

## On the Measurement of PANs by Gas Chromatography and Electron Capture Detection

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**Abstract.** A fast, automated, gas chromatographic system for the airborne measurement of PAN and a series of its homologues is described and its performance is evaluated. Response factors for PAN, PPN, APAN, PiBN, and MPAN have been determined and are discussed with regard to ECD response and to potential losses in the analytical system. Calibration methods used for these tasks are described and compared. The results from this work should help investigators who are employing the widely used GC/ECD method for the measurement of peroxyacyl nitrates to evaluate peaks of PAN homologues that cannot be calibrated for by using the reported response factors.

**Key words:** air pollution, atmospheric chemistry, gas chromatography, peroxyacetyl nitrate, peroxyacyl nitrates

### 1. Introduction

PAN (chemical formula:  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ) commonly named peroxyacetyl nitrate, is an important member of the reactive nitrogen family, and it is present throughout the global troposphere. Mixing ratios range from less than 2 pptv in the remote marine boundary layer to several ppbv in heavily polluted urban regions (Fahey *et al.*, 1986; Singh and Salas, 1989; Ridley *et al.*, 1990; Ridley *et al.*, 1990; Altshuller, 1993; Perros, 1994; Schmidt *et al.*, 1998; Watanabe *et al.*, 1998; Grosjean, 2003). A number of chemical homologues of PAN (hitherto also referred to as PANs,  $\text{RC}(\text{O})\text{OONO}_2$ ) have been measured in the atmosphere. These, less abundant, PAN-type compounds are PPN ( $\text{C}_2\text{H}_5\text{C}(\text{O})\text{OONO}_2$ , peroxypropionyl nitrate), PiBN ( $(\text{CH}_3)_2\text{CHC}(\text{O})\text{OONO}_2$ , peroxyisobutyryl nitrate), MPAN ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ , peroxymethacryloyl nitrate), APAN ( $\text{CH}_2=\text{CHC}(\text{O})\text{OONO}_2$ , peroxyacryloyl nitrate), PnBN ( $\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OONO}_2$ , peroxybutyryl nitrate), and PBzN ( $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONO}_2$ , peroxybenzoyl nitrate).

Other, more complex PANs have been predicted by atmospheric models, but they have yet to be detected in the ambient atmosphere.

PANs are formed during the photochemical oxidation of non-methane hydrocarbons in the presence of  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), which makes them by-products of the rate-limiting steps in photochemical ozone formation in the troposphere. This makes PAN species important for several reasons. The mix of the hydrocarbons involved in the photochemistry is reflected in the relative abundance of the different PAN species. For example, PAN arises from almost all non-methane hydrocarbon species, whereas PPN originates mainly from longer chain anthropogenic hydrocarbons like alkanes and alkenes and some biogenic hexene derivatives. MPAN, however, is formed primarily during the photooxidation of isoprene, which has predominantly biogenic sources such as trees and phytoplankton (Guenther *et al.*, 1995). Hence the absolute and relative concentrations of these PAN species provide an excellent tracer to determine the relative contributions of anthropogenic and biogenic hydrocarbon emissions (Williams *et al.*, 1997; Roberts *et al.*, 1998). PAN-type compounds often constitute a major fraction of available reactive odd nitrogen,  $\text{NO}_y$ , which is defined as the sum of  $\text{NO}_x$  and all  $\text{NO}_x$ -product species (e.g. nitric acid, nitrous acid, PANs, alkyl nitrates, etc.). Net PAN losses primarily occur via thermal dissociation followed by the reaction of the peroxyacyl radical with NO or with  $\text{HO}_2$  or other organic peroxy radicals and, to a lesser extent, via photolysis (Talukdar *et al.*, 1997; Kirchner *et al.*, 1999). The reaction with OH is very slow and constitutes a negligible loss of PAN throughout the troposphere (Talukdar *et al.*, 1997). The rate constant for thermal dissociation, however, has a very strong temperature dependence that controls atmospheric lifetimes of PANs in the lower troposphere. At  $\text{NO}/\text{NO}_2$  ratios typical for the troposphere, the lifetime of PAN varies from about 40 min at temperatures of 300 K to several months at temperatures characteristic of the upper troposphere. Thus, PANs are quite stable in the mid- and upper troposphere, and they can be transported over long distances from polluted continental regions into the remote troposphere such as over the Pacific Ocean. Singh and Hanst (1981) suggested that PAN acts as a temporary reservoir for  $\text{NO}_x$  and, through long range transport and subsequent release of  $\text{NO}_x$  especially in the lower troposphere, may control the photochemical production of  $\text{O}_3$  in much of the remote marine troposphere. Since then, a number of studies of PAN in remote marine environments such as over the Pacific or Atlantic Oceans have shown layers of polluted air at mid- to upper altitudes over the oceans, in which PAN is an important, and sometimes the dominant, fraction of the sum of all odd-nitrogen species. In the marine boundary layer PAN appears depleted relative to typical continental sites (Gallagher, 1990; Jacobi and Schrems, 1999; Roberts *et al.*, 2004). This indicates a loss mechanisms resulting in the release of  $\text{NO}_x$  (Walega *et al.*, 1992; Honrath *et al.*, 1996; Singh *et al.*, 1996; Kondo *et al.*, 1997). This may represent one of the most important mechanisms by which  $\text{NO}_x$  is transported globally and may control the  $\text{NO}_x$  budget and therefore the photochemical ozone production throughout large portions of the

remote lower troposphere (Fan *et al.*, 1994; Moxim *et al.*, 1996; Schultz *et al.*, 1999). In continental regions, PANs and complex organic nitrates resulting from oxidation of biogenic hydrocarbons may be important in the atmosphere-biosphere exchange of nitrogen (Shepson *et al.*, 1992; Sparks *et al.*, 2003). Thus, measurements of PANs provide information on photochemical processes occurring closer to source regions over the continent, as well as their impact on the global troposphere.

As a consequence, accurate and precise measurements of PAN and related compounds are crucial to the understanding of the  $\text{NO}_x$  budget and ozone photochemistry of the troposphere. Measurements of PAN and its homologues have most often been accomplished by gas chromatography with electron capture detection (GC/ECD) (e.g., Darley *et al.*, 1963; Singh and Salas, 1983; Müller and Rudolph, 1989; Ridley *et al.*, 1990; Schrimpf *et al.*, 1995; Volz-Thomas *et al.*, 2002; Whalley *et al.*, 2004) although other methods have been used, such as a Luminol based detector instead of an electron capture detector (Gaffney *et al.*, 1998), Negative Ion Chemical Ionization Mass Spectrometry (NICI-MS) (Tanimoto *et al.*, 1999), thermal dissociation laser induced fluorescence (Day *et al.*, 2002), Proton-Transfer Reaction Mass Spectrometry (PTR-MS) (Hansel and Wisthaler, 2000), and, very recently, Chemical Ionization Mass Spectrometry (CIMS) (Slusher *et al.*, 2004). The GC/ECD method is currently the best developed and most proven way to measure PAN and its homologues. The method has been improved by the application of capillary chromatography, and can provide an analysis of PAN species in 5 min or less (Roberts *et al.*, 1998; Williams *et al.*, 2000). The Fast-PAN-GC instrument described in this article is a compact dual channel gas chromatograph equipped with a common sampling loop and a common ECD detector. The instrument is configured for the measurement of PAN and PPN every 1.5 min and APAN, PiBN and MPAN every 2.5 min. This instrument has been successfully deployed on 5 aircraft campaigns between 1999 and 2002: The Southern Oxidants Study (SOS) in summer 1999, the Tropospheric Ozone Production during the Spring Equinox (TOPSE) Experiment in winter-spring 2000, the Texas Air Quality Study (TexAQS, summer 2000), the Transport and Chemical Evolution over the Pacific (TRACE-P) experiment in spring 2001 and the Intercontinental Transport and Chemical Transformation (ITCT) experiment in late spring 2002.

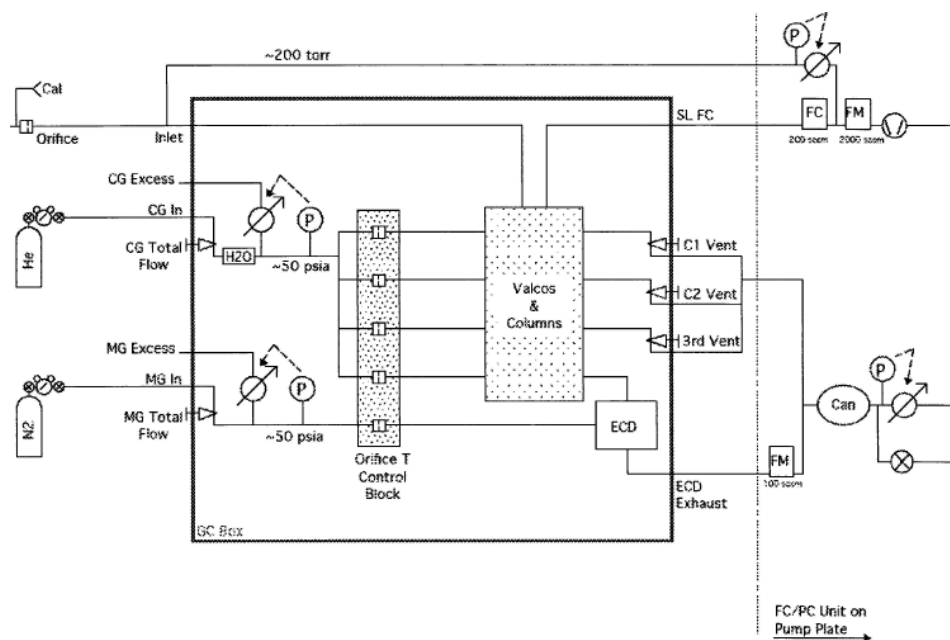
In this paper, we describe our instrument and its characterization using several different state-of-the-art calibration methods for all measured PAN species. Field intercomparison results are also presented. The relative response factors for different PANs obtained in this work should be of general use to the wide number of analysts that measure PANs by capillary GC/ECD. This is especially significant since, due to the commercial availability of an in-situ PAN source, most groups measuring PANs are only able to calibrate for PAN, but not for PAN homologues, on a regular basis in the laboratory or in the field.

## 2. The NCAR PAN Gas Chromatograph

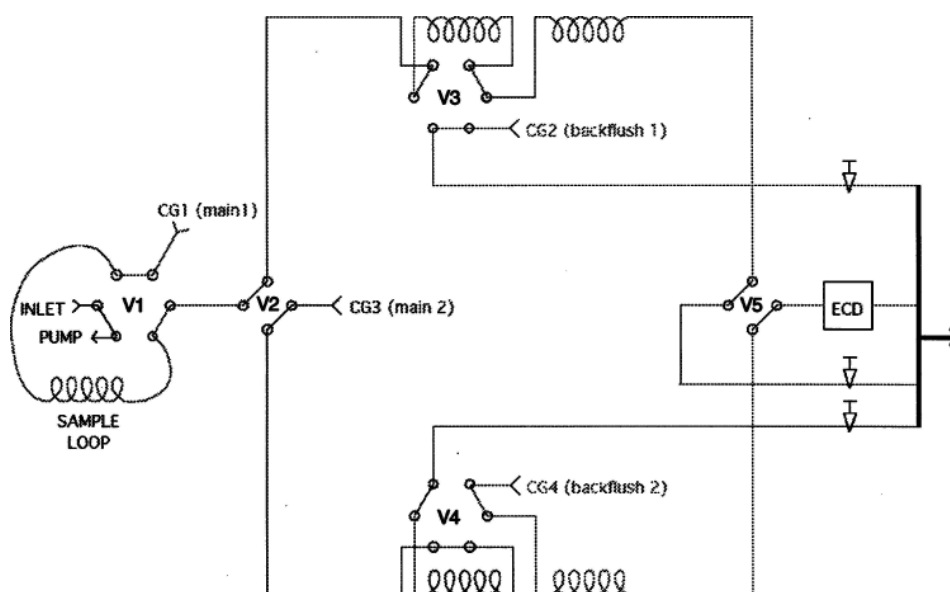
### 2.1. INSTRUMENT DESIGN

The Fast-PAN-GC instrument is based on capillary gas chromatography with electron capture detection (ECD). Through an array of stainless steel multi-port valves (Valco Nitronic 60 body, WE type rotors), a common sampling loop with an injection volume of about 1.3 cm<sup>3</sup> STP serves two independent separation channels and a common ECD. All connecting tubing between the Valco valves is 1/16" PEEK and the sampling loop material is 1/8" PEEK. PFA was found to be problematic for connecting tubing since oxygen diffuses through PFA quite easily and caused an elevated and more noisy baseline in the ECD. No losses of PANs were observed in the Valco valves or the PEEK tubing. Each column oven carries two widebore capillary columns, one of which serves as a pre-separation device and to remove lateeluting compounds and the other as the main column for separating the PAN species. The compact (12 × 12 × 15 cm incl. cooling fan) and lightweight ovens can be thermoelectrically cooled or heated to between 10 and 55 °C and controlled to ±0.1 °C. Two 2.5 by 2.5 cm peltier elements (Minco) and one 12 cm cooling fan are used in each oven. A schematic of the system is shown in Figure 1a. The gas flow diagram is shown in Figure 1b. The helium carrier gas flows are controlled by an array of four matched critical orifices (Lennox Laser, Inc.). The Helium pressure upstream of these orifices is controlled by a common back-pressure control system (MKS). The back-pressure control setup avoids exposing the carrier gas to the inner surfaces of pressure control valves or mass flow controllers before entering the GC system thus preventing contamination through out-gassing from seals and lubricants. Nitrogen is used as a make-up gas, back-pressure controlled in the same fashion. The carrier gas flow rate is 20–22 cm<sup>3</sup>/min STP, the make-up gas flow is 2–3 cm<sup>3</sup>/min STP. We found this very unusual ratio of carrier to make-up gas gave the maximum sensitivity with the Shimadzu Mini-2 detector, when using humidified carrier gas. Prior to entering the columns the carrier gas is humidified with about 100 ppmv water vapor by flowing it through a cartridge thermally controlled to 35 °C and filled with analytical grade CuSO<sub>4</sub>·6H<sub>2</sub>O. Prior to use in the system, these cartridges are flushed with a flow of around 100 sccm UHP Helium for 2–4 days. One 200 g cartridge lasts for several months of continuous operation. The added water vapor eliminates adverse effects of changing humidity levels in the sampling air and also minimizes PAN losses in the columns, the valve surfaces, and the connecting tubing. This was found to be a problem when very dry air masses were sampled (Ridley *et al.*, 1990). The presence of small amounts of water vapor in the carrier gas also allows for the unusually small make-up gas flow.

All valves and connecting tubing, as well as the sampling loop are situated in a thermally insulated compartment which is controlled to 25 ± 1 °C by means of a thermoelectric heat exchanger system. The thermoelectric heat exchange system is designed with a set of four 2.5 × 2.5 cm Peltier cooling elements (Minco) attached to an aluminum heat sink and two 12.5 cm blowers. The constant temperature ensures



(a)

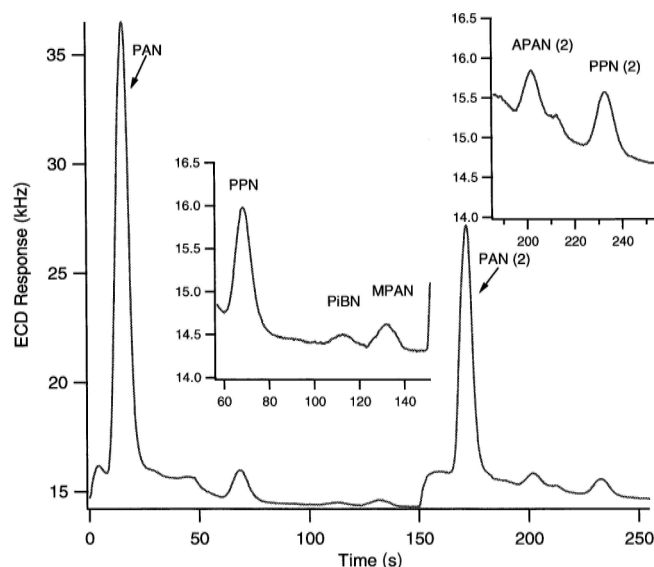


(b)

Figure 1. (a) Schematic of the NCAR 2-channel PAN-GC. (b) Schematic of the Valco valve system used in the NCAR 2-channel PAN GC. The valve numbers shown are referenced in the text and Table I.

a constant sampling volume and minimizes baseline drifts and changes in surface conditions in the tubing and valves that can be caused by external temperature fluctuations.

Samples are alternately injected onto each column. The pre-separation column is back-flushed after the compound of interest with the longest retention time has eluted from the pre-separation column. This ensures that heavier or more polar compounds are not transferred onto the main column, thus allowing for rapid injection sequences by avoiding the elution of potential contaminants during an analysis from the prior injection. The sample loop and inlet line typically is pressure controlled to 200 torr. This is always below ambient pressures encountered with the P-3B and C-130 aircraft that the system has flown on. The typical sampling loop volume is 5 cm<sup>3</sup> giving a sample volume of ~1.3 cm<sup>3</sup> STP. The samples are injected onto the columns sequentially, the injection timing depends on the particular separation setup (see below), and the eluent from each main column is connected to the ECD during the elution of the compounds of interest. To avoid an unwanted signal in the ECD baseline response upon switching of the valves, caused by the sudden change in flow resistance when switching a column to back-flush mode two needle valves (Hoke), adjusted to provide the same flow resistance as the GC columns, are employed at the vent ports. In addition, a buffer volume is used to decouple the ECD from the pressure control valve. The remaining baseline response, which can be seen in Figure 2 is mainly due to very slight flow differences between the



*Figure 2.* Chromatogram taken on May 13th, 2002, over California during ITCT. The insets show the same chromatogram, but on a different vertical scale to visually enhance the smaller peaks. The PAN, PPN, PiBN, and MPAN signals correspond to a mixing ratio of 1488, 149, 14, and 36 pptv, respectively. The PAN (2) and PPN (2) signals correspond to 816 and 84 pptv, respectively.

critical orifices that are within their specification. The exhaust of the ECD and all column exhausts are fed into a volume which is pressure controlled at 800 torr. This ensures a constant sensitivity of the ECD and stable retention times, independent of changes in an aircraft cabin pressure.

## 2.2. SEPARATION

The GC can be operated with two different, or two identical, sets of columns depending on the desired setup and analysis timing. For most of the recent field missions and during the instrument characterization work described in this paper, we have used the following setup: Oven #1 was equipped with a Restek Rtx-200 pre-column (1  $\mu$  film thickness, 0.53 mm I.D., 3.25 m length) and a main column of identical type, but 4.25m in length. Oven #2 was equipped with a Restek Rtx-1701 pre-column (5  $\mu$ , 0.53 mm I.D., 2.75 m length) and a Rtx-1701 main column (5  $\mu$ , 0.53 mm I.D., 3.25 m length). Normally, oven #1 is operated isothermally at  $20 \pm 0.1$  °C, while oven #2 is controlled at  $24 \pm 0.1$  °C. These operating parameters gave the best compromise between separation, peak shape, and total analysis time. Figure 2 shows a typical chromatogram, in this case of a sample taken on May 13th, 2002 on board the NOAA P-3 aircraft over Los Angeles, California, during the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) mission. The valve timing used during this mission is summarized in Table I. The chromatograms are divided into two parts. Between 0 and 150 s, the ECD is connected to oven #1. The injection for this first part of the chromatogram occurred at  $-48$  s relative to the time depicted on the  $x$ -axis. This not only allows faster analysis since during the first 48 s of the analysis the chromatogram from oven #2 can be analyzed, but also prevents the ECD from ever being exposed to the oxygen peak from the ambient air eluting immediately after injection. PAN elutes at 17 s analysis time, equivalent to a retention time (RT) of 65 s, the PPN elutes at 68 s (RT = 116 s), PiBN at 114 s (RT = 162 s) and MPAN elutes at 133 s (RT = 181 s). The signal drop near 45 s analysis time marks the point where the pre-column is changed

Table I. PAN GC valve timing as used during ITCT2K2

Start time (s)	Stop time (s)	Event	Description
207 (−48)	232 (−23)	Valve #1	Inject sample onto column #1
45	200	Valve #3	Backflush Column #1
233	142	Valve #2	Connect sampling loop valve to column #2
116	141	Valve #1	Inject sample onto column #2
150	255 (0)	Valve #5	ECD to column #2
210	112	Valve #4	Backflush column #2

*Note.* The description of the event corresponds to the valve switching at the start time.

into backflush mode by switching valve #3. Carrier gas #2 is now maintaining the flow through the main column #1 and carrier gas #1 is backflushing pre-column #1. Valve #2 is switched to ready the system for injection onto column #2. The trace between 150 and 255 s shows this part of the chromatogram. Injection occurs at 116 s analysis time, valve #5 is switched at 150 s, after elution of MPAN from oven #1. PAN elutes at 172 s (RT = 66 s), APAN at 201 s (RT = 95 s), and PPN at 233 s (RT = 117 s) from oven #2, thus marked with a (2) in Figure 2. The slight baseline perturbation near 210 s is due to pre-column #2 being switched into backflush mode. On column #1, the APAN signal is masked by the backflush switch. This timing is dictated by the desired fast analysis time for this mission, while allowing enough backflush time for the precolumn and at the same time not disturbing the PPN signal. This setup allows two measurements of PAN and PPN as well as one measurement each of PiBN, APAN and MPAN in a total analysis time of only 4.25 min. The PAN-GC can be setup in several different configurations dependent on the desired PAN analytes. We have used three primary alternative timing schemes: (1) two measurements of PAN, APAN, PPN, PiBN and MPAN every 6 min (injections equally spaced every 3 min); or (2) two measurements of PAN and PPN and one of PiBN, APAN, and MPAN every 4.25 min (injections spaced at 1.5 and 2.75 min, as depicted in Figure 2); or (3) A measurement of PAN, APAN and PPN every 1.75 min. These timing schemes can be easily changed on-the-fly by adjusting the valve timing accordingly.

### 2.3. DETECTION AND PEAK EVALUATION

A Shimadzu Mini-2 ECD, operated in constant-current, variable frequency mode, is used for the detection of PAN. An extensively modified electrometer is used, based on the design of the NOAA CMDL electrometer (Elkins *et al.*, 1996; Fred Moore, personal communication). The ECD frequency pulses are directly counted at a frequency of four Hertz, providing ample coverage for an eluting peak. All peaks are fitted using the Levenberg–Marquardt method applying Gaussian or exponentially modified Gaussian peak shapes. Figure 3 illustrates the sensitivity of the system. The peak shown is PAN from oven #2, corresponding to an ambient mixing ratio of 8.2 pptv, which was observed over Northern Colorado on 27 Feb. 2000 during the TOPSE project in air that originated over the Pacific Ocean. The dots show the raw signal, the black curve is the smoothed data (Savitzky-Golay, 21 point), the gray curve is the peak fit. The peak fitting software developed by us provided a much faster and much more reliable method of determining peak areas than a commercially available GC software package such as HP ChemStation. Based on this and other chromatograms that were taken in very clean air we estimate an in-flight limit of detection that is around 2 pptv or better for a signal peak height to average baseline noise ratio of 3. It should be noted that the detection limit is proportional to the sample volume injected, which is dependent on the inlet pressure. We normally operate at an inlet pressure of 200 (adequate to a maximum flying



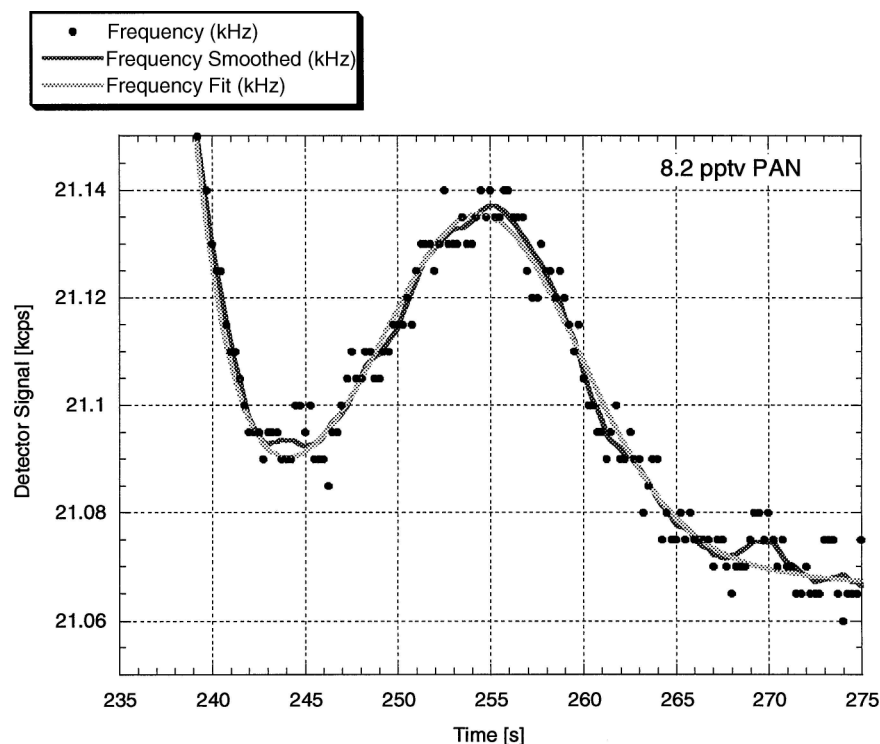


Figure 3. PAN peak in chromatogram taken on board the NCAR C-130 on 27 February, 2000. The signal is equivalent to an ambient PAN mixing ratio of 8.2 pptv.

altitude of roughly 8 km). In a higher flying aircraft the inlet pressure would be lowered, which can be offset by employing a larger sample loop. Data is recorded using National Instruments, Inc. hardware (DAQ) and software (LabView) and then analyzed with a C++ (Metrowerks) program developed by us.

#### 2.4. INSTRUMENT PERFORMANCE ON THE AIRCRAFT

The instrument setup as described above achieved a limit of detection of about 2 pptv using the 5 cm<sup>3</sup> sampling loop. This limits the maximum PAN mixing ratio that can be measured while in the linear range of the electrometer to 10 ppbv. For the TexAQS 2000 study we used a 2 cm<sup>3</sup> sampling loop because we expected very large mixing ratios over the Houston urban and industrial areas. This moved the limit of detection and the maximum measurable PAN mixing ratio to 5 ppt and 25 ppb, respectively. The highest mixing ratio ever observed with this instrument did occur over Houston at 14 ppbv.

The accuracy of an instrument on the aircraft generally is worse than under controlled conditions on the ground. Aircraft cabins often heat up close to or above

the manufacturer's stated temperature limits of electronic components, electrical power often fluctuates, or is lost completely for short periods of time and strong vibration is present on propeller aircraft like the C-130 and the P-3. In addition, electrical power to the instruments is typically not available when the aircraft is parked on the ground over night. We have taken several design steps to compensate for some of these problems. The instrument is designed so that carrier gas flows continue to flow without power at a reduced rate but enough to keep the analytical path and the ECD clean. The NO calibration gas also is flowing continuously through the calibration unit at a small flow rate ( $0.5\text{--}1\text{ cm}^3\text{ min}^{-1}$ ) because the tubing and the flow controller would have to be re-equilibrated for several hours every day without doing so. The valves and tubing inside the GC are temperature controlled and the ECD and electrometer are mounted using vibration isolators. These measures improved the instrument performance in the field but typically a factor of about 2 better precision can be achieved in the laboratory compared to when the instrument is installed on the aircraft.

The best way to assess the precision and accuracy of the instrument on the aircraft is to examine the stability of the calibrations. For example, during the TRACE-P and ITCT 2K2 mission, the average sensitivity of the system was around 100 area units per pptv PAN and varied between 79 and 125 area units/pptv. However, the sensitivity variations during single flights were significantly smaller. The instrument typically shows a gradual improvement of sensitivity over the course of a mission, which is most probably caused by the ECD slowly cleaning out from continuous operation and flushing with carrier gas. Calculated separately for each flight, the  $3\sigma$  standard deviation of the calibration peak area are between 7.5 and 11.1%. Typically, in-flight calibrations are done every 30 min using a fixed mixing ratio of 200–1000 pptv, depending on the expected pollution level. Linearity checks with mixing ratios of 20–10000 pptv are routinely done on the ground and in the laboratory.

Because calibration is done by overflowing the inlet with the calibration mixture, the observed variation of the calibrations takes into account all system uncertainties excluding a possible systematic error in the calibration unit output. Since we measured an absolute uncertainty of about 5% for the calibration unit, a conservative estimate for the total  $3\sigma$  uncertainty of our measurement would be 15% or 2 pptv, whichever is greater, to our PAN mixing ratios. In the laboratory, the total  $3\sigma$  instrument uncertainty is typically better than 10%.

### 3. Calibration and Instrument Characterization

#### 3.1. CALIBRATION METHODS

We use an *in-situ* photochemical method for PAN, in combination with diffusion cell sources for all the measured PAN species. While the former is our primary calibration method on the aircraft, the latter was used in the field on the ground as

a reference method and to verify calibration factors for the PAN homologues, but primarily and extensively in the laboratory for instrument characterization.

### 3.1.1. *The NCAR Photochemical PAN Source*

We have developed a photochemical calibration source for primary in-flight calibration of the PAN-GC system during field missions. The method is based on the photochemical production of peroxyacetyl (PA) radicals from the 285 nm photolysis of acetone in the presence of O<sub>2</sub>. A small, accurately measured flow of an NO calibration standard is added to the gas stream and efficiently converted first to NO<sub>2</sub>, then to PAN (Warneck and Zerbach, 1992). This method relies on a large excess of acetone and PA radicals to effect the conversion of NO to NO<sub>2</sub> and suppress the reaction  $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$ , i.e., to provide conditions such that  $\text{PA} + \text{NO}_2$  is the major reaction of NO<sub>2</sub>. We have made extensive design changes from a commercial design (METCON GmbH, described in Pätz *et al.* (2002) and Volz-Thomas *et al.* (2002)) to make the PAN calibration source aircraft ready and also significantly reduced the amount of acetone needed. The amount of acetone used by the commercially available source is not compatible with our columns because it overloads the column phase and interferes with the PAN peak. The reaction vessel in our system consists of a double quartz cylinder, externally aluminum coated, with a volume of 200 cm<sup>3</sup> and a 2-inch phosphorus-coated pen-ray lamp (Jelight Corp.) situated in the center. The phosphorus coating shifts the lamp output to 285 nm which photolyzes acetone very effectively (photolysis rates around  $2 \times 10^{-3} \text{ s}^{-1}$  can be achieved) but does not significantly photolyze PAN. For aircraft use the vessel is pressure controlled to 800 torr with a MKS model 248 solenoid valve and MKS model 1250 pressure controller. The solenoid valve is fitted with a PFA body, which was built in-house, to minimize PAN loss on metal surfaces. A mixture of 20 ppmv acetone in ultra zero air (Scott-Marrin) is used. Originally we tried to keep the acetone concentration as low as possible and we used a mixture of 10 ppmv acetone and 10 ppmv of CO, which was added to keep the OH mixing ratio in the reaction vessel sufficiently low to almost completely suppress the formation of HNO<sub>3</sub>, but we found that using 20 ppmv acetone instead was acceptable without causing any interference (the OH reaction rates of acetone and CO are similar). A 1 ppmv NO Standard (Scott-Marrin) in Nitrogen is used at flow rates between 0.25 and 2 cm<sup>3</sup> min<sup>-1</sup> STP and is added to 50 cm<sup>3</sup> min<sup>-1</sup> STP flow of the acetone mixture. The resulting NO mixing ratio in the reaction vessel is between 5 and 40 ppbv. The output from the calibrator is diluted with ambient air from which the PANs have been removed quantitatively by thermal decomposition. To achieve this, ambient air is drawn through a 2 m long stainless steel line filled with stainless steel wool heated to 140 °C at flow rates of 2–5 l min<sup>-1</sup> STP. This method (as opposed to using zero-air from a pressurized cylinder for dilution) saves weight on the aircraft but, more importantly, has the advantage that the air matrix used to calibrate the instrument remains very similar to ambient air in the respective sampling

region. In particular, humidity levels and VOC content are not altered. Through a Y-connector situated near the inlet tip, the inlet is overflowed with calibration gas during instrument calibration. Thereby, an in-flight calibration of the complete system is provided with PAN mixing ratios adjustable between 100 and 2000 pptv. Lower mixing ratios of PAN can be achieved on the ground by using larger flow rates of zero-air from a cylinder or PAN-stripped air using a larger pump.

### 3.1.2. Diffusion Sources

Diffusion sources from synthesized PANs have been used extensively to yield PANs of high purity in the cases of PAN, PPN and PnBN (Nielsen *et al.*, 1982; Gaffney *et al.*, 1984; Roberts, 1990). Typically, the PAN compound is diluted into a heavy alkane (such as tridecane) and placed into a diffusion tube at controlled temperature (most commonly 0 °C). The output of the diffusion cells is checked by a NO<sub>x</sub>/NO<sub>y</sub> measurement. We found a mixture of about 75% tridecane and 25% pentadecane most useful as it stays liquid down to about +2 °C so the synthesized, concentrated PAN solution in tridecane can be easily diluted into the mixture at low temperature. At 0 °C however, the mixture solidifies. We found the solid mixture to work just like a liquid as to the diffusion characteristics but this way the diffusion source becomes much less susceptible to mechanical shock, such as when the source is moved between laboratories (Williams *et al.*, 2000). Mixtures prepared in 100% tridecane would have to be recalibrated each time after transport but the solid diffusion source was found to remain stable even after longer transports in a vehicle – if air flow and pressure control was maintained during transport. More recently, calibration of APAN (Tanimoto and Akimoto, 2001) and MPAN (Roberts *et al.*, 1998) using diffusion sources was described, but the synthesis of the pure compounds is difficult.

For the PAN homologues from the diffusion sources, all of which are less than 100% pure, a preparative scale GC (prep-CG, see Section 3.2.1) is employed to separate the PAN compound of interest from potential contaminants in the standard (mostly NO<sub>2</sub>, see below). The chromatographically purified PAN compound is then injected from the prep-GC directly onto the Fast-PAN-GC. In this fashion the sensitivity of the PAN homologues versus PAN have been determined for wide-bore capillary CG/ECD.

## 3.2. LABORATORY CALIBRATION EXPERIMENTS

A two month period of comparison between the Fast-PAN-GC and a NO<sub>y</sub> instrument was carried out at the beginning of 2003 in the laboratory at NCAR. The Fast-PAN-GC is operated in the field using the photochemical in-situ PAN source described earlier that relies on an absolute NO standard for calibration. The peroxy acetyl nitrate is then calibrated based on the measured NO addition and a known production efficiency of PAN in the photochemical cell (see below). The PAN homologues

are then assigned response factors relative to PAN. Some research groups which measure other PAN species such as PPN and PiBN base their sensitivity on a decreasing response factor proportional to the compounds retention time through the column (Roumelis and Glavas, 1989; Roberts *et al.*, 2002) or a response factor equivalent to that of PAN is used, mostly because no separate calibration for any of the other PANs is available (Singh and Salas, 1983).

Both the production efficiency for PAN in our photolytic PAN source as well as the relative response factors for the PAN homologues need accurate measurement to decrease the uncertainty in the absolute measurements in the field. The following sections describe in detail how the response factors for a number of PAN homologue species were obtained in our laboratory.

### 3.2.1. Preparative GC System

The prep-GC is a very simple separation instrument. It has a large sample loop (20 cc) that is injected onto a short mega-bore capillary column (DB-5; 5 m, 0.53 mm I.D., 1  $\mu$ m film thickness) at a carrier gas flow of about 10 cm<sup>3</sup> min<sup>-1</sup> (STP). The column temperature can be adjusted to allow the separation of different PANs from each other and/or from NO<sub>2</sub>, which is a common impurity in both the photochemical PAN source and the diffusion tubes. At the same time, it produces very broad, flat-topped, peaks. The mixing ratio of the PAN species of interest in each signal is determined by eluting the column into the NO<sub>y</sub>-instrument. Reduction of the PAN (NO<sub>y</sub>) compounds to NO occurs by passing the PAN standards diluted in a zero air stream through a heated (325 °C) 6.4 mm molybdenum tube (Fehsenfeld *et al.*, 1987). The NO is then measured by chemiluminescence (Ridley and Howlett, 1974; Kley and McFarland, 1980). The NO<sub>y</sub> instrument was calibrated with a 0.970 ppmv NO standard (Scott Marrin). Conversion efficiency of the MoO catalyst for the PAN homologues to NO is assumed to be equal to that of NO<sub>2</sub> (Williams *et al.*, 1998). It was tested using an O<sub>3</sub> gas-phase titration device in which about 90% of the NO standard was converted to NO<sub>2</sub>. The converter efficiency was consistently 95 ± 0.5% ( $n \sim 50$ ) throughout the laboratory measurement period.

The bottom trace in Figure 4 shows the chromatogram of an injection of 20 cc of a synthesized MPAN diffusion source standard onto the prep-GC and eluted into the NO<sub>y</sub> instrument. The MPAN peak width is about 90 s and is separated from an unresolved peak of NO<sub>2</sub> and PAN by roughly 65 s. The eluent from a second injection of the same volume is then synchronously injected onto the Fast-PAN GC. Injection is timed roughly at the center of the nearly square shaped MPAN signal eluting from the prep-GC. The top trace in Figure 4 shows the MPAN peak, which was injected onto the Fast-PAN-GC in this fashion. This type of two-dimensional chromatography allows for the accurate quantification of the PAN homologue species. It also allows for the quantification of NO<sub>2</sub> impurity in both the PAN diffusion standards and the photochemical PAN source.

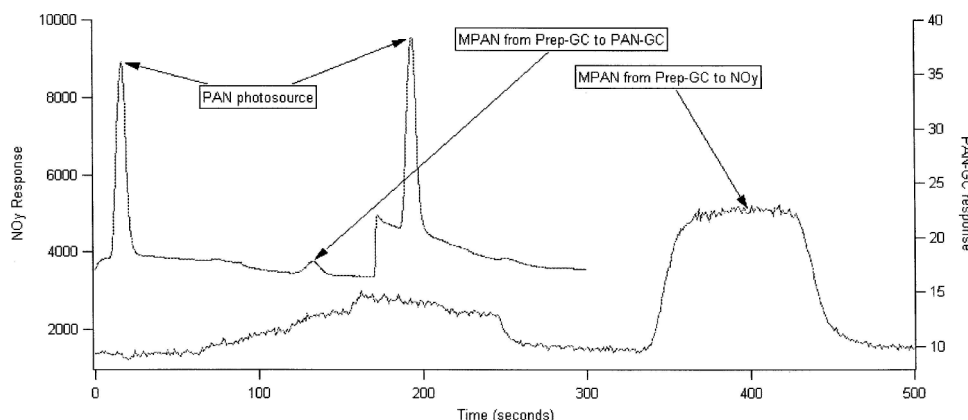


Figure 4. An example of MPAN injected on the Prep-GC and then onto the PAN-GC. Here, the  $\text{NO}_2$  and PAN signals are not resolved. To measure the  $\text{NO}_2$  content, the Prep-GC column temperature is lowered.

### 3.2.2. Calibration Results

PAN was calibrated using both, the photochemical PAN source and the diffusion source. Calibration of the PAN photolytic source and diffusion source output using the prep-GC/ $\text{NO}_y$  averaged  $95.5 \pm 1.5\%$  and  $97 \pm 1\%$  pure PAN to  $\text{NO}_2$ , respectively, throughout the calibration experiments ( $n = 9$ ). The main impurity in the output of both sources was  $\text{NO}_2$ . Use of a nylon wool trap on the  $\text{NO}_y$  instrument inlet verified that no detectable amount of nitric acid was produced by the photolytic standard technique. Calibrations for the PAN homologues PPN, MPAN, and PiBN were performed using synthesized standards in the diffusion source. Common impurities in the PiBN and MPAN standards are variable amounts of PAN and  $\text{NO}_2$ . The Prep-GC/ $\text{NO}_y$  instrument was used in all cases to purify and calibrate the standards. The results from the calibration experiments are summarized in Table II. Estimates of the sensitivity of the PAN-GC to APAN are also included, but a precise analysis of APAN could not be performed due to difficulty in producing a synthesized standard with sufficient purity. The response factor has been estimated based on the MPAN sensitivity and is therefore more uncertain.

### 3.2.3. Discussion

A previous study has found the sensitivity for the peroxy acetyl nitrates on a GC/ECD system typically to decrease with increasing retention time on the chromatographic column (Roumelis and Glavas, 1989). The same general trend was observed here, at least for the simple aliphatic PAN compounds. From PAN to PPN to PiBN the response factor decreases by almost half to 0.55. Similar to the findings in Roumelis and Glavas (1989) this could be explained by the column liquid phase undergoing an irreversible reaction with the PAN compound. While this possibility

*Table II.* Measured response factors of some PAN species relative to PAN. These numbers are an average from 20–50 single measurements of the response and the errors are 3- $\sigma$  standard errors of the means (except for APAN, please see text)

Compound	Structure	Standard purity <sup>a</sup>	PAN-GC Response factor <sup>b</sup>	PAN-GC Retention time (s)
PAN	$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$	$95.5 \pm 0.5^c$ $97.0 \pm 0.5$	1	65
PPN	$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}_2\text{NO}_2$	$97 \pm 1.0$	$0.90 \pm 0.02$	113
MPAN	$\text{CH}_2\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}_2\text{NO}_2$	78–85%	$0.64 \pm 0.03$	181
APAN <sup>d</sup>	$\text{CH}_2\text{CHC}(\text{O})\text{O}_2\text{NO}_2$	<10%	$0.8 \pm 0.15$	85
PiBN	$\text{CH}_3\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{O}_2\text{NO}_2$	30–60%	$0.55 \pm 0.02$	162
<i>i</i> -PrONO <sub>2</sub>	$(\text{CH}_3)_2\text{CHONO}_2$	100%	$0.70 \pm 0.01$	63

<sup>a</sup>Standard purity of synthesized compounds used in diffusion source.

<sup>b</sup>Response factor on PAN-GC corrected for purity.

<sup>c</sup>Photosource purity.

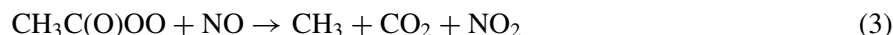
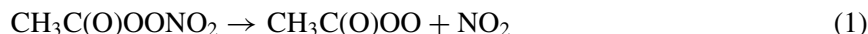
<sup>d</sup>Estimated.

cannot be ruled out, it is unlikely because the RTX-200 phase (a trifluoropropyl ester compound) has a very high inertness compared to other column phases used for PANs separation, especially carbowax packed column phases. The PANs could also react with the surfaces of the valves and internal connection lines and at commonly named “active sites” on the column. An active site is considered a piece of the column where there is no phase or the phase is very thin or where the phase has undergone chemical reactions with oxygen or other contaminants. We have evidence that such reactions occur since adding water to our carrier gas improved the reproducibility of the analysis. The emphasis here lies on reproducibility. The humidification most probably eliminates the activation of surfaces inside the system when very dry air is sampled at higher flight altitudes. This makes the system more reproducible.

However, the data in Table II show that the response factor of MPAN does not fall in line with the aliphatic PAN species since its response factor relative to PAN is higher (0.64) than that of PiBN (0.55), despite the longer retention time of MPAN. This is in contradiction to chemical losses on the column based on retention time being responsible for the observed response factor. We will therefore examine other factors, such as thermal loss of PAN compounds during analysis, and the ECD sensitivity to different PAN homologues, as potential explanations.

In the atmosphere, the effective PAN lifetime is governed not only by the thermal dissociation rate (R1) but also the NO to NO<sub>2</sub> ratio (Singh and Salas, 1983), since the loss reaction with NO (R3) competes with recombination of the peroxyacyl (PA) radical with NO<sub>2</sub> to reform PAN (R2). Under normal, lower tropospheric conditions the actual lifetime of PAN is therefore often considerably longer than the thermal dissociation lifetime. In a gas chromatographic system we can assume that all PA

radicals formed in the gas phase would be lost to the walls of connecting lines and valves or on the liquid phase on the column, making the actual PAN lifetime equal or at least very close to the thermal dissociation lifetime.



At 20, 25 and 30 °C, the characteristic time for the thermal dissociation of PAN is 1.42, 0.65 and 0.31 h, respectively. Given that PAN spends only about 70 s in the analytical system, a thermal loss of only about 2%, 4% or 8%, respectively of the injected amount of PAN would be expected. While this is in line with our observation of significant losses of PAN at column temperatures higher than 25 °C, it does not explain the decline in response factors for the larger PANs. For example, assuming the same thermal lifetime for PiBN as for PAN, at 20 °C the calculated thermal loss for PiBN is only about 2% larger than the loss for PAN. If the slightly longer thermal lifetime for PPN compared to PAN (Kirchner *et al.*, 1999) is assumed for PiBN, this difference would decrease further by about 30% making the expected loss only 1.5% larger than that for PAN.

A complication in estimating the expected loss of each PAN compound results from the fact that the compounds actually spend very little time in the gas phase while they travel through the analytical system. The total time an analyte spends in the gas phase is equal to the dead time of the chromatograph, in our case about 5 s. The rest of the time the analyte is dissolved in the liquid phase of the column. The PAN lifetime may actually be somewhat longer in solution than in the gas phase due to a possible cage-effect of the solvent, preventing the PA and NO<sub>2</sub> radicals from reaching a separation sufficient for dissociation fast enough before recombining (Roberts, 2005).

Since the thermal dissociation loss rates of PAN and MPAN are thought to be similar (Roberts and Bertman, 1992), this result is an additional indication that thermal loss of the PANs on the column is not the dominant contributing factor to their measured relative sensitivities. This leaves us to consider how the sensitivity of an ECD to each homologue might be influenced by its molecular structure. Both the physical size and also the electron donating effect of the alkyl group may contribute to a decrease in the effective cross section of the PAN species for an electron uptake reaction. We have observed a similar decrease of the ECD response of the thermally stable alkyl nitrates with increasing carbon chain length. The olefinic group on the MPAN molecule will have a strong electron donating effect because it forms a conjugated system, where the electrons are delocalized along the C=C–C=O bond. This electron donating effect should be stronger than that of the isopropyl group attached to the acyclic carbon of the PiBN molecule, thus causing the expected sensitivity for MPAN to be smaller or at least equal to that of PiBN. However, the methacryl group of MPAN is physically smaller in size and



is constrained in rotation compared to the isopropyl group attached to the acyclic carbon of the PiBN molecule. Therefore it appears likely that the physical size of the organic group is mainly responsible for the larger relative response factor of MPAN versus PiBN. Since this sterical effect is caused by the effective cross section of the molecule to capture a thermal electron in the ECD, the effect should, at first approximation, be independent of the manufacturer of the ECD used. Although we have not tested the relative responses of the PAN species on other brand ECDs in our laboratory, we think it is likely that the effect of each PAN homologue's effective cross section would result in approximately the same relative loss of sensitivity in different detectors.

We conclude that, in the case of capillary columns with inert phases, the system-internal losses of analyte are probably very small and the primary responsible factor for the different response factors of PAN homologues versus PAN is a lower sensitivity of the electron capture detector to PANs with larger carbon chain length. The difference between this finding and the finding of Roumelis and Glavas (1989) is most likely due to the fact that the manufacturing process of capillary columns has advanced significantly in the last 15 years and columns have far fewer imperfections and active sites than in the past.

#### 4. Comparison Measurements in the Atmosphere

##### 4.1. COMPARISON WITH OTHER PAN INSTRUMENTS

Our system has been extensively compared with NOAA's PAN GC system (Roberts *et al.*, 1998; Williams *et al.*, 2000) in the laboratory, and agreement was generally excellent, i.e. within 5% or better. However, both systems rely on the same calibration routine and use the same or similar chromatographic columns and detectors. Although the NCAR PAN gas chromatographic system has flown on six aircraft missions so far, there has only been one opportunity to compare the instrument with another PAN analyzer in flight. This comparison took place over the North Pacific Ocean in March and April 2001 during the NASA TRACE-P (Transport and Chemical Evolution – Pacific) experiment. The NCAR system was installed on the NASA P-3 aircraft, measuring PAN, PPN, APAN and MPAN and the NASA Ames PANAK system (Singh and Salas, 1983), measuring PAN and PPN, was installed on board the NASA DC-8. During 3 separate periods, each between 30 and 60 min long, the two aircraft flew within 1 km or less of each other at the same altitudes. Details about these comparison flights can be found in Eisele *et al.* (2003). Both instruments are GC/ECD systems but the NASA system uses packed columns. In addition the NASA system employs a cryogenic enrichment method which produces 5-min average mixing ratios which makes the direct comparison of results from the two instruments somewhat difficult.

The results for PAN are shown in Figure 5a. Because all comparison flights were carried out over the remote Pacific Ocean, the PAN values are generally quite

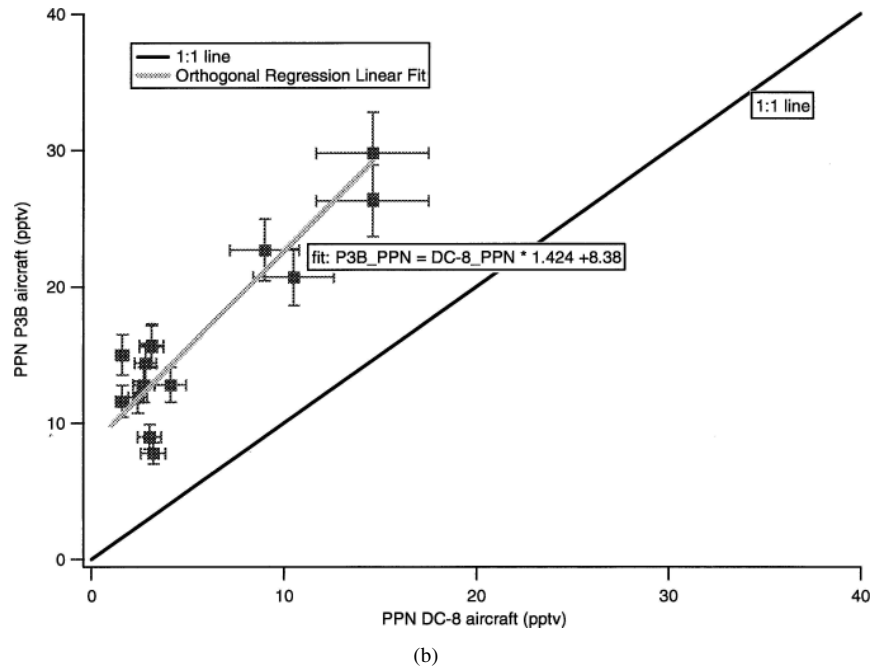
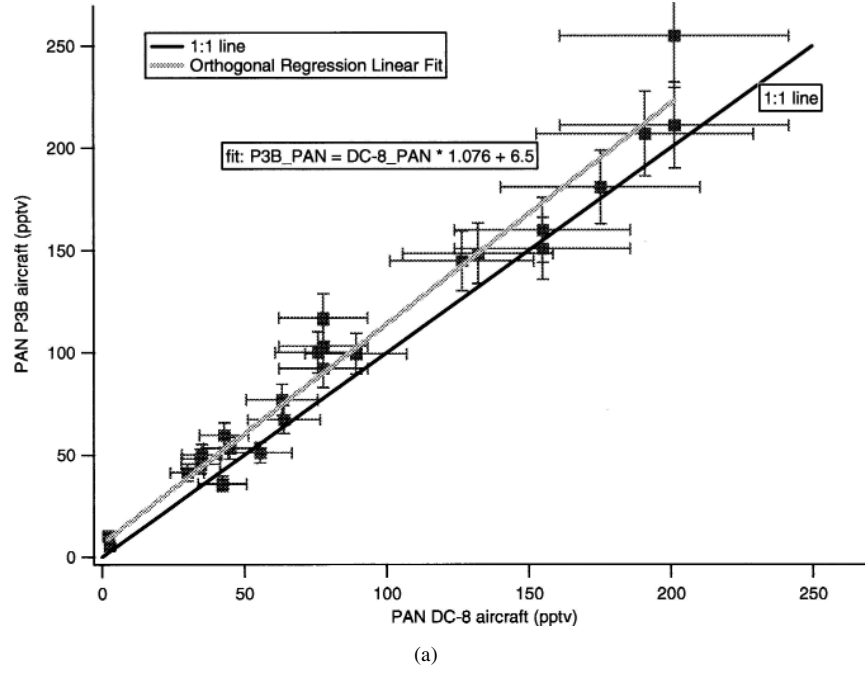


Figure 5. Plots of PAN (a) and PPN (b) as measured on board the NASA DC-8 with the NASA PANAK instrument and on board the NASA P-3B using the NCAR PAN-GC during three different comparison flights during the 2001 NASA TRACE-P experiment. The bars represent the stated uncertainties of both measurements.

low, ranging from the limit of detection (5 pptv for the NASA instrument, 2 pptv for the NCAR instrument) to about 200 pptv. These values are well below what would typically be observed in an urban area (Ciccioli *et al.*, 1988; Rappenglück *et al.*, 1993; Aneja *et al.*, 1999; Gaffney *et al.*, 1999; Glavas and Moschonas, 2001; Grosjean *et al.*, 2001; Roberts *et al.*, 2002) but within the range of PAN mixing ratios observed in the middle and upper remote troposphere (Singh and Salas, 1983; Ridley *et al.*, 1990; Atlas *et al.*, 1992; Singh *et al.*, 1994, 1996; Schmidt *et al.*, 1998; Thakur *et al.*, 1999; Zellweger *et al.*, 2000; Whalley *et al.*, 2004). The measurements are in very good agreement. Although there is a slight bias to higher mixing ratios in the NCAR data versus the NASA data, the slope is well within the combined uncertainty of the two instruments (15% or 2 pptv, whichever is greater, for the NCAR instrument; and 20% for the NASA instrument). There is a small offset of about 6 pptv that the NCAR instrument measures when the NASA instrument is extrapolated to zero, but it is insignificant compared to the uncertainty of the fit. The fact that 2-propyl nitrate coelutes with PAN on the RTX-200 column is not responsible for this offset. Normally 2-propyl nitrate is only a small fraction of PAN under most atmospheric conditions. However, in the marine boundary layer of the equatorial pacific, where 2-propyl nitrate mixing ratios can reach more than 10 pptv due to marine sources (Blake *et al.*, 2003) and PAN can be very low due to thermal loss, this interference can be significant. 2-propyl nitrate was measured during the comparison flights by the Blake group (Blake *et al.*, 2003) and at the lower PAN mixing ratios was between 1 and 2 pptv and did not exceed 6 pptv at the highest PAN mixing ratios (Blake, private communication). In addition, the response of the NCAR GC to 2-propyl nitrate is only 70% of that for PAN. This only explains a small fraction of the observed offset and also does not contribute significantly to the observed slope. One reason for the slight bias of the slope could lie in the sample timing issues of the two instruments. As mentioned above, the NASA instrument produces a 5-min average while the NCAR instrument uses direct injection and averages only over 2–5 s, depending on altitude. Only measurements were used where the NCAR measurement fell within the inner 4 min of the NASA measurement period and where  $\text{NO}_y$  values did not change more than 25% during the sampling period. More stringent criteria would have reduced the data to too few points. The measurement at around 200 ppt was taken while  $\text{NO}_y$  values were decreasing (Kondo, private communication). The NCAR GC took its measurement within the first minute of the NASA averaging period. It can be assumed that PAN mixing ratios were also decreasing during this period. If this value was eliminated from the comparison plot, the fitted slope would be 1.012 and the intercept would increase insignificantly to 7.2 pptv. In either case the measurements are in good agreement within the stated uncertainties. The point at 200 pptv PAN was included in the plot to be consistent with the analysis done in the Eisele *et al.* (2004) paper. Whether potential losses of PAN and PPN on the packed columns could be contributing to the observed positive offset of the NCAR instrument at very low PAN mixing ratios cannot be answered with the limited comparison data available.

Figure 5b shows the comparison for PPN. The data reported by the NASA group are considerably lower than the mixing ratios measured by NCAR. The slope of 1.46 is clearly outside of the combined instrument uncertainties. There is also a significant offset of the NCAR instrument over the NASA instrument. Similarly to the 2-propyl nitrate interference for PAN, there is a 2-butyl nitrate interference of the NCAR instrument for PPN. But also in this case, it can only explain a small fraction of the observed offset. At the low PPN mixing ratios, 2-butyl nitrate was below 2 pptv and did not exceed 3.5 pptv for the higher PPN values. The instrument response for 2-butyl nitrate was not tested, but in analogy to the PAN compounds, should be somewhat lower than that for 2-propyl nitrate. Thus the effect of the 2-butyl nitrate interference is well below the stated instrument uncertainty. If the point at 30 pptv PPN (measured by the NCAR instrument and coincident to the 200 pptv PAN measurement discussed above) would be removed from this analysis the slope would drop to 1.31 and the  $x$ -axis offset would increase to 10.5 pptv. The NASA instrument uses packed columns with a Carbowax stationary phase and has no separate calibration for PPN. The same sensitivity for PAN and PPN is assumed. It was shown by Roumelis and Glavas (1989) that packed columns tend to exhibit much larger loss rates compared to capillary columns. In addition, Carbowax is a quite reactive stationary phase. The differences in PPN observed here are consistent with enhanced packed column losses for PPN, resulting in a lower response factor than that for PAN.

## 5. Summary and Conclusions

A state-of-the-art fast-PAN-GC/ECD system has been developed and deployed to measure PAN compounds from an aircraft platform. Sampling and analysis timing can be optimized to capture PAN and PPN within a 1.5 min timeframe, and PAN homologues up to MPAN within 2.25 min.

We found that using a pre-separation column setup significantly reduces baseline variations during analysis, especially when polluted air is measured. This far outweighs the disadvantage of a short baseline disruption upon valve switching. We also found that the addition of water to the analytical path causes the system to run more stable as reflected in significantly reduced scatter in our calibration.

The response factors on the PAN-GC/ECD for synthesized PAN homologues have been accurately determined by the use of a preparative GC with  $\text{NO}_y$  and subsequently PAN-GC analysis. These response factors do not simply follow a retention time trend but show enhancements for MPAN sensitivity. We conclude that the main reason for the drop-off in sensitivity for aliphatic PAN compounds as well as the higher than expected sensitivity for MPAN is mainly due to the sensitivity of the ECD towards the different PAN species. Lower sensitivities to PAN compounds with larger aliphatic and olefinic groups appears to be caused by sterical reasons. From retention time and size of the olefinic rest, a sensitivity factor for APAN was estimated. We recommend for investigators using capillary columns

with inert stationary phases to measure PAN species to use these response factors if an individual calibration for PAN homologues is not possible. In the case of packed columns, however, it seems that significant losses of analyte do occur on the surfaces of the stationary phase or the column walls. In an aircraft comparison between our instrument and another instrument using packed columns PAN compared well while PPN values disagreed significantly beyond stated uncertainties. This discrepancy was consistent with potential losses of PPN on the packed column. A separate calibration for all homologues measured is necessary for each column and phase combination used in such systems.

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