Aerosol optical tweezers advance understanding of airborne particles

21 February 2020, by Ben Panko

Two studies led by faculty in Carnegie Mellon University's Center for Atmospheric Particle Studies show how aerosol optical tweezing can allow scientists to scrutinize the components of the atmosphere with new precision.

"What this allows us to do, really for the first time, is directly probe and understand how particles evolve in the atmosphere," said Ryan Sullivan, associate professor of chemistry and mechanical engineering, who is the first scientist in North America to make use of optical tweezer technology to study aerosol particles suspended in air.

Optical tweezers take advantage of the small forces exerted by light to trap and gently manipulate small particles or droplets. Arthur Ashkin won the 2018 Nobel Prize in Physics for developing this technique. In aerosol optical tweezing (AOT), individual particles are gently levitated, or "tweezed," in a laser beam, while a Raman vibrational spectrum of the particle is collected using the same laser light.

"With other techniques, you kind of get a static snapshot of the particle," Sullivan explained. But with AOT, researchers can watch the same particle for hours as it changes in response to different stimuli, which is a much more realistic way to observe how they might behave in the real atmosphere.

"Particles float around in the atmosphere for at least a week on average," Sullivan said. "They're so dynamic—their composition and other properties are constantly evolving."

That evolution can result not only in the changing of particles emitted into the atmosphere from Earth, but in entirely new ones that are being formed. Secondary organic aerosols (SOAs) are molecules formed directly in the atmosphere from the oxidation of organic molecules, such as those emitted by trees, vehicles and consumer products. These particles are an important but highly variable component of the atmosphere and can have effects on pollution, air quality, clouds and climate, and human health.

In a 2017 study in the journal Environmental Science & Technology, Sullivan's lab captured and analyzed secondary organic aerosol for the first time with AOT. He was assisted by Neil Donahue, a professor of chemistry and chemical engineering, and Kyle Gorkowski, a postdoctoral researcher at McGill University who worked on his Ph.D. under Sullivan and Donahue.

"It's very complex material," Sullivan said of working with SOA, which they generated directly in the AOT chamber from ozone reacting with the organic vapor ?-pinene, a terpene molecule released by trees. "You will get dozens or hundreds of different chemical products as a result—it's like a runaway chain reaction with all sorts of branching."

This SOA is a major component of atmospheric particulate matter and the AOT approach provides a unique way to directly study its properties and chemistry.
Using their tweezed SOA particles, Sullivan and his collaborators published a study the following year in the journal *Environmental Science: Processes & Impacts* reporting their new method to analyze the properties and morphology of particles that separate into two separate chemical phases based on the Raman spectra collected from the AOT. In most cases the SOA formed a separate shell phase around another core phase, and their new analysis allowed them to determine the properties of both phases as they change through continued chemical reactions.

The results were the first direct confirmation of what researchers had suspected about SOA droplets—that they would "phase separate" in the atmosphere, forming a core of aqueous or hydrophobic organic material surrounded by a shell of oxidized secondary organic material.

Understanding the exact morphology of SOAs is important, Sullivan noted, because what's at the surface of a particle can determine how easily it reacts with other gases, water vapor and light in the atmosphere. For example, many important trace gases in the atmosphere react much more quickly with aqueous phases than with organic material.

"If I'm a molecule that really wants to react with water, and I have to burrow and diffuse through this organic shell, I may not reach the aqueous phase that I want to react with in time," Sullivan explained. These organic shells can thus shut down important gas–particle reactions.

In a new study published in the journal *Chem*, Sullivan, Donahue and Gorkowski restaged the experiments behind the team's 2018 work showing phase separation of SOA but under different conditions.

"We wanted to see if the conclusions we had drawn about phase separation and morphology for secondary organic aerosol at higher relative humidity held at lower relative humidity when there is less water vapor around," Sullivan said. "And they do."

Furthermore, the study compiles results and observations from previous research to build a predictive formula for when a phase separation would occur when different organic materials are oxidized under different conditions, and what the morphology of that resulting complex phase-separated particle including SOA would be. Sullivan believes this new insight can be incorporated into current chemical models that predict the behavior and evolution of atmospheric particles over global scales.

In another new study, Sullivan, Gorkowski, and Hallie Boyer, an assistant professor of mechanical engineering at the University of North Dakota and former postdoctoral researcher at Carnegie Mellon, developed a technique to precisely measure the pH of tweezed droplets to determine their acidity. The research was published in the journal *Analytical Chemistry*.

"The pH of droplets is a huge open question in the atmospheric chemistry of particles because acidity is such a key property for essentially all chemical behavior," Sullivan said. The property can not only affect how and if reactions occur between different particles, but it can also determine whether a particle ends up becoming phase separated or not.

While determining pH is not a difficult process
under normal circumstances, measuring it directly from suspended picoliter aerosol particles has challenged the atmospheric chemistry community for decades, Sullivan noted. In particular, the high concentration of ions in atmospheric particles leads the ions to interact with each other more so than in most substances, producing "nonideal" chemical interactions that can significantly alter the droplet's acidity.

By combining two different pieces of information uniquely determined from the Raman vibrational spectra of the particles, the team was able to develop a technique to overcome these challenges and measure the pH of each droplet directly with high accuracy. In addition, they were able to track changes in the droplet's pH. In forthcoming work, they also demonstrate the ability to observe changes in the pH of both the core and shell of phase-separated particles independently over time.

With all of the tools now in place, Sullivan is looking forward to building on all of this aerosol optical tweezing work by using the technique to study a wide variety of particles and chemical interactions in Earth's atmosphere in a realistic way.

"The optical tweezers allow us to for the first time directly probe the dynamic evolution of all these critical properties of atmospheric particles and how they feedback on each other as each particle continues to evolve," Sullivan said.

**More information:**


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