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AIRCRAFT MEASUREMENTS OF NITROGEN DIOXIDE AND PEROXYACYL NITRATES USING LUMINOL CHEMILUMINESCENCE WITH FAST CAPILLARY GAS CHROMATOGRAPHY

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1. INTRODUCTION

Peroxyacyl nitrates (PANs) and nitrogen dioxide (NO_2) are important trace gas species associated with photochemical air pollution. Peroxyacyl nitrates are a class of organic oxidants that have the general chemical structure RC = OO-O-NO2. The most common family members of the PANs are peroxyacetyl nitrate (PAN, $R = CH_3$-), peroxypropionyl nitrate (PPN, $R = CH_3CH_2$-), and peroxybutyl nitrate (PBN, $R = CH_3CH_2CH_2$-).

The PANs are in thermal equilibrium with the peroxyacetyl radical ($RC = O\text{-}OO^{\cdot}$) and NO_2 (Gaffney et al. 1989). Because PANs are trapped peroxy radicals, they are an important indicator species of the photochemical age of an air parcel, as well as being a means of long-range transporting of NO_2, leading to the formation of regional ozone and other oxidants. Typically, PANs are measured by using a gas chromatograph with electron-capture detection (ECD). Once automated, this method has been shown to be reliable and quite sensitive, allowing the levels of PANs to be measured at low parts per trillion in the troposphere (e.g. Gaffney et al. 1993). Unfortunately, a number of other atmospheric gases also have strong ECD signals or act as inferences (e.g., O_2, freons, H_2O) and limit the speed in which the analysis can be completed. Currently, the shortest analysis time for PAN is approx. 5 minutes with ECD (e.g. Williams et al. 1997).

We recently examined the luminol detection of NO_2 and PANs using gas capillary chromatography for rapid monitoring of these important trace gases (Gaffney et al., *Atmos. Environ.*, in press). Analysis of the PANs (PAN, PPN, and PBN) and NO_2 in one minute has been demonstrated in laboratory studies by using this approach. Reported here are modifications of this instrument for aircraft operation and preliminary results from test flights taken near Pasco, Washington in August of 1997.

2. EXPERIMENTAL

The details of the instrumental design are given in detail in Gaffney et al., in press, but will be briefly described here. A luminol nitrogen dioxide detector (Scintrex LMA-3) has been modified to make the NO_2 and PANs measurements. An air sample is pulled through an inlet tube into a six-port sampling valve which is electronically actuated (Valco timer and Cheminert valve). For these studies a 5 cm^3 sampling loop was used and injected into a 3 m DB-1 capillary column for separation of the PANs and NO_2. Retention times for NO_2 and PAN at 125 cm^3/min carrier gas flow (5% O_2 in He) were 0.23 and 0.32 minutes, respectively. The recording integrator (Hewlett-Packard 3395) has been interfaced to a lap top computer (Toshiba) using Hewlett Packard Peak96 software, which allows automated collection of the data onboard the aircraft. The instrument consisted of a mounting rack, the modified-LMA-3 with capillary column operated at ambient temperature, sampling valve and associated electronics (automated timing system), carrier gas bottle and regulator, peristaltic pump for the LMA-3 (external), recording integrator, and lap-top computer. Instrument weight with the rack included was approx. 190 lb.

PAN and NO_2 retention times were checked using a PAN synthesized standard (Gaffney et al. 1984).

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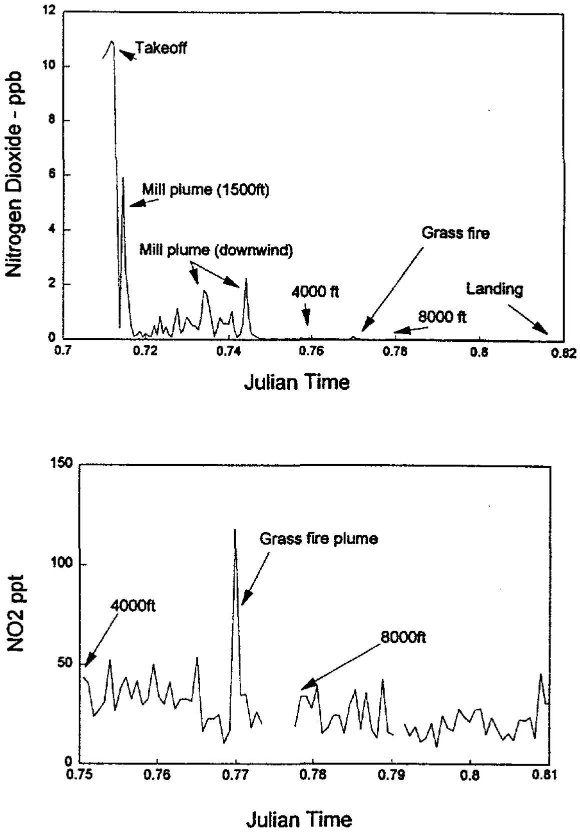
Calibrations were performed using certified NO_2 standards and standard dilution techniques. PAN was assumed to have approx. the same sensitivity for these preliminary analyses using the 5% O_2/He carrier gas (Gaffney et al. in press). Samples were taken into the sampling loop using a small air pump operated at 825 cc/minute flow by pulling the outside air from inside a 1 inch Teflon Sampling Pipe which was inside an external sampling inlet (ram-air) on the aircraft while in flight. The 5 cm^3 samples were injected for 10 s followed by 50 s for the completion of the analysis before the next analysis was initiated. NO_2 and PAN analysis were completed in one minute for the flights during this testing program.

The aircraft used for these studies was the G-1 aircraft owned by the U.S. Department of Energy and operated by Pacific Northwest National Laboratory. The flight no. 3 described in this work was a flight originating at Pasco airport and conducted on August 13, 1997 from approx. 1700 to 1945 GMT. The instrument was initially started on the ground and was operated from takeoff until shortly before landing during this flight at one minute intervals.

3. RESULTS AND DISCUSSION

In Figures 1a, 1b, and 2 the results of one minute analyses are presented for the flight no. 3 taken on August 13, 1997 from Pasco airport for NO_2 and PAN, respectively. As expected the initial NO_2 levels were observed to be quite high at the airport and during the takeoff period and rapidly fell to background levels. The flight took us around a paper mill in the area where we were able to detect the plume from the mill at 1500 ft altitude. The later part of the flight involved measurements at 4000 ft and 8000 ft altitude. At the 4000 ft altitude a plume from a grass fire below was detected using the instrument indicating a small source of NO_2 from the fire, as anticipated.

Figure 3. shows the results of PAN/NO_2 analysis for the flight. Note the increase in the PAN/NO_2 ratio with time follows the altitude of the flight path. This is consistent with the lower temperatures at the higher altitudes leading to thermal stabilization of the PAN. The air quality during these studies over this area was very clean. NO_2 levels outside of the plumes were on the order of 100 ppt at 1500 ft and dropped to around 50 ppt at 8000 ft.



Figures 1a. (ppb) and 1b. NO_2 (ppt) levels observed during flight no. 3 from Pasco, WA on 8/13/97. Figure 1b. shows the levels at 4000 ft and 8000 ft. and indicates detection of NO_2 source from grass fire below.

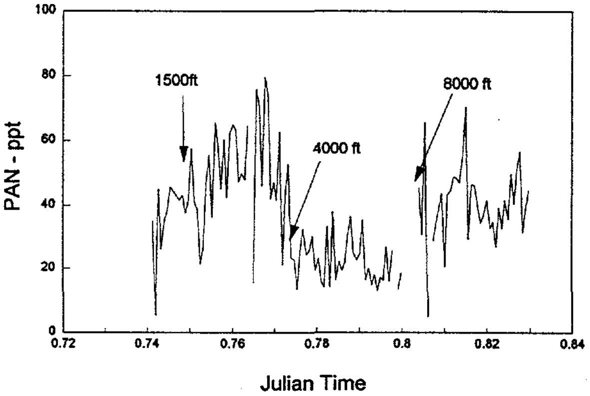


Figure 2. Peroxyacetyl nitrate (PAN) levels in ppt observed during aircraft flight no. 3 near Pasco, WA on August 13, 1997.

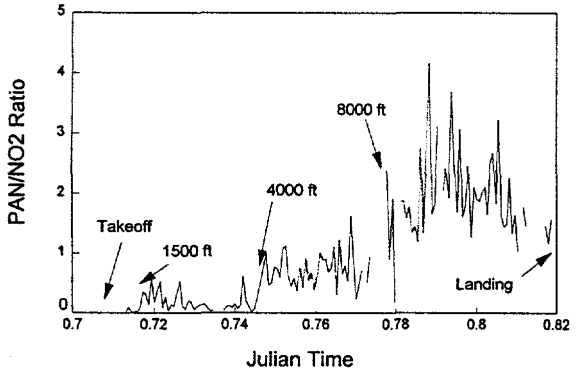


Figure 3. PAN/NO_2 ratio for the flight no. 3 taken on 8/13/97.

PAN levels were observed to be higher at the higher altitudes and at or below detection levels at the lower altitudes. This is likely due to the weather conditions at the time with approx. 40 C ground temperatures. The levels aloft indicated that at least for this flight the upper air mass may have been marine sourced or representative of clean continental air with little impact from any sources.

These results, we believe, are the fastest analyses of PAN that has been accomplished to date. The improvement from 5 to 1 minute resolution, dramatically improves the potential for aircraft measurements of PANs and for low level, unambiguous, NO_2 measurements. Further improvements in the reduction of the analysis time may be accomplished by redesigning the luminol detection chamber to remove the dead volume associated with the LMA-3 detection cell. Improvements may also be accomplished by using a cooled column to improve the separation while minimizing the retention time.

It should be noted that the luminol system is inherently more sensitive than the NO chemiluminescent reaction with ozone. This is due to the fact that the luminol emission is in the visible, while the NO_2* emission is in the far visible, near infrared. By coupling chromatography to the luminol detector a number of interferences can be used to advantage, i.e. they can be measured as well as the species of interest. This system does not require high vacuum or any toxic reagents and lends itself well to aircraft operations for these species by allowing lighter and safer equipment operation. Detection sensitivities in the low tens of ppt are readily accomplished using this approach. By using chromate converters or converting NO to peroxynitric acid it is anticipated that this type of instrumentation could also be used for NO as well as NO_2 and PANs. Thermal conversion of organonitrates, nitro-aromatics, etc. to NO or NO_2 could also be performed using this approach which will be useful in unraveling the various contributions of these species to tropospheric nitrogen oxides.

4. ACKNOWLEDGMENT

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5. REFERENCES

Gaffney, J.S., R. Fajer, and G.I. Senum, 1984: An Improved Procedure for High Purity Gaseous Peroxyacetyl Nitrate Production: Use of Heavy Lipid Solvents. *Atmos. Environ.* **18** 215-218.

Gaffney, J.S., N.A. Marley and E.W. Prestbo, 1989: Peroxyacyl Nitrates (PANS): Their Physical and Chemical Properties. the *Handbook of Environmental Chemistry,* **Volume 4/Part B. (Air Pollution)** edited by O. Hutzinger, 1-38, Springer-Verlag, Berlin, Germany.

Gaffney, J.S., N.A. Marley, and E.W. Prestbo, 1993: Measurements of Peroxyacetyl Nitrate (PAN) at a Remote Site in the Southwestern United States: Tropospheric Implications. *Environ. Sci. Technol.* **27** 1905-1910.

Gaffney, J.S., R.M. Bornick, Y.-H. Chen, and N.A. Marley, in press: Capillary Gas Chromatographic Analysis of Nitrogen Dioxide and PANs with Luminol Chemiluminescent Detection. *Atmospheric Environment.*

Williams, J., J.M. Roberts, F.C. Fehsenfeld, S.B. Bertman, M.P. Buhr, P.D. Goldan, G. Hubler, W.C. Kuster, T.B. Ryerson, M. Trainer, and V. Young, 1997: Regional ozone from biogenic hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN. *Geophys. Res. Lett.* **24** 1099-1102.