An Optimized Method for Airborne Peroxyacetyl Nitrate (PAN) Measurements

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Abstract. In this paper we describe a gas-chromatographic method for PAN measurements in the background atmosphere, which has been adapted to the special requirements of aircraft based campaigns. The instrument is installed in a 1.21 m high, 19 inch rack which has a total weight of 70 kg and a power consumption of 750 VA. The gas chromatograph is equipped with a commercial liquid injector and a valve system for injection of gaseous samples. The gas-inlet system allows automatic injection of samples with defined and constant mass, independent from ambient pressure variations. Two different methods are used for calibration: Liquid PAN calibration samples and a diffusion source for gas-phase calibrations. Both methods have reproducibilities better than 90% and agree with each other to better than 85%. An optimum selectivity of the gas-chromatographic separation is obtained by a combination of two short megabore capillary columns of different polarity. The flow rates are 15 cm^3/min, the column temperature is 26 °C. For detection an electron-capture detector, operated at 30 °C, is used. To allow a reliable control of these relatively low temperatures the instrument is equipped with peltier cooling. To avoid baseline or signal drifts caused by pressure variations in the aircraft cabin an electronic control of the system pressure is integrated into the instrument. The lower limit of detection is better than 15 ppt (3 σ), the time needed for one measurement is less than 4 min. Preliminary results from a flight campaign conducted in June 1994 demonstrate the suitability of the instrument for airborne PAN measurements.

Key words: peroxyacetyl nitrate, gas-chromatographic optimization, airborne measurements.

1. Introduction

Peroxyacetyl nitrate (PAN), a photochemical product of non-methane hydrocarbons (NMHC) and NO_x (= NO + NO_2), plays an important role in atmospheric chemistry. Two aspects are of interest: (1) Due to its strongly temperature dependent rate of thermal decomposition (Atkinson *et al.*, 1992) PAN can act as a significant reservoir for nitrogen oxides. This way it can influence regional as well as large-scale NO_x distributions by long-range transport in the upper troposphere (Crutzen, 1979). Also in situ formation can occur in some tropospheric regions both leading to maximum PAN to NO_x ratios of 25 (Singh *et al.*, 1992a). (2) The formation of PAN indicates photochemical smog (Carter *et al.*, 1981; Rappenglück *et al.*, 1993). PAN is a more reliable indicator than ozone because it originates solely from photochemical reactions, within the troposphere.

For the investigation of the transport of air pollutants not only measurements of the latitudinal PAN distribution are important (Müller and Rudolph, 1992), but also the variations in PAN concentration with altitude must be taken into account because in cold tropospheric regions PAN shows a longer lifetime than NO and NO_2. Thus, the number of airborne PAN measurements has considerably increased during the last years (Rudolph *et al.*, 1987; Singh *et al.*, 1990, 1992b; Ridley *et al.*, 1990). Still, data are scarce, especially measurements above 6 km altitude. Measurements in the 10-km altitude range are of special interest because the rising volume of flight traffic in the Northern Hemisphere enhances the concentration of NO_x in the upper troposphere.

Airborne instrumentation for PAN measurements has to meet several requirements. For minimum thermal decomposition and therefore highest sensitivity and reproducibility the instrument has to be operated at ambient temperature or less. To minimize PAN loss due to surface contact the analysis has to be fast. In addition, on board of an aircraft the analysis time should be as short as possible to obtain a good spatial resolution of the measurements. To save measuring time preconcentration steps which are necessarily time-consuming should be avoided. This implies a higher detection limit due to smaller sample volumes which must be compensated by improving the detector sensitivity. Further problems to be handled are pressure variations in the aircraft cabin which can lead to signal and baseline shifts. Also the decreasing ambient pressure with increasing flight altitude will reduce the injected air sample mass if the injection system does not allow a compensation for pressure changes. Finally aircraft operation places limits on weight, size and electric power consumption of the instrument.

2. Instrument Description

The general instrumental setup is depicted in Figure 1. The single components are integrated into 19 inch slide-in units which guarantee easy handling and higher safety on board of an aircraft. These slide-in units are attached to a rack of the dimensions $1.21 \times 0.56 \times 0.86$ m which has a total weight of 70 kg. Since European standard 220 V/50 Hz power supply is limited on most of the research aircrafts only few components of the instrument need 220 VAC while all others are operated with 110 V/100 Hz or 28 VDC. The total power consumption adds to 750 VA. The gas supply is provided by a 10-l gas cylinder placed in another 19 inch rack which contains the gas supply for all experiments on board.

The sample inlet system that allows three different operation modes is shown in Figure 2. It is used for dynamic dilution of the calibration gas with air purified by passing air from the aircraft cabin through a molecular sieve cartridge. This is necessary to obtain PAN concentrations in the calibration gas that are relevant for background air measurements and which are within the linear range of the detector. With a mass flow controller the exact dilution factor can be adjusted. For this mode the manual three-way valve is in the 90° clockwise-turned position while

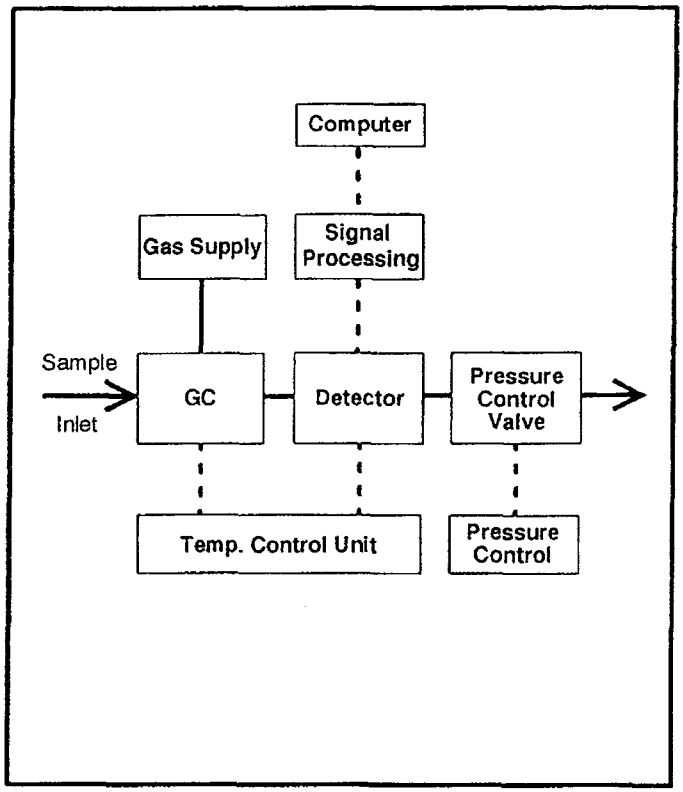

Fig. 1. Flow diagram of PAN instrumentation during the flight campaign. The dotted lines indicate electrical connections, the solid lines indicate gas flow connections.

the pneumatic four-way valve is in the position as indicated by solid lines and the gate valve is closed. The second function is to flush the inlet line during ambient air measurements. The three-way valve then is in the 180° position, the four-way valve is in the position as indicated by dotted lines and the gate valve is open. The third operation mode allows flushing of the inlet line in the opposite direction with purified air. In this way contaminations of the inlet line during take-off and landing procedures at highly frequented airports can be avoided. For this purpose the three-way valve is in the 90° clockwise-turned position while the four-way valve is in the position as indicated by solid lines and the gate valve is open. Furthermore, the mass flow controller is turned off. All connection lines in this system are 4-mm i.d. Teflon tubes.

Figure 3 shows the gas-flow scheme of the instrument. It is an improved version of an instrument designed for ground based operation (Müller and Rudolph, 1989). As carrier gas we use nitrogen. For laboratory measurements, nitrogen of 99.999% purity which is for further purification passed through an adsorption cylinder containing molecular sieve of different pore sizes, activated carbon, and silica gel kept at –80 °C. On board of the aircraft the gas chromatograph is operated with nitrogen of 99.9999% purity without further purification. Since water vapor has a positive effect on PAN sensitivity (Watanabe *et al.*, 1978) the carrier gas is passed through

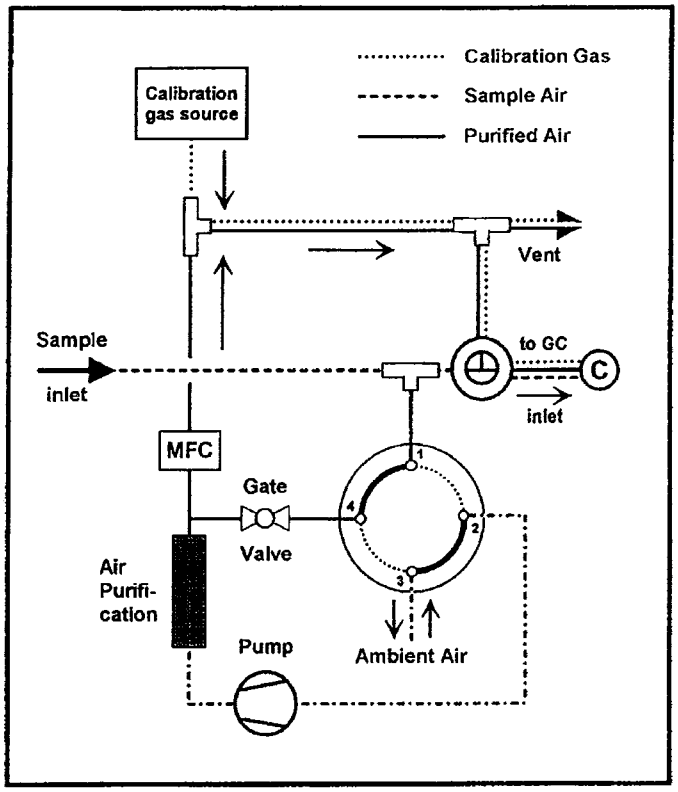

Fig. 2. System for flushing the ambient air inlet line and for dynamic dilution of the calibration gas. Note that the manual three-way valve is in the 0° position.

a glass cylinder filled with 340 cm^3 $CuSO_4 \cdot 5H_2O$. This results in a constant and defined water vapor mixing ratio of 15 ppm. The different gas pressures are controlled by stainless-steel membrane pressure regulators (Siemens).

Two possibilities for sample injection are integrated into the gaschromatograph: (1) A liquid injector (Siemens) allows the measurement of liquid PAN calibration samples. Via the pneumatic 4-way valve (III) the injector can be connected to the carrier gas stream (see Figure 3). (2) The inlet system for gaseous samples consists of a 7.5-cm^3 STP sample loop of borosilicate glass and three pneumatic metal bellow valves (a)–(c). The connections to a pump, a pressure regulator for nitrogen and the inlet line are made of Teflon tubes with 4 mm i.d. To guarantee the injection of gaseous samples of constant mass independent from ambient pressure variations and thus flight altitude, a Teflon 'compression tube' of 2.5 m length and 4 mm i.d. is located between inlet valve and sample loop. With valves (a) and (c) open and ten-way valve (I) in the position as indicated by dotted lines (see Figure 3), ambient air (or calibration gas) is passed through the 'compression tube' and the sample loop at a flow rate of typically 50 cm^3/min STP, regulated by the mass flow controller. After closing valves (a) and (c) and simultaneously opening valve (b) the air in the sample loop is compressed to the pressure preset on the regulator R_3 by carrier gas N_2. Subsequently switching back the ten-way valve (I) leads to the injection of

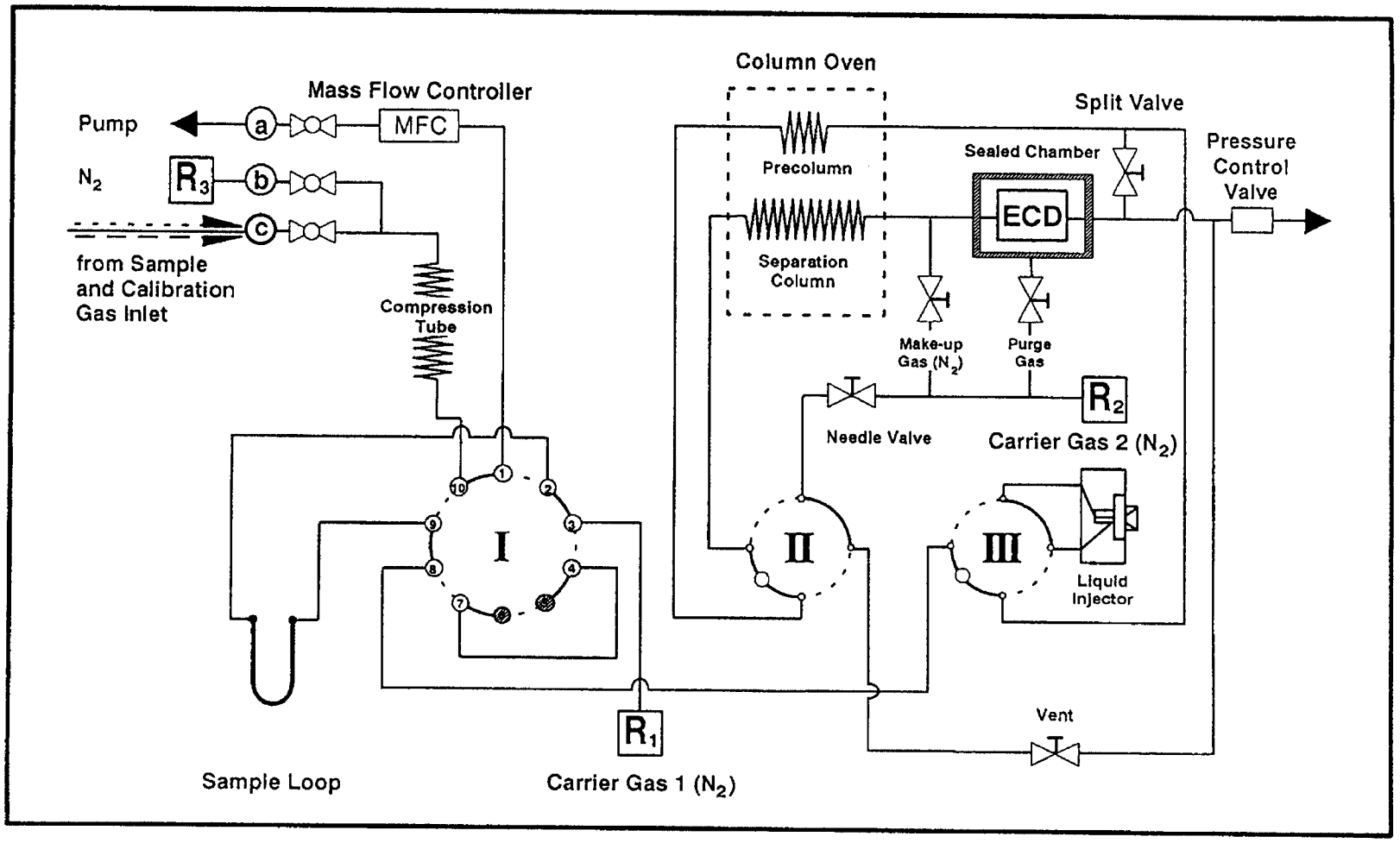

Fig. 3. Gas-flow scheme of the gas chromatograph.

a defined and constant gas amount. Moreover the pressure regulated by R_3 is set equal to the column-head pressure. So a pressure surge is prevented, when gaseous samples are injected. The six pneumatic valves are controlled by magnetic valves which can be switched automatically. This allows a time programmed, automatic operation of the gas chromatograph.

The connections between the inlet, the multiport valves and the separation columns are made of 1/16 inch stainless steel tubes. To obtain an optimum separation we use an arrangement which combines a ten- and a four-way valve with a precolumn and a main column. During the preseparation process on the precolumn (position of valve (I): solid lines; position of valve (II): dotted lines) this combination allows the sample fraction of lower retention than PAN to be vented. By switching the valve (II) into the position as indicated by solid lines, PAN is transfered to the main column. During the next preseparation process the sample fraction of higher retention than PAN can then be eliminated by 'flushing' the main column with carrier gas 2 (at a higher flow rate than carrier gas 1). This shortens the analysis time and will allow a two-dimensional separation if pre- and main columns of different polarity are used. The 'vent' needle valve provides the possibility to optimize the flow rate during preseparation on the precolumn independent of the flow through the main column. Unlike the standard chromatographic setup with a ten- and a four-way valve combined with a pre- and a main column (Müller and Rudolph, 1989) this modified version has no connection lines between the precolumn and the ten-way valve and back to the four-way valve. This setup does not allow blackflushing of the precolumn but leads to shorter dead times and smaller dead volumes. The split valve installed between the four-way valve (III) and the precolumn permits the use of capillary columns instead of packed columns without variation of the sample loop volume. During the optimizing process of the instrument we tested packed as well as capillary columns. For details, see Table I.

The instrument is equipped with a constant-current, frequency-modulated electron capture detector (ECD) from Siemens. To achieve an acceptable performance of this ECD a minimum flow rate of 15 ml/min in the detector is necessary. Therefore this ECD offers a make-up gas connection (make-up gas is nitrogen) to maintain a sufficient flow rate in the detector during operation with capillary columns at flow rates lower than 15 ml/min. A signal amplifier and an analog to digital converter process the ECD signal.

To avoid baseline and signal shifts from pressure variations in the aircraft cabin the various gas flows are combined at the exit of the gas chromatograph (see Figure 3). At the common GC exit we installed a proportionally working valve (MKS) to control the system pressure. The system pressure can be adjusted to a constant level independent from variations in ambient pressure by a set point control combined with an electronic pressure sensor (Setra). For an optimum stability of the pressure regulators (R_1–R_3) their reference side is also connected to the system pressure control (not shown in Figure 3). To reduce the pressure load on the ECD-

TABLE I. Column combinations tested during instrument development. The column oven temperature always was 26 °C. The detection limit is based on an optimized sample volume corresponding to [half-intensity width/2 × flow rate] Rtx-1, 100% dimethylpolysiloxane (Restek); Rtx-5, 5% diphenyl-/95% dimethylpoysiloxane (Restek); Rtx-1701, 14% cyanopropylphenyl-/85% dimethylpolysiloxane (Restek); SPB-5, 5% diphenyl-/95% dimethylpolysiloxane (Supelco).

Precolumn	Separation column	Flow rate	Retention time	Detection limit	Theoretical plates	Make-up-gas
0.3 × 2 mm glass packed with 5% PEG 400 on Chromosorb WHP 80/100 mesh	1 m × 2 mm glass packed with 5% PEG 400 on Chromosorb WHP 80/100 mesh	40 cm^3/min	275 sec	60 ppt	575	10 cm^3/min
	10 m × 0.32 mm fused silica capillary column SPB-5, film thickness 1 μm	4 cm^3/min	189 sec	140 ppt	6895	45 cm^3/min
5 m × 0.53 mm fused silica capillary column Rtx-1, film thickness 5 μm	10 m × 0.53 mm fused silica capillary column Rtx-1, film thickness 5 μm	15 cm^3/min	252 sec	20 ppt	2144	–
5 m × 0.53 mm fused silica capillary column Rtx-5, film thickness 5 μm	10 m × 0.53 mm fused silica capillary column Rtx-5, film thickness 5 μm	15 cm^3/min	393 sec	40 ppt	2495	–
2 m × 0.53 mm fused silica capillary column Rtx-5, film thickness 5 μm	3 m × 0.533 mm fused silica capillary column Rtx-5, film thickness 5 μm	15 cm^3/min	159 sec	30 ppt	1684	–
5 m × 0.53 mm fused silica capillary column Rtx-1701, film thickness 3 μm	10 m × 0.53 mm fused silica capillary column Rtx-1701, film thickness 3 μm	15 cm^3/min	419 sec	50 ppt	2603	–
3 m × 0.53 mm fused silica capillary column Rtx-1, film thickness 5 μm	3 m × 0.53 mm fused silica capillary column Rtx-1701, film thickness 3 μm	15 cm^3/min	146 sec	15 ppt	1448	–

cell by ambient pressure drops and because the ECD is known to be sensitive to O_2-diffusion into the ECD-cell the detector is housed in a sealed chamber. The chamber is purged by nitrogen (see Figure 3) and the exit is also connected to the MKS valve.

Three components of the gas chromatograph are operated temperature-controlled: the liquid injector, the ECD and the column oven. Due to the strongly reduced lifetime of PAN at temperatures above 30 °C the ECD and the column oven must be kept at temperatures in the range of 15–30 °C. To maintain a reliable temperature control in this temperature range they are cooled by peltier elements. The liquid injector is operated at higher temperatures, depending on the solvent of the PAN calibration solution.

To calibrate the instrument we use a solution of PAN in n-heptane which is synthesized similar to the method of Nielsen *et al.* (1982) and stored at –20 °C. Regularly, the PAN concentration in the solution is determined by alkaline hydrolysis and subsequent photometric measurement of the nitrite ion concentration (Saltzmann, 1954). Nitrate ions are also measured photometrically to obtain a measure for the degree of PAN decomposition in the solution. The PAN calibration standard is used for two calibration methods: (1) This stock solution is further diluted with n-hexane and samples of a few microliters are injected. This method enables us to calibrate the gas chromatograph with different PAN concentrations which are comparable to those expected from injection of ambient air samples. (2) Gas-phase calibration of the instrument is achieved by utilizing a diffusion system similar to the one which is described in a previous article (Müller and Rudolph, 1989). To determine the PAN mixing ratio in the calibration gas about 100 l are passed through a small impinger filled with 20 cm^3 of a diluted NaOH solution. The concentration of the formed nitrite ions is also determined photometrically. A formation of nitrate ions will not be observed if the alkalinity of the NaOH solution is sufficiently high (pH > 13).

In June 1994, we participated in a flight campaign on board of the DLR (Deutsche Forschungsanstalt für Luft- und Raumfahrt) aircraft FALCON along the European West coast. The specific setup of the gas chromatograph for the flights was as follows: For sample separation we used a combination of 3 m × 0.53 mm Rtx-1 as a precolumn and 3 m × 0.53 mm Rtx-1701 as main column. For practical reasons we decided to keep our diffusion system for gaseous calibration only at 0 °C. n-Propyl nitrate (NPN) was added to the PAN solution in the diffusion system. NPN is known to be a thermally stable substance which shows no relevant loss due to surface reactions, has a slightly higher retention time than PAN and a similar ECD response. Therefore NPN is useful for checking the stability of the calibration gas and the detector response.

TABLE II. Selected optima of the operating parameters of the gas chromatograph

Operating parameter	Selected optimum
Oven temperature	26 °C
Detector temperature	30 °C
Injector temperature	45 °C
Carrier-gas flow rate	15 cm^3/min
Make-up gas flow rate	No make-up gas added
Carrier-gas humidity	Water vapor mixing ratio = 15 ppm
Column polarity	Precolumn: nonpolar
	Main column: medium-polar
Column length	6 m
Sample volume	About 2 cm^3 STP for gaseous samples
	About 0.3 mm^3 STP for liquid samples

3. Results and Discussion

The special optimizing problem of airborne PAN measurements is to reach a short analysis time combined with a low detection limit and a sufficient selectivity. The selected optimized conditions are listed in Table II. In the following part of this article we will briefly discuss the most important and PAN-specific considerations.

The injector guarantees a sufficiently fast evaporation of the PAN/n-hexane calibration samples and an acceptably low thermal decomposition of PAN during sample evaporation when it is operated at 45 °C. The detector shows highest sensitivity at an operating temperature of 30 °C. Finally, the column oven temperature for lowest thermal PAN decomposition at still reasonable retention times is 26 °C. Due to the peltier cooling these temperatures can be easily controlled within a range of ±0.2 °C.

The unusually high flow rate of 15 cm^3/min for the megabore capillary columns with no make-up gas added was chosen because the Siemens ECD has to be operated at a minimum flow rate of 15 cm^3/min. A further dilution of the sample by make-up gas and therefore an increase of the detection limit can thus be avoided. On the other hand the lack of a make-up gas excludes the possibility to use helium as carrier gas which would lead to a higher separation efficiency but would also reduce the size of the possible sample volumes. However, the enhanced flow rate leads to a desirable acceleration of the chromatographic separation without severe reduction of the selectivity.

The linear range of the Siemens ECD for PAN detection extends from 0.1 pg to 600 pg. This corresponds to PAN mixing ratios of 15 ppt to 90 ppb for the instrument setup during the flight campaign.

After testing several columns and column combinations (see Table I), it was found that 3 m × 0.53 mm Rtx-1 combined with 3 m × 0.53 mm Rtx-1701 provide

satisfactory results as is shown in Figure 4 where the performance of Rtx-1 alone is compared with Rtx-1 + Rtx-1701. The use of a nonpolar precolumn seems to be reasonable for venting the sample fraction of higher volatility like oxygen which otherwise would lead to a broad, interfering peak. Moreover, 'flushing' of the main column during the next preseparation process eliminates the sample fraction of lower volality than PAN including water. The use of a medium-polar main column then provides a better separation between PAN and the sample components of similar volatility but different polarity. Actually, this combination gives the best PAN detection limit and the shortest retention time concerning our special problem of airborne measurements. The lower limit of detection is 15 ppt (3σ), the retention time is about 2.5 min. Thus the total analysis time does not exceed 4 min.

We performed extensive investigations to understand the effect of water vapor on PAN detection. First we checked the sensitivity of the inlet surfaces to water vapor by injecting humidified as well as dry calibration gas. Signal deviations between both injection operations were found to be within the range of the overall measurement reproducibility which is better than 90%. Then we compared three different setups of carrier and make-up gas humidification. The $(5 + 10)$ m $\times$ 0.53 mm Rtx-1 separation column was operated at 15 cm^3/min flow rate plus 15 cm^3/min make-up gas flow rate, first without any humidification, secondly humidifying only the make-up gas and finally moistening both gases. Moistening only the make-up gas causes the appearance of an additional peak in the chromatograms of liquid calibration samples. This peak also occurs when the whole system is moistened. In both cases the additional peak does not interfere with the PAN peak. The signal to noise ratio and also the detector response for the PAN peak increases in both humidification types by 18% compared to the unhumidified setup. Earlier investigations on that subjet using packed columns (Schrimpf, Master Thesis, 1992) showed an increase in the signal to noise ratio of PAN by 43% and a decrease of the reference signal of NPN (n-propyl nitrate) by 25%. Moreover, an increase in the reproducibility is observed. Moistening only the make-up gas changes the reproducibility during ten consecutive calibration gas measurements insignificantly from 91% to 92%. However, if the total GC system is humidified an improvement of the reproducibility by 6% to 97% will be achieved.

These results permit two conclusions: First, the chemistry in the detector cell must be influenced by the presence of water vapor. This will explain the occurrence of an additional peak if only the make-up gas is moistened. This gives also an explanation for the reduced NPN and increased PAN signal. Secondly, the surface activity inside the gas-chromatographic system must have been reduced. This explains why the signal to noise ratio of PAN which is known to show surface reactions is rising. We propose a combination of both effects to explain the consequences of carrier-gas humidification. But still further investigations are needed to establish to what extent such improvements of response and measurement reproducibility can be attributed to the changes in the chemistry occurring in the ECD or to deactivation of the active sites present on the column surface.

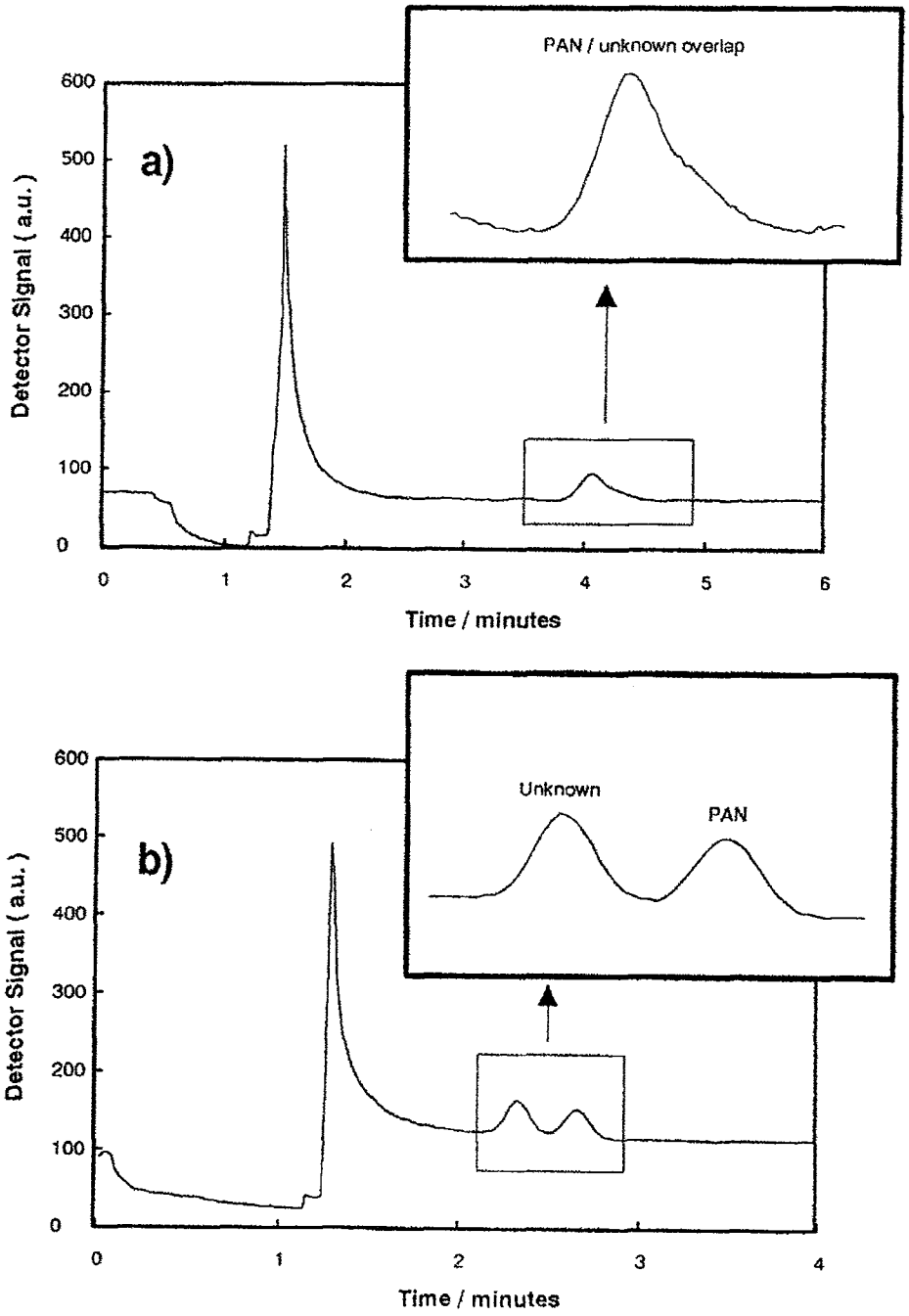

Fig. 4. Ambient air chromatograms. (a) Separation on a Rtx-1 column, 15 m (5+10 m) × 0.53 mm, 5-μm film thickness. (b) Separation on a 3 m × 0.53 mm Rtx-1 precolumn, 5-μm film thickness plus 3 m × 0.53 mm Rtx-1701 main column, 3-μm film thickness.

Preliminary tests in our laboratory as well as the results from the flight campaign showed the suitability of the MKS valve for system pressure control. Generating a pressure drop of 400 mbar at the GC exist leads to system pressure deviations of less than 1 mbar. Thus no pressure effect on the baseline can be observed.

The two calibration procedures we use have been thoroughly studied. During the last three years we participated in an European PAN calibration intercomparison (CEC STEP PAN intercalibration project). Details will be given in a forthcoming paper. In summary, for both methods first intercomparison results gave an agreement with the average values of the other participating groups of better than 90%. In addition, our two methods coincide to better than 85%. The reproducibility during ten consecutive injections is better than 90%. The gaseous calibration with the diffusion system shows a reproducibility of about 93% and the decrease of the PAN concentration in the diffusion gas will be only 10% per month if it is kept at –15 °C. The reproducibility of liquid calibrations varies in the range of 91–97% depending on the routine of the experimentalist. The PAN decomposition rate in the stock solution (PAN concentration about 3 g/cm^3) stored at –20 °C is lower than 5% per year.

Preliminary results from the FALCON flight campaign are shown in Figures 5 and 6. The chromatograms in Figure 5 demonstrate the excellent performance of the instrument during the campaign. Both show that the separation efficiency, the analysis time and the sensitivity of our instrument are sufficient for high-frequency airborne PAN measurements in the Northern Hemisphere. n-Propyl nitrate, our reference standard, can be identified in the calibration gas chromatogram at a retention time of 3.5 min. The apparently corresponding peak in the ambient air chromatogram at 3.6 min can not be attributed to NPN alone. Supposing a similar detector response as for PAN the mixing ratios were mostly higher than those of PAN throughout the whole campaign. This would contradict our present understanding of the atmospheric chemistry of organic nitrates. Further investigations are needed to find out whether this peak as well as the others in the ambient air chromatogram can be attributed to organic nitrates, halogenated hydrocarbons or other volatile compounds.

Figure 6 presents a preliminary profile of the PAN mixing ratios measured over the Atlantic near Prestwick, Scotland on 21 June 1994. These measurements were made during a 2.5-h flight with a residence time of about 5 min at each altitude level. Thus the measurement frequency gives a sufficient spatial resolution of the PAN measurements. The results of the measurements during the FALCON flight campaign will be presented elsewhere. A presentation and discussion of these data would be beyond the scope of this paper.

4. Summary and Conclusions

We describe a compact and light-weight instrument of low power consumption. For airborne PAN measurements humidified nitrogen of high purity (water vapor mixing ratio = 15 ppm) is used for carrier-gas supply since the results of an extensive investigation on the influence of carrier-gas humidification showed an increase in sensitivity and reproducibility of the PAN measurements. The valve system allows the injection of liquid as well as gaseous samples and can be operated automatically.

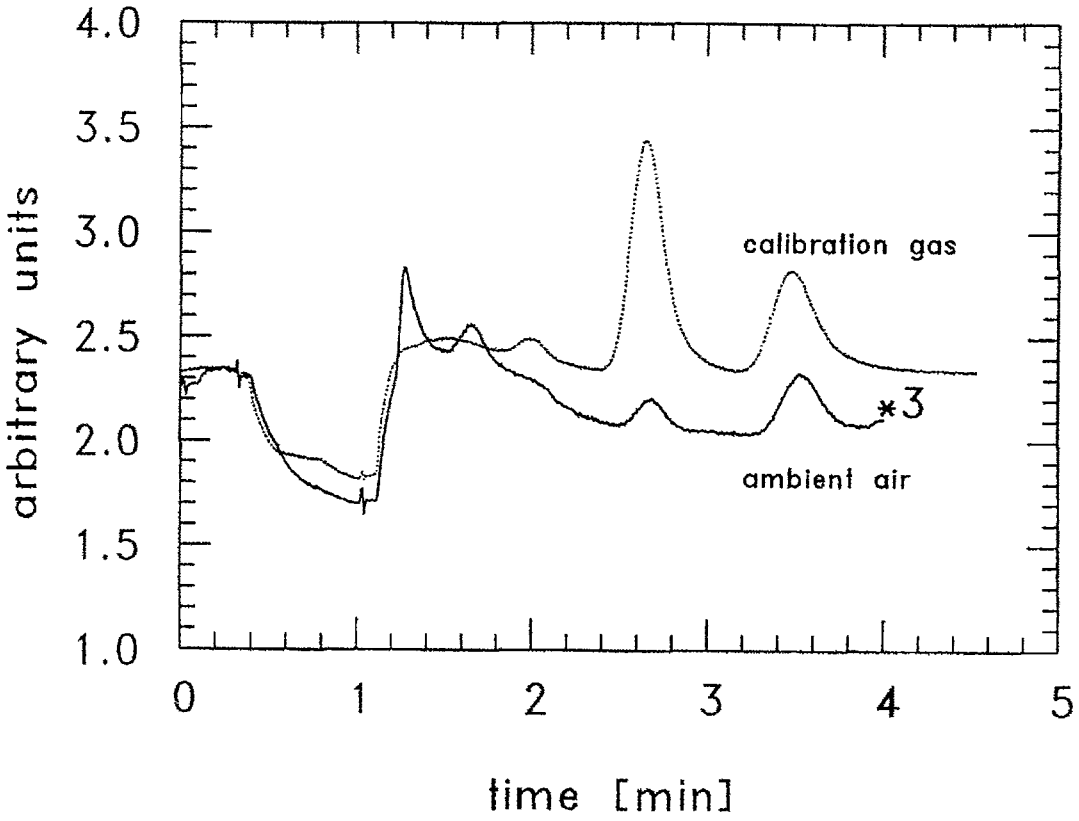

Fig. 5. Chromatograms of calibration gas and ambient air during the FALCON flight campaign. The calibration gas injection was made during routine calibration on the ground. The ambient air chromatogram results from a measurement at about 12 km altitude and is enlarged by a factor 3. The two peaks correspond to PAN mixing ratios of about 5 ppb and 200 ppt respectively.

The injection of air samples of constant mass independent from external pressure variations is achieved by integration of a 'compression tube' connected to a pressure regulator for nitrogen as 'compression gas'. The tests of several separation columns showed that an optimum separation with respect to selectivity, retention time and detection limit of PAN is accomplished by a combination of a 3 m × 0.53 mm Rtx-1 capillary precolumn and a 3 m × 0.53 mm Rtx-1701 capillary main column. A ten- and a four-way valve allow 'venting' and 'flushing' steps to be carried out. The columns are operated at a carrier gas flow rate of 15 cm^3/min with no make-up gas added. An electron capture detector (Siemens) with a linear range between 0.1 pg and 600 pg PAN is used. To eliminate baseline or signal shifts due to pressure variations in the aircraft cabin the system's various gas flows join at the GC exit where a pressure control valve is installed. This valve allows a system pressure control within deviations of less than 1 mbar. The optimum operating temperatures of the column oven, the ECD and the liquid injector were determined to be 26 °C, 30 °C and 45 °C, respectively. For a reliable control of the oven and the detector temperature peltier cooling elements are applied.

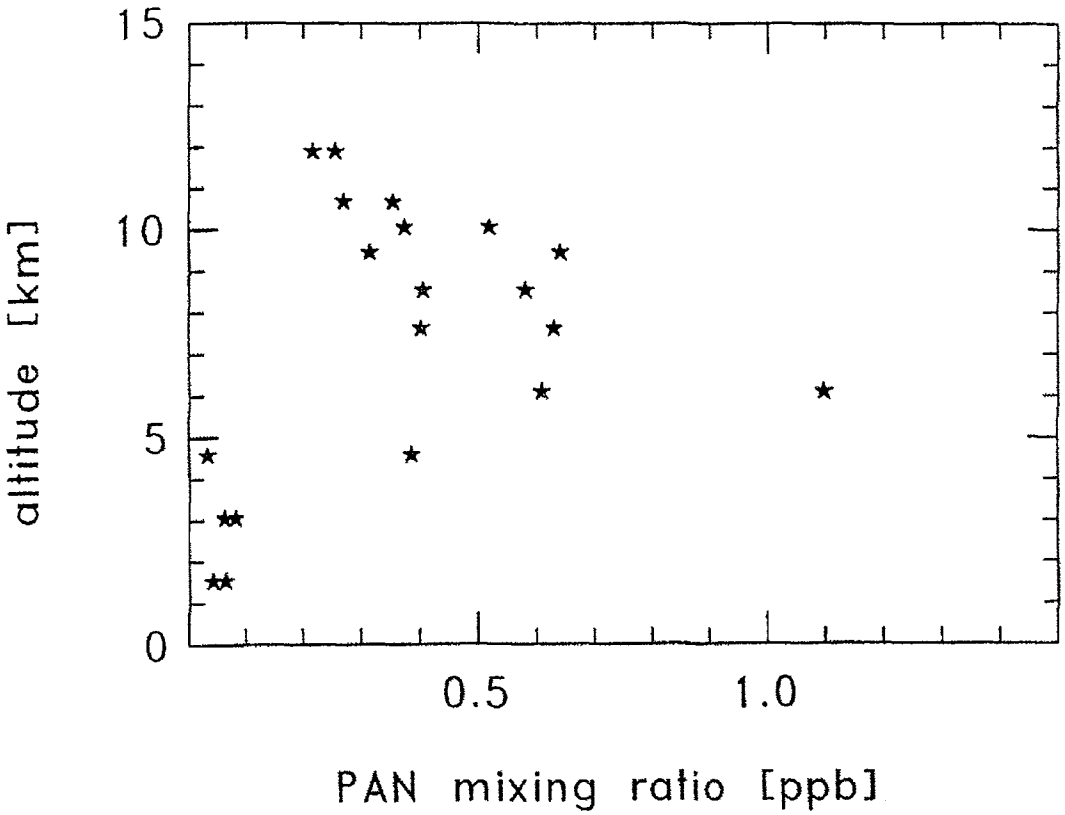

Fig. 6. Airborne PAN measurements at 57° N, 9° W on 21 June 1994 during the FALCON flight campaign.

We calibrate the instrument using two procedures: liquid injection of a few microliters of a diluted PAN/n-heptane solution (synthesis of PAN and determination of the concentration are conducted at our laboratory) and injection of gaseous calibration samples originating from a diffusion source. The short- as well as long-term reproducibility of both methods is better than 90%. They agree with each other to better than 85%.

The general instrument performance is characterized by the lower limit of detection of 15 ppt (3σ) and the total analysis time of about 4 min. The preliminary results from the FALCON flight campaign in June 1994 proved the suitability of the instrument for airborne PAN measurements. However, the instrument's sensitivity is certainly sufficient for measurements in the Northern Hemisphere but still has to be improved for measurements in the Southern Hemisphere.

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