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TROPOSPHERIC HO_2 DETERMINATION BY FAGE

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In contained-flow HO analyzers, ambient HO_2 can be detected by its conversion to HO via

$$HO_2 + NO \text{ --> } HO + NO_2$$

The detection efficiency is greatest at low pressures, where the subsequent removal of the HO product by the NO reagent (via $HO + NO + M \text{ --> } HONO + M$) is relatively slow. Moreover, nozzle expansion of the air from ambient to low pressures produces a turbulent zone that assists in mixing the reagent with the sample. If the HO product is observed by laser-excited fluorescence, then the other advantages of low-pressure detection by FAGE (Fluorescence Assay with Gas Expansion) also apply.

The method and some of its potential interferences are set forth in Reference 1. Regarding RO_2, we incorrectly assumed that the intermediate reaction $RO + O_2 \text{ --> } R'CHO + HO_2$ is instantaneous in our pressure range; correction reduces this interference considerably. When NO is the modulating reagent, any contaminant that fluoresced (or gave photolytic HO) would produce a false positive HO_2 signal. This can be prevented by using a steady NO flow, modulating the resulting ambient HO_2 + HO signal with an HO-removing reagent, and performing a parallel determination of ambient HO in another channel.

We have calibrated the FAGE instrumental response to external HO_2 by observing NO decay in the photolysis of $HO\text{-}CH_2O$ mixtures and by choosing conditions in which $HO_2 + NO$ is the only significant NO destruction path. We have determined HO_2 in urban air.

Reference

T.M. Hard, R.J. O'Brien, C.Y. Chan and A.A. Mehrabzadeh, Environmental Science and Technology 18 768-777 (1984).

Comments

Using this chemical conversion/LIF detection of OH method, this group estimates that HO_2 can be detected at levels of 60 to 120 × $10^6/cm^3$ in a 6-minute average. They claim it is specific to HO_2 in that other peroxyl radicals, such as methyl peroxyl, can be prevented from yielding OH at low pressure due to kinetic freezing out. Current calibrations are by NO decay due to HO_2 + NO in the absence of O_3, and HO_2 decay due to HO_2 + NO_2 in the absence of NO, NO_2, and O_3. These two methods give differing results by a factor of 2, and it will be necessary to resolve such discrepancies. The workshop participants felt that the method appeared sound from a spectroscopic/laser basis, but that there remained questions concerning its chemical aspects.