Georgia Tech

Research News

Georgia Institute of Technology
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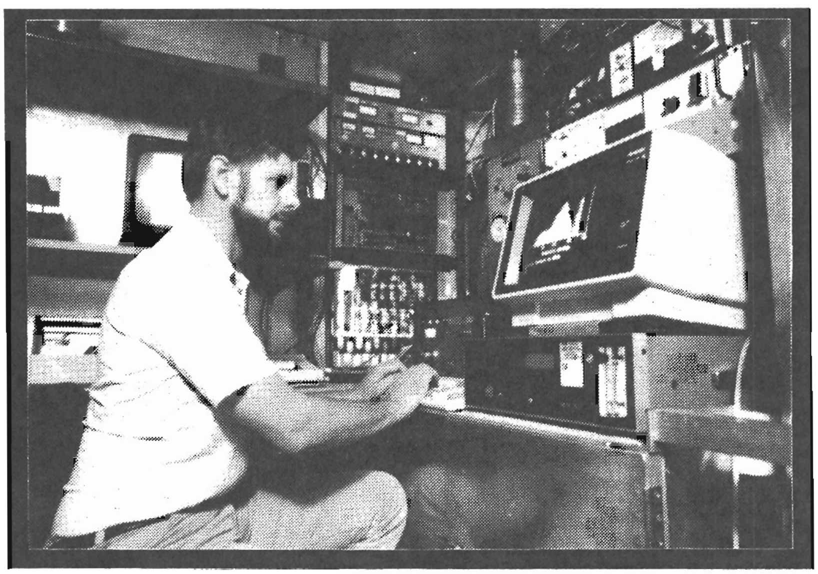
For Immediate Release
May 3, 1991

UNDERSTANDING THE ATMOSPHERE: CHANCE OBSERVATION LEADS TO BETTER METHOD FOR MEASURING KEY CLEANSING MOLECULE

A chance observation made four years ago under some Massachusetts power lines may provide scientists with a sensitive new technique for measuring an elusive atmospheric compound that plays a key role in cleansing the Earth's atmosphere.

Inspired by their observation, scientists at the Georgia Institute of Technology have developed a new technique to measure the hydroxyl (OH) radical. This highly-reactive molecule provides the single most important means for removing a number of persistent greenhouse gases from the atmosphere.



In his mobile laboratory, Dr. Fred Eisele uses mass spectrometry as part of a new technique for measuring concentrations of the OH radical. (Color slides/B&W prints available)

For instance, OH provides the primary means for initiating the destruction of many unwanted atmospheric species such as carbon monoxide, hydrocarbons like methane, and nitrogen dioxide. It will also play a key role in breaking down the newly-formulated refrigerants designed to replace current freons -- which are damaging the Earth's ozone layer.

As more and more compounds are released into the atmosphere, an accurate understanding of the role played by OH therefore becomes increasingly important. An improved ability to measure OH would help scientists better understand the complex photochemical reactions which take place in the atmosphere, helping clear up some of the mysteries that surround the global warming and ozone depletion issues.

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"As far as we have tested it, the technique looks very promising and has considerably more sensitivity than other methods available," said Dr. Fred Eisele, principal research scientist at the Georgia Tech Research Institute (GTRI). "People are very interested in the ability to measure OH on a very rapid time scale for modeling. This new technique should help improve our understanding of atmospheric photochemistry."

Formed in the atmosphere by a photochemical reaction, the OH molecule exists for less than a second before it reacts with other atmospheric constituents. It is therefore found in very low concentrations -- parts per quadrillion -- making it very difficult to measure. Three techniques were developed for measuring OH during the 1970s, but all suffer from problems with background interference, and none has yet provided a rapid measurement capability.

The GTRI ion-assisted technique takes advantage of the hydroxyl's highly reactive nature to initiate a chemical reaction with sulfur dioxide. Sulfur dioxide is added to air samples containing OH until all of the hydroxyl molecules are converted to sulfuric acid. The sulfuric acid can then be measured continuously by a highly sensitive mass spectrometer to provide an indirect measurement of how much hydroxyl was present.

Air containing OH is drawn into a special sampling device under conditions designed to maintain laminar flow -- keeping the center of the air column away from contact with the equipment walls. The technique relies on the use of isotopically-labelled sulfur dioxide, which allows Eisele to differentiate between sulfuric acid created in the measuring device and naturally-occurring sulfuric acid.

Since OH could reform catalytically within the measuring chamber, Eisele introduces propane to destroy any hydroxyl molecules that may be regenerated within the apparatus. The entire measurement cycle can be completed in less than a second.

"Our technique represents a totally new approach," he explained. "The advantage is that our total background interference is only about a third the height of the peak measurement of OH."

Eisele and research technician David Tanner have used their experimental apparatus to measure OH at the Mauna Loa Observatory in Hawaii, and at Sapelo Island on the Georgia coast. With support from the U.S. Environmental Protection Agency (EPA), they are currently working on an improved version which they hope will provide even more sensitive readings.

"Our goal is to convert the present very sensitive OH monitoring apparatus into a carefully tested, well-characterized and well-calibrated measurement instrument," said Eisele. "Our goal is a tool capable of measuring the OH radical with sufficient sensitivity and certainty that it will provide a meaningful test of photochemical models."

This summer, the Tech researchers plan to participate in a study comparing their readings to those provided by long-path absorption, one of the three existing techniques for measuring OH.

Eisele and Tanner hit upon the new technique while measuring ions under high-voltage power lines near Pittsfield, Massachusetts. While conducting background measurements, they noticed sharp changes in sulfuric acid concentrations whenever clouds passed overhead. Because OH is formed by a photochemical reaction which occurs only in the presence of sunlight, the two scientists suspected OH as the cause of the fluctuations.

"As the OH concentration rose and fell with the amount of incident sunlight, corresponding changes occurred in the amount of sulfuric acid," Eisele recalled. "A similar but more controlled sulfuric acid production mechanism was then used to measure the OH concentration."

The experimental Georgia Tech technique will be described in a paper accepted for publication in the Journal of Geophysical Research -- Atmospheres. The research was sponsored by the National Science Foundation (NSF) under grant # ATM 8717675 and with internal funding from the Georgia Tech Research Institute.

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