

## 熱分解 / キャビティ減衰位相シフト分光法を用いた大気中有機硝酸塩の測定 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 ( $\text{NO}_x$ ) in the atmosphere. Since their lifetime is longer than that of  $\text{NO}_x$ , 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  $\text{NO}_2$  and then  $\text{NO}_2$  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)  $\text{NO}_2$  line, (2) PANs line, and (3) ANs line. The  $\text{NO}_2$  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  $\text{NO}_2$ ,  $\text{NO}_2 + \text{PANs}$  and  $\text{NO}_2 + \text{PANs} + \text{ANs}$  can be obtained from the  $\text{NO}_2$ , PANs and ANs lines, respectively. These concentrations are sequentially measured by switching solenoid valves and then  $\text{NO}_2$ , PANs and ANs concentrations are obtained. Since a part of  $\text{HNO}_3$  is pyrolyzed in the ANs line, annular denuder coated with NaCl to remove  $\text{HNO}_3$  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  $\text{NO}_x$ ,  $\text{NO}_y$ , total inorganic nitrate,  $\text{O}_3$  and CO concentrations simultaneously observed are introduced.

キーワード: 反応性総窒素酸化物, 有機硝酸エステル, キャビティ減衰位相シフト分光法

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