The fluorometric gas-phase hydrogen peroxide procedure is based on the technique used by Lazrus et al. (1) for the determination of H$_2$O$_2$ in the liquid phase. The analytical method utilizes the reaction of H$_2$O$_2$ with horseradish peroxidase and p-hydroxphenylacetic acid (POPHA) to form the fluorescent dimer of POPHA. The analytical reaction responds stoichiometrically to both H$_2$O$_2$ and some organic hydroperoxides. To discriminate H$_2$O$_2$ from organic hydroperoxides, catalase is used to preferentially destroy H$_2$O$_2$. Using a dual-channel flow system the H$_2$O$_2$ concentration is determined by difference.

For the determination of H$_2$O$_2$ in the gas-phase, the liquid-phase analytical procedure is used with an inlet system which concentrates H$_2$O$_2$ in the aqueous phase. The following figure details the inlet system.

Sample air at 2 slpm along with 0.042 ml/min of aqueous solution is drawn through the scrubbing coil. The H$_2$O$_2$ is extracted into solution and analyzed directly using the fluorometric procedure. The detection limit for gas-phase H$_2$O$_2$ is better than 50 pptv. The system has been tested for potentially interfering species commonly found in the atmosphere. Minor interferences from sulfur dioxide (SO$_2$) and ozone (O$_3$) are observed. Sulfur dioxide gives an interference at a level of 1% of the H$_2$O$_2$ signal for each 10 ppbv of SO$_2$. The O$_3$ interference generates a H$_2$O$_2$ signal equivalent of 30 pptv for each 100 ppbv of O$_3$.

The gas-phase analytical system has been used on a number of ground and aircraft based field studies in the past year. Measured levels of H$_2$O$_2$ range from the detection limit to several ppbv.

This instrument has received much flight time and appears capable of detection limits < 50 ppt with minimal interference (chief culprits are SO₂ and O₃). Future improvements include the inlet system, the response time, and the ability to separate H₂O₂ from RO₂H. A calibration between this instrument and the tunable-diode laser determination has been performed at the 3-5 ppb level, which was near the detection limit for the diode system. It was reported at the workshop that satisfactory agreement between the two instruments was observed. This is important in that the spectroscopic method is very specific for H₂O₂ but not as sensitive as the fluorometric method.