Application of a Gas Chromatography/Luminol Detection System for Peroxyacetyl Nitrate Airborne Measurement

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ABSTRACT
We constructed and tested an airborne peroxyacetyl nitrate (PAN) monitoring system based on luminol chemiluminescence detection with fast gas chromatography. This system allowed for simultaneous measurement of PAN and nitrogen dioxide (NO₂) with a time resolution of <2 min. Actual sample masses within the fixed volume sample loop at various altitudes and temperatures were adjusted to standard atmosphere, using measured pressures and temperatures. The airborne PAN measurement system was evaluated during two field studies above the southern Korean Peninsula in August and October 2009. The detection limit based on the ISO approach was 0.035 ppbv PAN, well below the observed concentrations of 0.185-1.49 ppbv during these studies. Under these conditions, the PAN mixing ratios were positively correlated with O₃ (O₃=O₃+NO₂), with slopes varying between 0.014 and 0.033 and intercepts between 22.6 and 55.1 ppbv O₃. The intercepts corresponded roughly to background O₃ mixing ratios in central Europe; however, the slopes were above the range of slopes reported in other studies. We also enhanced the durability, safety, and ease of maintenance of the PAN monitoring system by redesigning the structure of the conventional luminol cell.

Key words: PAN, Airborne measurement, Luminol detection, Fast GC, Ozone

1. INTRODUCTION

Peroxyacetyl nitrate (PAN) is one of a class of common air pollutants formed by the action of sunlight on volatile organic compounds (VOCs) and nitrogen oxides (NOₓ). PAN is also present in polluted atmospheres and has been suggested as an indicator of photochemical smog along with ozone (O₃). Unlike O₃, PAN does not have abundant natural sources in the stratosphere (Stephens, 1969). PAN is produced only from VOCs whose oxidation leads to acetyl radicals in the presence of nitrogen oxides, whereas O₃ is formed through the oxidation of all VOCs. PAN and nitrogen dioxide (NO₂) play major roles in the chemistry of the troposphere at urban, regional, and global scales (Singh, 1985). PAN is in equilibrium with NO₂ and the peroxyacetyl radical. This equilibrium is strongly temperature-dependent; PAN is more stable at colder temperature (Fischer and Nwankwoala, 1995; Roberts, 1990). At cold temperatures, PAN can act as an important transport mechanism for NOₓ and a source of remote NOₓ (Gaffney and Marley, 1993; Gaffney et al., 1989; Singh, 1987). Among its chemical properties, low solubility in water (Gaffney et al., 1984) and low OH reactivity (Talukdar et al., 1995) give PAN a long atmospheric lifetime. Therefore, both PAN and NO₂ are important atmospheric oxidants formed in the troposphere that affect air quality and can lead to global climate change (Gaffney and Marley, 1992).

PAN has been measured using a variety of methods (Gaffney et al., 1989). The most widely used method is the electron capture detector (ECD). This method has detection limits in the tens of ppt and uses packed or capillary columns for the analysis (Roberts, 1990; Gaffney et al., 1989). However, many atmospheric gases interfere with ECD signals, limiting the speed of the analysis to 10-30 min. Luminol detection of NO₂ and PAN has been conducted using packed columns with air as a carrier gas (Burkhardt et al., 1988). Measurement of PAN after chromatographic separation and thermal conversion of PAN to NO₂, followed by luminol detection of the generated NO₂, has also been shown to be a sensitive method (Blanchard et al., 1990). Luminol methods using packed and capillary columns have been compared with the more conventional ECD chromatographic approach and have been found to agree to within 15-20% (Blanchard et al., 1990). Be-
cause luminol detection of PAN does not suffer from the oxygen interference that affects ECD, separation of NO2 and PAN can be accomplished in a much shorter analysis time (Gaffney et al., 1999; Gaffney et al., 1998). Marley et al. (2004) developed the prototype for simultaneous fast-response measurement of NO2 and PAN.

Airborne instrumentation for PAN measurement must meet several requirements. To apply the luminol method, improvements in sensitivity and increased contact of the column effluent with the luminol solution is needed. In addition, when on board an aircraft, the analysis time should be as short as possible to obtain good spatial resolution of the measurements and minimize thermal decomposition of PAN. Further challenges to be addressed include: 1) pressure variations in the aircraft cabin, which can lead to signal and baseline shifts; 2) decreasing ambient pressure with increasing flight altitude will reduce the injected air sample mass if the injection system does not compensate for pressure changes; and 3) aircraft operation places limits on weight, size, and electric power consumption of the instrument. The objective of this study was to construct and test an airborne PAN monitoring system based on luminol chemiluminescence detection with fast gas chromatography (GC), meeting the requirements stated above.

2. MATERIALS AND METHODS

We constructed a capillary fast GC with luminol detector optimized for high sampling frequencies to measure airborne PAN (Fig. 1). We selected all components based on the review paper of Marley et al. (2004) and designed the instrumentation to fit into a 19-inch sub-rack case for mobility, portability, and ease of installation. The sampling pump (Fig. 1k) was connected directly to the aircraft sampling manifold, which was held at a constant pressure of 12.1 psi by a mass flow controller (Fig. 1e). Two milliliters of ambient air were injected every 2 min through a 6-port valve (Fig. 1b) with a Teflon sampling loop (Fig. 1g). The analyzer was equipped with a capillary column (DB-1, 10 m, 530 μM i.d., 1 μM film thickness; Fig. 1f) for separation of PAN and NO2. Nitrogen gas (purity 99.999%) was used as carried gas at a flow rate of 20 cc/min. The chemiluminescence signal was detected by a gated photon counter (HC135-01, Hamamatsu) set at 850 V. All peaks were stored on a computer and analyzed with LabVIEW software (National Instrument Co.). The PAN monitoring system was operated at <35°C. In previous study, combined uncertainties based on the ISO approach were quantified to identify the major sources for measurement uncertainty during the determination of PAN concentrations using this system (Khang et al., 2010).
these conditions, the detection limit based on the ISO approach was 0.035 ppbv PAN and the retention times of NO₂ and PAN were 0.45 and 1.16 min, respectively. O₃ was measured with an ultraviolet absorption photometer (Model 49; Thermo Environmental Instruments, Inc.). The detector was equipped with a rapid-update EEPROM by the manufacturer, which allowed for a 4-s cycle time, 0 to 95% response time of 10 s, and precision of 2 ppbv. The sensitivity of the UV photometer was quite stable, but instrument calibration was conducted between flights.

Previously developed PAN detectors have generally had a single quartz window between the photomultiplier tube (PMT) and the reaction cell (Marley et al., 2004). 1 mM luminol solution is prepared in the strong base of 0.5 M NaOH. If the quartz window is exposed to the luminol solution over the long term, the luminol can break the glass in the reactor cell. For this reason, the reactor cell must be washed with pure water after analysis. Because this solution is not entirely safe for long-term operation, we improved the durability of the PAN monitoring system by redesigning the luminol cell with double quartz glass windows between the luminol solution and the PMT. Fig. 2 shows the luminol cell as redesigned in this study, based on the luminol cell designed by Marley et al. (2004). PAN and NO₂, after separation by the capillary column, enter the reaction cell in a carrier gas with stable flow, then are pumped out of the cell with luminol solution. The luminol cell has a symmetric structure front to back. The chemiluminescence reaction occurs in the front cap, which has three holes connected to the capillary column (Fig. 2a), waste reservoir (Fig. 2b), and luminol supply pump (Fig. 2c). The chemiluminescence emission is captured by the PMT, located in the PMT bracket (Fig. 2e). In addition, we added an o-ring and quartz window to the reactor frame to isolate the luminol reaction cell from the PMT. This duplicate structure enhances the safety and durability of the PAN measurement system, while poten-

Fig. 2. Structure and assembly of the luminol cell. (A) Sample inlet, (B) Waste Outlet, (C) Luminol solution inlet, (a) Luminol reactor, (b) O-ring, (c) Window, (d) Reactor frame, (e) PMT bracket.

Fig. 3. Flight areas in this study. A region was above an industrial and urban area and B region was above the sea at southwest of Korea.
tially reducing the sensitivity of the PMT. For an aircraft platform, a mass flow controller is needed to compensate for the temperature and pressure of the sample. The temperature and pressure are measured by a digital flow controller when the samples are taken, which enables stabilization of the sample pressure in
flight. The airborne PAN system was contained in a
19-inch rack case designed to fit in a standard instru-
mment rack. The carrier gas was provided by a refill-
able gas cylinder attached to the back of the rack mount.
The overall system weight was under 21 kg for port-
ability and safety in the aircraft.

3. RESULTS AND DISCUSSION

3.1 PAN Airborne Measurement

We evaluated the performance of the airborne PAN
monitoring system during two field studies above the
southern Korean Peninsula in August and October
2009. Fig. 3 and Table 1 show the flight areas and
altitudes. Field A was above an industrial complex
and urban area in southern Korea and field B was above
the sea at southwest of Korea. Warm air was transport-
ated into the study area due to a high-pressure system
originating in China. Much of the experimental period
was under the influence of a continental anticyclone,
carrying yellow dust from China on westerly winds.

Figs. 4-9 show the horizontal and vertical tracks of
all flights with altitude, as well as the measured PAN,
NO2, and O3 mixing ratios. Table 1 summarizes the
average mixing ratios for PAN, NO2, and O3 during the
individual flights. All flights were conducted below
an altitude of 1,000 m during the day on dry sunny
days. PAN and NO2 were measured simultaneously
with time resolution of < 2 min, an improvement of
5-fold over ECD. NO2 and PAN were detected sepa-
rate at 0.2 min and 1.3 min. During the three flights
on 1, 2, and 10 August, the air temperature was 23-
29°C. The PAN mixing ratios were 0.1-0.6 ppbv, simi-
lar to the average of ratios measured in European air-
craft studies at similar altitudes (Schmidt et al., 1998).
The maximum concentrations of O3 and NO2 occurr-
ed at the same position (127.1° E, 34.5° N) over the
industrial complex. During the three flights on 16, 18,
and 19 October, the air temperature was about 21.2
°C. The PAN mixing ratios were > 1.1 ppbv, higher
than the flights in August.

Fig. 6. Horizontal and vertical flight tracks and PAN, NO2,
and O3 measurements on 10 August 2009.

Fig. 7. Horizontal and vertical flight tracks and PAN, NO2,
and O3 measurements on 16 October 2009.
3.2 Relationship between PAN and O₃

Airborne studies of the relationship between PAN and O₃ mixing ratios are influenced by the horizontal and vertical variability of both compounds in air masses differing by precursor load and photochemical age. Rappenglück et al. (1993) reported that the mean ratio of O₃ to PAN is about 15-30 in polluted air masses (Shepson et al., 1992; Altshuller, 1983), and Kourtidis et al. (1993) reported that the correlation between PAN and O₃ at ground level is typically strongly positive (Shepson et al., 1992; Wunderli and Gehring, 1991; Ridley et al., 1990). As a result, classification of airborne PAN and O₃ data by air mass origin, precursor load, and degree of photochemical processing is generally necessary if PAN-O₃ relationships are to be investigated (Ridley et al., 1990). In practice, reliable classification of aircraft data according to these criteria can rarely be achieved. However, without such classification, PAN-O₃ correlations that may exist in photochemically aged air masses are less pronounced due to the loss of O₃, which reacts with NO in freshly polluted air masses, while PAN is much more stable in cold air parcels. Kley et al. (1994) demonstrated that comparing PAN with O₃ (O₃+NO₂) rather than O₃ can reduce this interference. In meteorological terms, strong positive correlations between PAN and O₃ are expected in stable wind fields, leading to formation of well-defined regions upwind and downwind of anthropogenic sources within the flight area. Such situations provide the large range of PAN and O₃ mixing ratios needed to establish significant correlations.

Data for most of the flights showed relatively poor correlations between PAN and O₃, except for 16 and 18 October. Both of these flights were conducted at various altitudes, while the other flights maintained a similar altitude throughout. Fig. 10 shows correlations between PAN and O₃. The slopes of the correlations varied between 0.014 and 0.033 ppbv O₃/ppbv PAN, wider than the range previously reported (0.015-0.030; Schmidt et al., 1998; Rappenglück et al., 1993; Shepson et al., 1992; Ridley et al., 1990; Altshuller, 1983). When the PAN mixing ratios were 0 for the October flights, the background values of (O₃)₀ were...
22.6 and 55.1 ppbv, varying more than the European background O₃ mixing ratio in September of about 35 ppbv reported by Volz and Kley (1988). Despite high O₃ with or without PAN correlations, the August flights did not yield background values, whereas the October flights showed strong correlations between PAN and Oₓ, yielding background values. We suggest that urban and industrial areas may be more favorable for generation of PAN than O₃. It appears that the VOCs emitted from urban areas are important sources of PAN production compared to in the marine environment. PAN is also a strong indicator of photochemical oxidant production from anthropogenic pollutants.

The best correlation between PAN and Oₓ was found for the afternoon flight on 16 October. Fig. 11 illustrates the relative importance of NO₂ and temperature in determining the relationship between PAN and Oₓ. From the lower left to the upper right, the correlation between PAN and Oₓ was strengthened by increasing concentrations of NO₂, temperature, and altitude. PAN and Oₓ were highly correlated when the NO₂ concentration was > 3 ppbv at high altitude.

4. CONCLUSIONS

We constructed an airborne PAN monitoring system based on chemiluminescence detection with fast GC. We modified the structure of the luminol cell with a duplicate quartz window to protect the PMT against the luminol solution and enhance the safety and durability of the instrument. The instrument allowed for continuous measurement of PAN and NO₂ within 2 min. Further improvement in the instrumentation will be accomplished by cooling the system to minimize the thermal decomposition of PAN and to reduce the background noise from the photomultiplier tubes.

Airborne observations were conducted to evaluate this instrument over the southern Korean Peninsula in August and October 2009. The two flight areas were characterized as marine and urban/industrial environments. We measured the concentrations of PAN, NO₂, and Oₓ throughout all flights. The relationship between PAN and Oₓ was more sensitive to NO₂ than to altitude, with a threshold of 3 ppbv NO₂ on the afternoon flight of 16 October. We found that the (Oₓ)₀ background value for the urban/industrial environment was higher.
than that of the marine environment. We conclude that urban or industrial areas are sources with higher potential for generation of PAN than the marine environment, confirming that PAN is a strong indicator of photochemical oxidant production from anthropogenic pollutants.

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