions of the aroma components to determine odor thresholds. They formulated aroma recombinates by adding the odorants to carbonated tap water adjusted to pH 4.2 (wheat beer pH). A panel of trained assessors evaluated the original beers and the recombinates in separate sessions. They used a seven-point scale to evaluate the intensity of flowery, clovelike/phenolic, malty, cabbage-like, pungent, caramel-like, and fruity/banana-like attributes. They confirmed that the recombine aromas were very similar to the original beers.

Almost all odorants were identical in the two beer samples. The most pronounced differences were in 2-methoxy-4-vinylphenol (clovelike odor) and 4-vinylphenol (smoky, leather-like odor), which were present in higher concentrations in beer A. Beer B had higher odor activity values for (*E*)- $\beta$ -damascenone (cooked apple-like), ethyl methylpropanoate (fruity), and linalool (flowery, citruslike).

Although ales and lagers contain ferulic acid, the precursor to 2-methoxy-4-vinylphenol, only in wheat beer is this compound's concentration higher than the odor threshold. The yeast strain used for fermentation affects the degree to which ferulic acid is decarboxylated to produce 2-methoxy-4-vinylphenol. Other contributors include various yeast metabolites, alcohols, and carboxylic acids. Dimethyl sulfide, another important aroma compound in wheat beer, has a positive influence on the overall beer aroma, but high concentrations may lead to off-flavors.

The results of this study can serve as a basis for further research into varying recipes or processing conditions to maintain a good beer flavor or to establish alcohol-reduced, alcohol-free, or gluten-free wheat beers. (*J. Agric. Food Chem.* **2013**, *61*, [11303–11311](#); Nancy McGuire)

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December 2, 2013

**Why are sulfone-based electrolytes stable at high voltages?** High-voltage cycling of batteries or capacitors can oxidatively decompose the electrolyte and degrade the device's performance. In lithium-ion batteries, traditional organic solvent-based electrolytes have oxidation potentials (vs Li/Li<sup>+</sup>) of  $\approx 4.3$ – $4.5$  V. Sulfone-based electrolytes are stable at 5 V or higher, which makes them an attractive alternative.

In contrast to the experimentally observed stability of sulfone electrolytes, the ab initio-calculated oxidation potentials ( $E_{ox}$ ) for isolated sulfones are lower than those for carbonates. W. Li and coauthors at South China Normal University (Guangzhou) and the University of Utah (Salt Lake City) investigated this apparent contradiction by using density functional theory (DFT) calculations to compare several sulfones and carbonates.

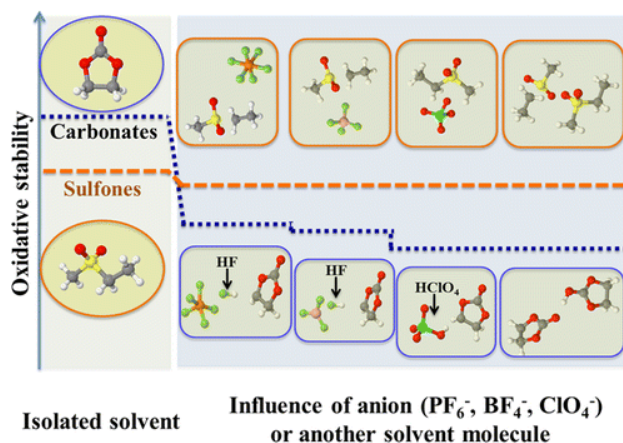
Single-molecule DFT calculations that use an implicit solvent shell produce oxidation stabilities for the investigated sulfones that are lower than for the investigated carbonates. This is inconsistent with experimental observations, which show higher anodic stability for sulfone-based electrolytes.

The inconsistency is resolved by including anions or additional neighboring solvent molecules in the calculation. The molecules in the first coordination shell strongly influence the potential and stability of the electrolyte molecules.

Anions and additional solvent molecules generally lower the oxidation stability of an electrolyte by participating in oxidation and decomposition reactions. For some of the sulfones, the calculated oxidation potentials are dramatically lowered in the presence of anions (PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, or BF<sub>4</sub><sup>-</sup>) or neighboring solvent molecules, which is similar to the carbonates' behavior. Other sulfones, however, are surprisingly stable in the presence of anions and neighboring solvent molecules, resulting in overall higher calculated oxidation potentials than those of carbonates.

When the authors compared  $E_{ox}$  for a series of solvent-anion clusters, they found that LiPF<sub>6</sub> is a more suitable lithium salt than LiBF<sub>4</sub> or LiClO<sub>4</sub> for a high-voltage electrolyte. LiClO<sub>4</sub> actually reduces the oxidation stability of the electrolyte and thus was the least suitable.

The authors also were able to design new oxidation-stable sulfones by modifying their functional groups. This is an important development in designing high energy-density lithium-ion batteries. (*J. Phys. Chem. Lett.* **2013**, *4*, [3992–3999](#); Nancy McGuire)



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