

Measurement of organic nitrates in the atmosphere using thermal dissociation/cavity attenuated phase shift spectroscopy

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Peroxyacyl nitrates (PANs) and alkyl nitrates (ANs) act as one of the reservoirs of nitrogen oxides (NO_x) in the atmosphere. Since their lifetime is longer than that of NO_x , they can be transported over a long-distance and would be important as trans-boundary pollutants. PANs and ANs are generally observed using GC/ECD (gas chromatograph / electron capture detector) or GC/NICI-MS (gas chromatograph / negative ion chemical ionization-mass spectrometry) method. While these GC methods can measure concentrations of each constituent in PANs and ANs, they have low time resolution. Measurements by GC/ECD which has radioisotope are very difficult in Japan because of laws and regulations. On the other hand, frequent maintenances are required for measurements using GC/NICI-MS. Thus observation data of PANs and ANs in Japan are quite low.

In this research, continuous measurement system of total PANs and ANs in the troposphere has been developed by using a thermal dissociation / cavity attenuated phase shift spectroscopy (TD/CAPS) method. Both PANs and ANs are thermally decomposed to produce NO_2 and then NO_2 is measured by CAPS method. This system can observe PANs and ANs with high time resolution while this system cannot separate constituents of PANs and ANs.

This system has three lines; (1) NO_2 line, (2) PANs line, and (3) ANs line. The NO_2 line consists of a quartz tube without heating. The PANs and ANs lines have quartz tubes heated at 433 K and 633 K, respectively. Concentrations of NO_2 , NO_2 + PANs and NO_2 + PANs + ANs can be obtained from the NO_2 , PANs and ANs lines, respectively. These concentrations are sequentially measured by switching solenoid valves and then NO_2 , PANs and ANs concentrations are obtained. Since a part of HNO_3 is pyrolyzed in the ANs line, annular denuder coated with NaCl to remove HNO_3 is set before the heated quartz tube in the ANs line.

The decomposition efficiencies of PANs and ANs were investigated and obtained to be 100 and 90%, respectively, for all kinds of PANs and ANs examined.

Continuous field observations of PANs and ANs concentrations have been being carried out at NOTOGRO supersite at Suzu, Noto Peninsula, since November 2012. In this presentation, the observational results and preliminary analyses of PANs and ANs concentration variations with NO_x , NO_y , total inorganic nitrate, O_3 and CO concentrations simultaneously observed are introduced.

Keywords: total odd nitrogen species, organic nitrates, cavity attenuated phase shift spectroscopy