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THE DETERMINATION OF THE GLOBAL AVERAGE OH CONCENTRATION USING A DEUTEROETHANE TRACER

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It is proposed to measure the decreasing global concentration of an OH reactive isotopic tracer, C_2D_6, after its introduction into the troposphere in a manner to facilitate uniform global mixing. Analyses at the level of 2×10^{-19} mole fraction, corresponding to one kg uniformly distributed globally, should be possible by a combination of cryogenic absorption techniques to separate ethane from air and high sensitivity isotopic analysis of ethane by mass spectrometry.

Aliquots of C_2D_6 totaling one kg would be introduced at numerous southern and northern latitudes over a 10 day period in order to achieve a uniform global concentration within 3 to 6 months by the normal atmospheric circulation. Then samples of air of 1000 ℓ (STP) would be collected periodically at a tropical and temperate zone location in each hemisphere and spiked with a known amount of another isotopic species of ethane, $^{13}C_2H_6$, at the level of 10^{-11} mole fraction. After separation of the ethanes from air, the absolute concentration of C_2D_6 ($C_2D_6/^{13}C_2H_6 \sim 10^{-8}$) would be analyzed using the Argonne 100-inch radius mass spectrometer. The effective global average concentration of OH is determined by

$$[\overline{OH}] = \frac{1}{kt} \log \frac{[C_2D_6]_o}{[C_2D_6]_t}$$

where the rate constant for the oxidation of C_2D_6 by OH, $k = 3.06 \times 10^{-11}\, \ell^{-\frac{1834}{T}}$ cm^3 $molecule^{-1}$ sec^{-1} (C. M. Stevens and Bunschul, unpublished). For an average OH concentration of 10^6 molecules/cm^3 the lifetime is 1.1 years.

Concentration differences of C_2D_6 due to hemispheric and seasonal differences in OH concentration should be observable within the expected accuracy of the analyses of ± 1 to 3%.

The principal technical difficulties are expected to be non-uniformities in the mixing of the tracer and the uncertainty of the competitive scavenging of C_2D_6 by Cl radicals (Chiltz et al., 1963), estimated at 20% of the OH removal rate (Aiken et al., 1982).

Chiltz, G., R. Eckling, P. Goldfinger, G. Huybrechts, H. S. Johnson, L. Meyers, and G. Verbeke, J. Chem. Phys. 38, 1053 (1963).

Aiken, H. C., J. R. Herman, E. J. Maier, and C. J. McQuillan, "Atmospheric Chemistry of Ethane and Ethylene," J. Geophys. Res. 87, 3105-3118 (1982).

Comments

This concept received widespread approval from many workshop participants, not as a check on current levels of OH but as a method to set a series of measurements to be carried out over many years. The idea is to repeat the measurements over each 5 to 10 year period for several decades. It can then be used to obtain a determination of any change in the oxidizing capacity of the atmosphere, a parameter of direct utility in forecasting future changes (one estimate places a 25 percent decrease in this quantity over the last 35 years). For example, has the increase in tropospheric ozone increased or decreased OH?

With a large mass spectrometer as suggested here, 10^{-10} mole fraction of the released reactant can be determined in 5 minutes. A fully globally mixed 1 kg sample will yield 6 molecules/cm^3. The choice of C_2D_6 is a good one but should be looked at further. Are there any possibilities that it will be released outside this experiment, thus contaminating the results? (What are other uses for this compound?) Background measurements should be made to address this; these should be easy to do. There is concern about the effects of $C\ell$ atoms in the atmosphere; at likely concentrations worldwide and with probable reaction rates, they will account for about 20 percent of the total C_2D_6 loss rate according to some estimates. Another participant however felt there was too little $C\ell$ in the troposphere to cause any loss.

Perhaps less ambiguity can be achieved using other compounds, for example $CD_3CF_2CD_3$, which is less common and will have far less contamination. Of course, reaction rates will need to be carefully determined in the laboratory. Multiple releases using different reactants (the use of three was suggested) may be valuable in this regard. Unsaturated compounds react with O_3 not OH, so saturated hydrocarbons are better.

Of major concern are large nonuniformities in concentration resulting from release and subsequent circulation patterns. These could cause a large error in the decay rate if not properly accounted for including nonuniformities in the oxidizer concentrations. Calculations with a global circulation model are needed here. For example, the concentration of C_2H_6 has been found to vary at certain locations by a factor of 3 on a seasonal basis. Nonreactive tracers would help here although no suitable species has been found for this purpose yet. Some participants were concerned about errors in the measurements, that is, nonrepeatability due to differences in tropospheric circulation and chemistry. This was estimated as high as 15 percent for a given measurement for a homogeneously released compound with a chemical lifetime of one year, measured one year after release. For the C_2D_6 considered here, things could be worse. Again, calculations with a global circulation model need to be performed to address these questions.