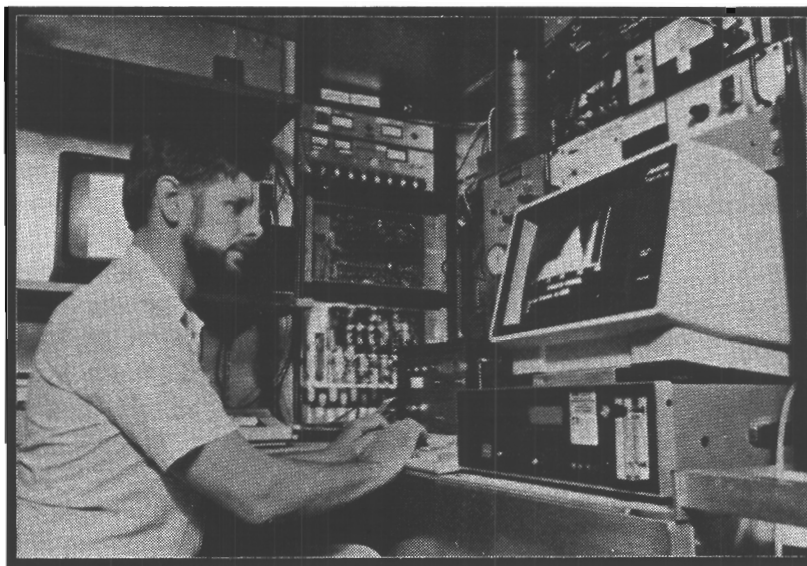


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UNDERSTANDING THE LOWER ATMOSPHERE: COMPARISON OF MEASURING TECHNIQUES ALLOWS BETTER TESTING OF ATMOSPHERIC MODELS

A comparison of two independent analytical techniques based on different physical principles has given scientists new confidence in their ability to measure concentrations of a molecule which plays a key role in controlling several greenhouse and ozone-depleting gases in the lower atmosphere.

The comparison demonstrated that atmospheric chemists can now measure the OH (hydroxyl) radical well enough to test complex atmospheric photochemistry models, researchers from the National Oceanic and Atmospheric Administration (NOAA) and the Georgia Tech



Dr. Fred Eisele uses a mass spectrometer in Georgia Tech's mobile laboratory as part of an ion-assisted technique to measure concentrations of the hydroxyl radical. (Color/B&W Avail.)

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Research Institute (GTRI) reported in the May 22 issue of Science magazine.

"For the first time, there is sufficient confidence in the accuracy of the OH measurements that scientists are starting to use them to test their photochemical models," said Dr. Fred L. Eisele, a Georgia Tech principal research scientist who collaborated with NOAA's Dr. George H. Mount in the study.

In addition to the confidence resulting from the comparison, the OH concentrations measured by the scientists were lower than expected, presenting "a new challenge to chemical theories of the lower atmosphere," Mount noted.

The OH radical provides the primary means for destroying many atmospheric

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gases such as hydrocarbons, carbon monoxide and nitrogen oxides. It will also be the primary mechanism for breaking down the new generation of refrigerants designed to replace CFCs. Before scientists can obtain a complete understanding of photochemistry in the troposphere, they must be able to accurately measure OH.

But because hydroxyl is so reactive, it exists in extremely low concentrations, making it difficult to measure. At least three techniques have been developed to study OH, but because of their complexity, many doubts have remained about their precision.

To verify the accuracy of existing measuring methods, NOAA and Georgia Tech scientists measured OH concentrations simultaneously at NOAA's Fritz Peak Observatory in Colorado during the summer of 1991 using two techniques: a long-path laser spectroscopic absorption technique and an ion-assisted chemical analysis method. Despite the differences in the two techniques, the researchers found surprisingly good agreement in results, lending strong credibility to the two experiments.

"The two measurements seem to agree well, certainly within the limits of errors of the two instruments," said Eisele. "The agreement is very encouraging. I think the fact that these different measuring techniques agree suggests that neither technique is probably in error by very much."

The study was the first to successfully measure OH using two independent techniques. Eisele and Mount believe the results of the comparison will reduce much of the skepticism concerning accuracy of OH measuring techniques. Both techniques were developed within the past five years.

The results, which provided comparable results in the study of both polluted and unpolluted air, may also lead to a review of models scientists now use to study atmospheric photochemistry.

The instruments measured less OH than was predicted by the models, suggesting that another unknown reaction may be depleting OH from the air. In the past, said Eisele, scientists studying such results would have questioned the OH measurement, but new confidence from the comparative studies may instead prompt a search for previously-unknown chemical reactions which may be causing the discrepancy.

"It has brought us to the point that we are testing the models rather than questioning the measurements," he explained. "I think there is still some skepticism, but it has died down tremendously with the comparison of these two dramatically different techniques."

NOAA's Mount used an ultraviolet laser to illuminate a retroreflector array at 10.3 kilometers distance, and measured the return signal for OH absorption using a very high resolution spectrograph and solid state array detector.

Eisele and Research Technologist David Tanner used an ion-assisted technique to indirectly measure OH by studying its reaction with isotopically labelled sulfur dioxide. By measuring the resulting gas-phase sulfuric acid with a sensitive mass spectrometer, Eisele could determine the concentration of OH.

Because Mount was observing OH over a 20 kilometer path, his results did not always match the results Eisele obtained at a single site on the ground. Those discrepancies can be explained by the varying conditions in the areas being measured, particularly fluctuations in the amount of sunlight -- which promotes the formation of OH.

Even though the results suggest good comparison between the methods, Eisele and Mount hope to obtain additional funding to repeat the studies for OH and related photochemical species. They would also like to include a third OH measurement technique.

Because existing techniques measure OH near the ground where chemical reactions can be affected by surface conditions such as vegetation, scientists want to know how well the data represents atmospheric reactions which occur above the surface. To remove the effects of local vegetation, Eisele and Tanner are monitoring OH concentrations at the Mauna Loa Observatory in Hawaii this summer.

Because of the observatory's altitude and remote location, it often receives unpolluted air from the middle of the troposphere -- the lower atmosphere. Eisele believes the results from Mauna Loa will be more representative of the chemistry which occurs in unpolluted areas of the lower atmosphere.

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The Georgia Tech measurement technique was earlier described in a May 3, 1991 news release.

The opinions, findings, conclusions and recommendations expressed herein are those of the authors and do not necessarily reflect the views of the National Science Foundation or Environmental Protection Agency.