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TUNABLE-DIODE LASER ABSORPTION SPECTROMETRY

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Tunable-diode laser absorption spectrometry (TDLAS) affords a number of advantages for atmospheric measurements. It is a universal method, applicable, in principle, to all gases of atmospheric interest. Because of its extremely high spectral resolution it provides unequivocal identification of the target species, with no interferences from other gases. It provides real-time, in situ measurements with time resolutions better than 1 minute.

We have constructed TDLAS systems suitable for both ground-based and airborne measurements. Although great improvements have been made in the detection limits achievable by these systems they are currently incapable of measuring HO at atmospheric concentrations. However, the addition of the new megahertz modulation techniques (proposed by D. E. Cooper) may make HO measurements attainable by TDLAS.

The sensitivity of the current TDLAS system is marginally capable of measuring HO_2. This species exists in the troposphere at concentrations which are up to 2 orders of magnitude higher than those of HO and, in addition, is much less susceptible to removal by the surfaces of the instrument and its sampling system. HO_2 is an important HO_x species in its own right but can also give direct information on the HO concentration by virtue of the rapid partitioning between these two species. The addition of the high-frequency modulation technique to the TDLAS system would ensure its ability to measure HO_2 under most atmospheric conditions.

On the other hand, we have demonstrated (Slemr et al., J.G.R.), the ability of the TDLAS to measure hydrogen peroxide (H_2O_2) in the ambient atmosphere. With the airborne system the detection limits should be better than 0.1 ppbv, which is sufficient to measure this species under most atmospheric conditions. H_2O_2 measurements give a clear indication of HO_x mixing ratios and are also important as a photolytic source of HO and as an important oxidant for other atmospheric consitituents such as SO_2.

Reference

Slemr, F., Harris, G. W., Hastie, D. R., MacKay, G. I., and H. I. Schiff. J. Geophys. Res., vol. 9, no. D5, pp. 5371-5378, April 1986.

Comments

This instrument can be used for both NO_2 and H_2O_2, with current limits of detectability at 40 and 300 ppt, respectively. This is acheived in 1 to 10 minutes of averaging, using a 0.7-m path length multipassed for a total absorption path of 40 m, allowing absorption at the 10^{-5} level to be measured. Improvements in the multipass capability should increase the path length to 200 m, lowering the detection limits to below 20 and 100 ppt for these two species.

Detection of HO_2 is marginal at the 10^8 per cm^3 level, but a combination with frequency modulation spectroscopy, such as discussed at the workshop by D. E. Cooper of SRI, may make this a viable method.