

SEEING THROUGH SOOT

Soot: it's a serious matter. Far from its charming appearance in the movie *Mary Poppins*, this fine particulate has been linked to both human and environmental health problems. Yet for all the growing body of evidence of its impact, soot remains a pestilentially difficult substance to study.

Soot is primarily carbon-based chemical by-products formed from incompletely combusted or uncombusted hydrocarbon-based fuels. It is produced by the burning of fossil fuels, especially coal, in power-generating facilities, as well as by diesel-powered vehicles, aircraft, wood-burning stoves and fireplaces, and the smelting of metals.

Soots differ from one another depending on their source, even as soots from the same source can differ depending upon the conditions of their formation, says Michael Zachariah, a professor of mechanical engineering and chemistry at the University of Minnesota in Minneapolis. "The soot that an auto diesel engine produces while pulling a trailer uphill will be very different from the soot that same engine produces in level highway driving," he says. "And soots from diesel engines are very different from soots from fireplaces or jet engines."

Soots are complex and variable mixtures of chemical compounds, says Michael Verkouteren, leader of the Atmospheric Chemistry Group at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, and that makes them difficult to characterize. Whereas some soot and particulate matter (PM) analyses are performed according to agreed-upon standards, others are not, he says, and the physical and chemical idiosyncrasies of different soots can bias many analytical methods.

Verkouteren says the immediate concern with design-based methodological protocols is that they provide precise results of unknown accuracy, because their design is usually based on incomplete information. "As further information and advanced technologies become available, the protocols tend to become modified and improved," he says. "The eventual result is many

methods used to generate data that are extremely difficult to intercompare.”

Verkouteren and Cary Presser, leader of the NIST Thermal and Reactive Processes Group, are now setting their sights on a new way to look at soot. They are in the earliest stages of a new project they believe will lead to the creation of a suite of synthetic soot particles that could allow for improved calibration of the analytical instruments used to measure PM.

Soot: A Spreading Health Hazard

Soot, which is classified as PM_{2.5} (2.5 µm in diameter or smaller), has been linked to significantly increased risk of death from lung cancer and other severe respiratory ailments. A study in the 6 March 2002 issue of the *Journal of the American Medical Association* by a coalition of health care and environmental groups and funded largely by the NIEHS found that the number of deaths from lung cancer increases 8% for every 10 µg/m³ PM_{2.5}. Fine particles of this size and smaller are of particular concern, as

several studies have indicated 2.5 µm as a possible threshold size at which particles are able to evade the body's natural defenses and migrate deep into the lungs. PM_{2.5} costs an estimated \$250,000–\$1 million in health care expenses per ton of emitted product, according to Mark Jacobson, an associate professor of civil and environmental engineering at Stanford University.

PM is classified as a “criteria pollutant” by the U.S. Environmental Protection Agency (EPA), Verkouteren explains, or an air pollutant for which the EPA has established a National Ambient Air Quality Standard. These pollutants are measured in air quality control regions to determine whether the area meets federal air quality standards.

“The problem is that [PM is] the only criteria pollutant without a chemical identity,” says Verkouteren. “Regulation is based solely on the mass of PM—the amount trapped on a filter over a given period of time. But there's no distinction based on its composition.” He says that industry's concern has been that if the measurements used to determine compliance with air quality regulations have unknown uncertainties, the decisions and costly actions subsequently taken to reduce the problem could be compromised and ineffective.

Jacobson says worldwide soot production is on the order of 7–10 billion kilograms annually. Soot has been labeled as perhaps the second-largest contributor to global warming after carbon dioxide.

Jacobson estimates that because of its ability to absorb and reradiate the sun's heat, soot may be responsible for 15–30% of global warming.

“These particles can have an environmental lifetime of one to three weeks,” he says. “That means they can drift thousands of kilometers, so you can have emission sources impacting health and the environment far away from the original source. Soot has been found at the South Pole, with no major emission source for thousands of kilometers.”

This extended lifetime leads to another potentially serious problem—combination with other chemicals in the atmosphere. Jacobson says soot can start out as simple black carbon, but can serve as a collection/mixing point for a wide range of other chemicals, including sulfates and nitrates—soot not only serves as a platform where these compounds can mix with one another, but also combines with them to form different substances.

The exact nature of this mixing and the possible environmental impact of the substances formed is still a matter of study. A study by scientists at the research organization SRI International, published in volume 24, issue 4 (1997), of *Geophysical Research Letters*, showed that soot particles are able to catalyze a variety of chemical reactions that do not occur in their absence. For example, soot surfaces are able to convert nitric acid to nitrogen dioxide and nitric oxide. This phenomenon could have a serious effect on the atmosphere, because atmospheric ozone levels are very sensitive to concentrations of nitrogen dioxide and nitric oxide.

Once this carboniferous PM enters the atmosphere, says Verkouteren, it encounters a stew of other substances.

“We see that PM is dominated in the western United States by nitrates, and in the eastern United States by sulfates,” he says. “But there are hundreds of organic compounds involved, not to mention molds, pollens, trace metals, and so on. It's all part of a very complex system of interaction, which can vary even within a single location by time of day, temperature, humidity, and so on.”

According to Presser, soot measurements from the field currently are compared with standard reference PM that is collected at specific EPA sites around the country and then characterized with various analytical instruments. This method does not allow a clear traceability to the



source of each PM sample or enable reproducibility of the PM characteristics. Thus, what is needed, says Presser, is a suite of PM samples in which the pedigree of each PM class is clearly traceable to the source operating conditions and associated uncertainties, and in which the PM can be reproduced with specified uncertainties so that intercomparison of results from different analytical instruments can be made on an equal footing.

A New Look at Measuring Soot

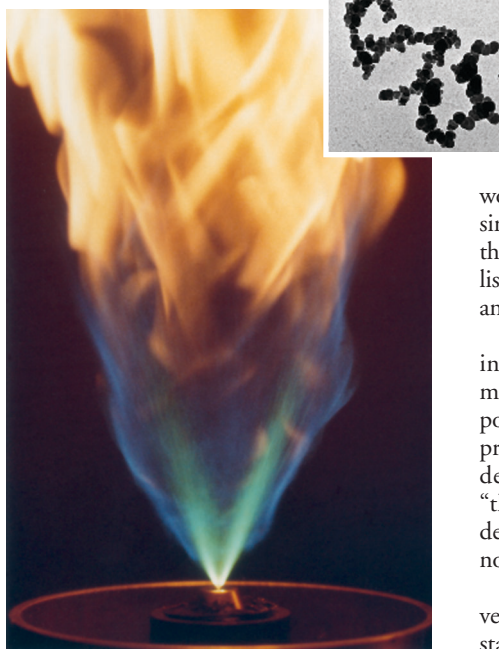
Verkouteren and Presser's project involves producing soot under very controlled conditions, in which temperature of combustion, fuel source, fuel composition, and other factors are all known and controllable. "We want to be able to control what we put in," Presser says, "which will enable us to control what we produce. Then we can also characterize any uncertainties, so we can provide industry with materials with certain clearly specified uncertainties, materials we can reproduce in a controlled fashion." He adds, "We don't want to try to measure everything under the sun, but will instead focus on more relevant physical and chemical parameters that will clearly be of value to industry."

"One of the most uncertain measurements is for black carbon," says Verkouteren. "No one really knows exactly what black carbon is, but we do know it's a rather reactive substance, in that it absorbs all sorts of toxic organics and other substances from the air. So the amount of black carbon [in the air] could be a good indicator of health risks. But we've sent samples to different labs, and come back with black carbon readings of anywhere from eight percent to fifty percent, which underscores the need for reference materials to standardize measurements and improve interlaboratory reproducibility."

The NIST research spray combustion facility, where the synthetic soots will be created, does not emulate real-world conditions of industrial reactors such as furnaces

or gas turbines; such systems are far too complex to reproduce in the lab. Instead, the facility simulates different phenomenological conditions, such as air swirl intensity and fuel-air stoichiometry, that are found within real-world industrial combustion systems.

Ultimately, says Presser, he wants to simulate as closely as possible the type of soot found in the environment. This will require as much flexibility in the system as possible, so that the operating conditions can be changed to influence and control the soot characteristics.



A burning question. A heptane flame is used to create synthetic soot that researchers hope will help to characterize these enigmatic particles. An electron micrograph shows a typical soot structure (inset) that was formed by the aggregation of particles. Such structures make up a significant portion of particulate air pollution.

The first synthetic soot has come from burning heptane (C_7H_{16}). Heptane is convenient for its simple composition,

and a lot is known about its chemistry and its soots. "We started with liquids because they're more representative of reality, and we can more accurately control the composition of what we put into the reactor," Presser explains. "The next step will probably be something more complex, such as toluene, which is a highly sooting fuel."

What about something solid, such as coal? "Probably not," Presser says. "As you add more chemicals into the mix, things become much more complex. If you look at something like high-sulfur coal or diesel oil, there's a tremendous number of organics and other substances involved, which makes it a more difficult process to study. You can't make things so complicated that you can't control and interpret what goes on, or too simple that it won't reflect reality. Our plan was to start simple and build from there." Presser says that benchmark data obtained will be published in archival journals, as NIST reports, and on the Internet.

Typical users of such a product would include any industry requiring reference materials, Presser says—for example, transportation, construction, power and energy producers, and health, environmental, and defense groups. "In addition," he says, "these products would be useful for model development and for calibration of diagnostic tools."

The project is ambitious and potentially very valuable, says Zachariah. "Developing standards is certainly worth taking a crack at, because those standards could be invaluable steps on which to base future measurements. And they'd help provide valuable historical records," he says. "If lab X did a study on soot, then when lab Y does a study on soot from a different source, they could reference back to that project. That would allow two different research groups to compare instrumentation and results. You need to have standards to be able to regulate anything, and the more you can put to rigorous standards, the better your regulatory results will be."

For a variety of reasons, Presser admits, any synthetic soot will be only moderately representative of environmental PM. Because of the exceptional complexity of soot, and the many unknown and uncontrollable variables of its interaction with the environment, soot will remain a complex and illusive product. Presser's hope is to make what we do know of it both clearer and more precise.

Lance Frazer

Suggested Reading

- Science Assessment and Integration Branch, Meteorological Service of Canada. 2001. Precursor contributions to ambient fine particulate matter in Canada. Toronto, Ontario: Meteorological Service of Canada.
- Widman JF, Presser C. 2002. A benchmark experimental database for multiphase combustion model input and validation. *Combust Flame* 129:47–86.
- Anderson JW. 1997. Revising the air quality standards: a briefing paper on the proposed National Ambient Air Quality Standards for particulate matter and ozone. Issue brief. Washington, DC: Resources for the Future. Available: http://www.rff.org/issue_briefs/PDF_files/NAAQS_primer.htm [accessed 15 July 2002].