C-1.2.3 Development of Sampling and Analytical Method for Peroxyacyl Nitrates and Related Compounds at Low Concentration in the Air

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Abstract

Peroxyacyl nitrates (PANs), such as peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN), are important components of tropospheric reactive-N and potential carriers of global NOx. Atmospheric measurements of PANs in remote sites, however, are rare and are virtually non-existent in Asian region.

The methods and the instrument of sampling, carrying and keeping for atmospheric PANs with dryice-ethanol and pulverized-dryice are developed for field studies at remote sites and by aircraft. They were used for the field studies at Tushima Is. and Oki Is., and for aircraft study. PAN and PPN were detected in all of the 129 samples. Good correlations were observed between PAN and PPN for all samples, and PANs and NOx in aircraft survey. From aircraft survey, the slopes of the regression lines of PAN/NOx for upper 2000m altitude were higher than those for lower 1300m altitude. PANs are considered to be the potential carriers of global NOx in the background area.

Key Words East Asia, Nitrogen cycle, Nitrogenous compounds, PAN, PPN

Introduction

The oxides of nitrogen play a important role in a variety of atmospheric processes such as acid formation, tropospheric and stratospheric ozone production and destruction, and urban- and regional-scale oxidant formation[1].

Peroxyacyl nitrates (PANs), such as peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN), are the principal members of a family of nitrogenous compounds produced by the action of sunlight and are important components of tropospheric reactive-nitrogen and potential carriers of global NOx over regional and continental scales[2]. Atmospheric measurements of PANs in remote sites or in upper layer, however, are rare and are virtually non-existent in Asian region.

There were some difficulties to measure PANs, that is, the preparation of PANs, lability of PANs in analytical procedures. And besides, a more critical problem is exist in Japan or some other countries, that is, ECD, the most common detector of PANs, can not be practically carried to the remote sampling sites by the governmental regulation for radioactive materials.

In addition, the sampling methods used in most of past studies had the serious disadvantage that the sample might be taken so rapidly as to yield an unrepresentative sample of the atmosphere.

Thus, the reliable methods of sampling and carrying, and keeping for atmospheric PANs are developed for field studies at remote sites and by aircraft in this study. They were used for the field studies in Tushima Is. and Oki Is. and for aircraft study.

Experimental

PANs in the air are collected by the U-shape Teflon trap [tube (30cm L, 1.5mm I.D.) packed with *ca.* 0.2g Teflon beads] chilled with dryice-ethanol or pulverized-dryice. The sampling duration is 10 to 120 minutes, depending on the sampling volume (100 to 1000ml) and the purposes. Two kinds of collecting Technique are developed and used for the survey, as described later.

The collected samples were carried to the laboratory and PANs are analyzed by Simadzu Model 4CM gas chromatograph (GC) with two electron capture detectors (^{63}Ni, 10mCi, 50°C) between which the Teflon tube (30cm*2mmI.D.) packed PANs absorbent (10% KOH on Teflon beads) was installed[3)4)]. Two glass tubes (30cm*2mmI.D. and 100cm*2mmI.D.) packed with 5% PEG 400 on Chromosorb W (AW/DMCS, 60/80) was used for a precut column and a analytical column, respectively, at room temperature (20-25°C). Water vapor in sample was eliminated by the precut column prior to the separation of PANs. The carrier gas was high purity nitrogen (40 mL/min).

Results

One of two collecting techniques that were developed in this study is composed with the U-shape trap attached to a Teflon four-way valve and a 200ml glass syringe mounted vertically. Sample air is constantly sucked through the chilled trap by the smooth fall of the plunger under gravity[5)]. This is adequate to the temporary sampling or to the circumstance without any electric power sources. We used this method for the field study at Tushima Is. where is located between Kyushu and Korean Peninsula during Oct. 4-8 in 1991.

Another is composed with the U-shape trap attached to the valve, a mass flow control system, suction tanks (1 ℓ x2), a evacuation pump, and the electric recorder for monitoring of the sampling flow rate and the temperature and pressure of the tanks. This is adequate to the reliable sampling by aircraft or the continuous ground sampling. This method was used for the field study in Oki Is. in Sea of Japan and by aircraft over the Yellow Sea and over the sea off Oki Is.

Twelve traps which same amount of PAN was introduced were prepared for the test of stability of PAN in the trap chilled with dryice-ethanol. The result shows that the decomposition of PAN in the traps is less than 15 % for seven days (see Fig.1) and the cryogenic collection methods developed here can be used for the PAN aircraft sampling or for ground-based sampling at remote area.

The decay rate of PANs in the chilled trap by pulverized-dryice was also checked to be below 1.5%/day, and the sublimation rate of dryice is less than 15%/day in the plastic box of thick walls. The keeping technique of PANs samples in the traps chilled by pulverized-dryice permits carrying them from remote sites to the central laboratory by aircraft or by commercial delivery systems without any virtual decay. This technique is also useful for the interlaboratory comparison and for the sampling in the simultaneous survey over several countries.

We used the special detection system, ECD-(PANs Absorbent)-ECD, for PANs analysis, because of the avoid the miss determination. Actually a small peak, 50% in peak area at most, which are coincident with the peak of PPN, were often observed on the chromatograms after the PANs absorbent. The detection limits of PANs are *ca.* 5 ppt(v) for 500ml sample.

The developed methods were used for the field studies at Tushima Is. (Oct, 1991), Oki Is. (Nov. 1992) and by aircraft (Nov. 1992) and yield 129 observations.

PAN and PPN were detected in most of the samples. Good correlations between them were observed and PPN is 5-9% of PAN (see Fig.2-4).

The concentrations of PAN and PPN were 0.02-0.8 ppb and 0.002-0.056 ppb, respectively, in Tushima Is. and several times of gaseous nitrous acid and nitric acid, which were measured by KEIO groups there. PAN and PPN were 0.10-0.35 ppb and 0.005-0.035 ppb, respectively, in Oki Is. Good correlations were also observed between PANs and NOx (which was measured by NIES groups) in aircraft survey. The slopes of the regression lines of PANs/NOx for upper 2000m altitude were higher than those for lower 1300m altitude (see Fig.5,6). PANs concentrations drastically decreased in upper layer over 2000m altitude in two surveys over Sea of Japan.

PANs are considered to be the potential carriers of global NOx in the background area from these field surveys.

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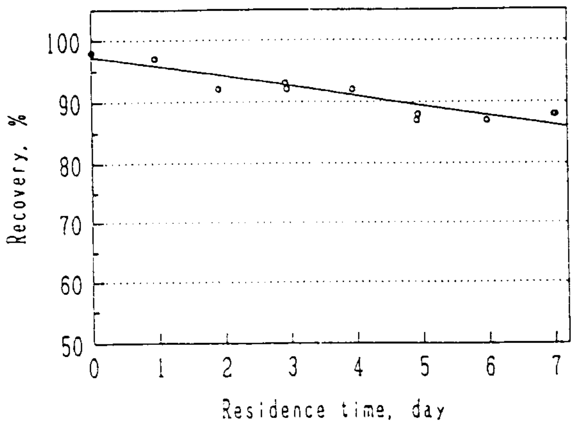

Fig. 1 Stability of PAN in the Teflon trap chilled with dryice-ethanol

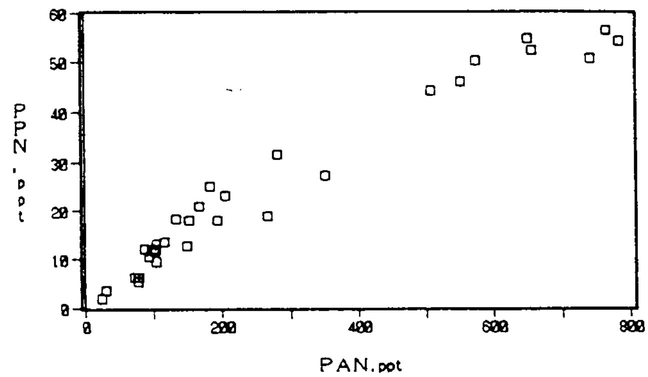

Fig. 2 Relationship between PAN and PPN in Tushima Island.

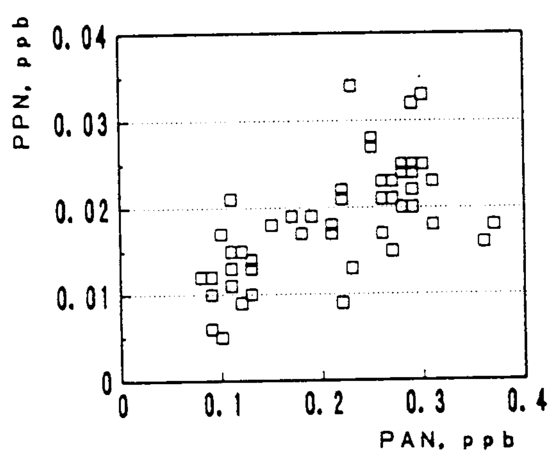

Fig. 3 Relationship between PAN and PPN in Oki Island.

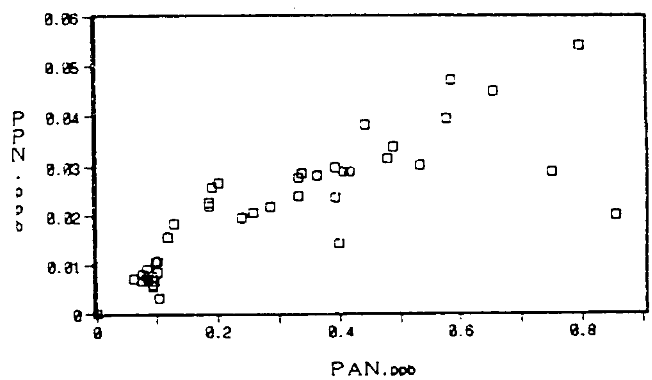

Fig. 4 Relationship between PAN and PPN in samples taken by an aircraft.

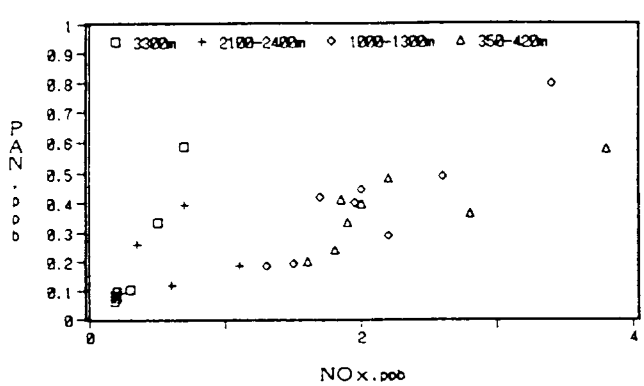

Fig. 5 Relationship between PAN and NOx in samples taken by an aircraft. (NOx was measured by NIES group)

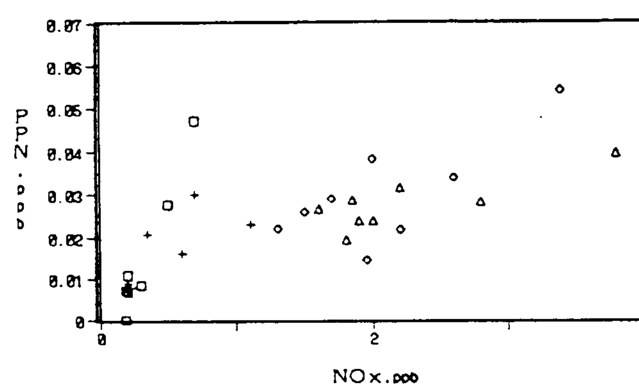

Fig. 6 Relationship between PPN and Nox in samples taken by an aircraft. (NOx was measured by NIES group)