

## EDITORIAL

**The Measurement of HO<sub>x</sub> Radicals in the Atmosphere**

This special issue of the *Journal of the Atmospheric Sciences* is devoted to measurements of the HO<sub>x</sub> family of radicals, OH and HO<sub>2</sub>, and the interpretation of these measurements so as to understand atmospheric photochemistry. Closely linked chemically, OH and HO<sub>2</sub> play key roles in the chemistry of both the troposphere and the stratosphere. The hydroxyl radical is the major oxidizer in the atmosphere; its concentration is buffered by the hundredfold larger HO<sub>2</sub> reservoir. Measurements of either or both species on a local (in situ) scale constitute excellent tests of our understanding of fast atmospheric photochemistry: OH has a very short lifetime, on the order of 1 s, and is present at very low concentration, on the order of 10<sup>6</sup> molecules per cubic centimeter, significantly less than one part per trillion. Its interference-free determination, with sensitivity and precision adequate to test atmospheric models, has posed an extreme experimental challenge over many years. Recently, there has been dramatic improvement in OH instrumentation, including the emergence of new concepts for its measurement, and at the same time steady improvement in the capabilities of HO<sub>2</sub> instruments. Several measurements have been made, both in the boundary layer and the stratosphere, which appear quite credible and provide important new information about atmospheric photochemistry. Thus, this is an excellent time to survey the topic of the determination of HO<sub>x</sub> in the atmosphere.

These papers have resulted from a symposium on OH and HO<sub>2</sub>, organized for the purpose of surveying the current state of the art of the measurement capabilities and the interpretation of field results on these radicals. The symposium was part of the Conference on Atmospheric Chemistry at the meeting of the American Meteorological Society, held in Nashville, Tennessee, in January 1994. The symposium participants were researchers engaged in measurements of OH and/or HO<sub>2</sub> and modelers who use these data to test our understanding of the pertinent chemistry. This combination is important because we need to have results that are not only believable but also meaningful; that is, they must be planned and performed in such a way to enhance our knowledge of the atmosphere.

The order of articles in this issue follows the order in the symposium. Following an article by myself that gives an overview of currently available OH and HO<sub>2</sub> methods and recent measurement results, Thompson discusses comparisons of measured and model-predicted OH and factors affecting precision in prediction. The next seven papers include all but one of the tropospheric OH instruments deployed in the field as of the time of the symposium. These seven papers discuss laser-induced fluorescence (Brune et al.; Hard et al.; Holland et al.), long-path laser absorption (Mount and Harder; Dorn et al.; Armerding et al.), and chemical conversion with mass spectrometry (Eisele). Both instrumentation and OH field measurements are described; some of the results raise interesting questions concerning tropospheric photochemistry. Poppe et al. follow these experimental papers on OH with a discussion of correlations and sensitivities in comparing measured and modeled OH.

For HO<sub>2</sub> determinations, three methods exist, two of which are represented in this issue (the third is matrix isolation/electron spin resonance practiced at Jülich). Conversion to OH and detection via laser-induced fluorescence is discussed in the articles on that topic in connection with OH. Cantrell et al. describe the technique of chemical amplification and recent results with their instrument.

Wennberg et al. then describe their laser-induced fluorescence instrument, which measures stratospheric OH and HO<sub>2</sub> aboard the ER-2 aircraft, and the striking new results that it has provided. Campbell et al. discuss a field intercomparison of two tropospheric OH instruments; one technique, not described above, relies on reactive conversion of <sup>14</sup>CO, and the other is based on laser-induced fluorescence. As described in the overview article and discussed in other papers as well, intercomparison missions such as this are essential

to establishing credibility for OH measurements. Finally, Heal et al. describe a new laser-induced fluorescence-based instrument not yet field tested but currently under development in the laboratory.

These 14 papers in the *Journal of the Atmospheric Sciences* thus provide a nearly comprehensive view of current OH and HO<sub>2</sub> measurement capabilities and recent results. Although many of the instruments are undergoing continued development and improvement, it appears that the ability is established to make reliable OH measurements on ground-based instruments in the boundary layer and in the stratosphere aboard the ER-2. Is it worth all the trouble? The results presented here convincingly demonstrate that direct, local measurement of OH is providing us with surprises, questions, and a far more definitive comprehensive picture of atmospheric photochemistry than we had before. The answer to the question is clearly affirmative.

*David R. Crosley*  
Guest Editor  
SRI International