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Short communication

Improvement in the use of capillary columns for ambient air peroxyacetyl nitrate monitoring

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Abstract

The use of the HP-1 wide bore capillary column for the ambient monitoring of peroxyacetyl nitrate (PAN) was found to be limited by the presence of a coeluting peak when the oven temperature was at 30°C. Lowering the oven temperature to 10°C yielded baseline resolution of the two peaks, in addition it increased the sensitivity in the detection of PAN by an average 55%. Lower oven temperatures in the range of −50°C during sample loading and initial analysis time, offered very increased sensitivity for PAN but the method lacks linear response; however at these conditions with the same chromatogram one can determine nitrogenous constituents of air as well as chlorofluoronated compounds. © 1997 Elsevier Science B.V.

Keywords: Air analysis; Environmental analysis; Peroxyacetyl nitrate

1. Introduction

The use of capillary columns for the determination of the components of ambient air can offer high resolving power, lower analyses times and higher sensitivity, through the optimization of the detector's response independent of the carrier gas flow-rate. Indeed the analyses of hydrocarbons in air are carried out exclusively with capillary columns, due to their high resolving capabilities [1]. In contrast, for the analyses of nitrogenous constituents of ambient air (such as the peroxyacyl- and alkyl nitrates) very few studies exist which used capillary columns [2–5] even though higher sensitivity has been proposed for the analyses carried out with capillary columns [3,6]. In addition, capillary columns have been shown to cause less on-column destruction of peroxyacetyl nitrate (PAN), (the most significant of these nitrogenous compounds) and peroxypropionyl nitrate (PPN), compared to packed columns [7], thus resulting in improved sensitivity.

One of the reasons why researchers do not choose capillary columns, is the possible interference of other electron-capturing compounds, mainly chlorofluoronated type compounds, in the detection by the electron capture detector (ECD) used in these analyses. Automatic ambient air measurements of PAN and PPN carried out by our laboratory showed abnormally high PAN values at specific periods of day and night, not correlated with other secondary photooxidants such as ozone. Tests discussed in Section 2 showed that these high peaks were not PAN.

In the present paper we report how a simple change in the chromatographic parameters solved the

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interference problem and also resulted in higher sensitivity in the analysis of PAN.

2. Experimental

A Hewlett–Packard 5890A gas chromatograph equipped with ECD, operated in the constant current mode, was used. The analytical column was a HP-1 100% methyl silicone non-polar, 10 m×0.53 mm I.D. and film thickness 2.65 μm. The oven temperatures below room temperature were achieved with liquid nitrogen cryogenic cooling. The detector was set at 45°C and the packed injection port at 35°C. Helium of purity 99.999% was the carrier gas at a flow-rate of 5 ml/min and 10% CH_4 in argon the make-up gas (both from Linde Hellas) at a flow-rate of 35 ml/min. Both gases were further purified with an oxisorb trap from Messer (Griesheim, Düsseldorf, Germany).

A laboratory-made timer switched on/off a membrane pump (Charles Austen Pumps, Surrey, UK) which pulled the sample through the 2-ml sample loop, which was located inside the GC oven, of a six port gas valve (Valco Europe, Schenkon, Switzerland) pneumatically actuated via the chromatograph's split/splitless injector controls. This configuration allowed the automatic operation of sampling and analysis of ambient air samples. Manual injections were also possible by placing the six-port valve in the inject mode and making the injection at the packed injection port with gas tight syringes (Precision Sampling, Baton Rouge, USA). The chromatographic data were acquired and evaluated by a HP-3396A integrator and/or the HP-3365 CHEMSTATION software.

The identification of PAN was made through comparison of the retention time of the assumed PAN peak with the retention time of pure PAN prepared in the laboratory by nitration of the acetylperoxy acid according to the method of Gaffney et al. [8]. The acetylperoxy acid was prepared according to the method of Nielsen et al. [9]. Additional checks of the purity of PAN peak involved: (1) the heating of the detector to 150°C – at this detector temperature the pure PAN peak disappears; (2) replacement of part of the PTFE sample line with a glass tube 1 m×4 mm I.D. and heating it with a resistance to about 160°C – at this temperature the thermally unstable PAN decomposes; (3) the PAN sample passed through an impinger containing a 0.1 *M* solution of NaOH. When these tests were carried out on pure laboratory synthesized PAN samples, 0.1–10 ppb were tried, in pure air, all the PAN peak disappeared; however, when these tests were carried out on ambient air samples, the peak eluting at the pure PAN retention time was decreased by 10–90%, indicating the presence of a compound with the same retention time as PAN but not affected by the processes which destroy PAN. The percent decrease depended on the contribution of the coeluting compound to the observed peak.

3. Results and discussion

Since the analyses dealt with here are aimed to be applied to field studies, cryogens necessary for subambient temperature operation of the GC should be avoided. Thus the first oven temperature tried was 30°C. Unfortunately at this temperature the PAN peak coeluted with a thermally stable electron-capturing compound. In order to identify the coeluting compound – most likely a chlorofluorocarbon – injections were made of the following: $CHClF_2$, CF_2CCl_2, $C_2H_2F_4$ and CCl_3CH_3. Unfortunately their retention times did not match that of the interfering compound. A GC–MS system was also used but its sensitivity was not sufficient. To improve the resolution, the oven temperature was decreased from 30 to 20, 15 and 10°C. The results are shown in Fig. 1. The chromatograms shown in Fig. 1 are ambient air in our area, sampled on the same day within approximately 1 h from the beginning to the end. This sampling assured little variation of the concentrations of PAN and the interfering compound, thus diminishing the bias of the resolution by the variation of the concentration. The resolution, defined as $R=2\Delta t_R/W_a+W_b$, where Δt_R is the difference in the retention times of the two peaks, interfering and PAN, and W_a and W_b their baseline peak widths, was 1.57, 1.38 and 1.20 at oven temperatures of 10, 15 and 20°C, respectively.

An additional advantage of employing lower oven temperature was the improvement in the sensitivity of PAN detection. Ambient air sampling at oven

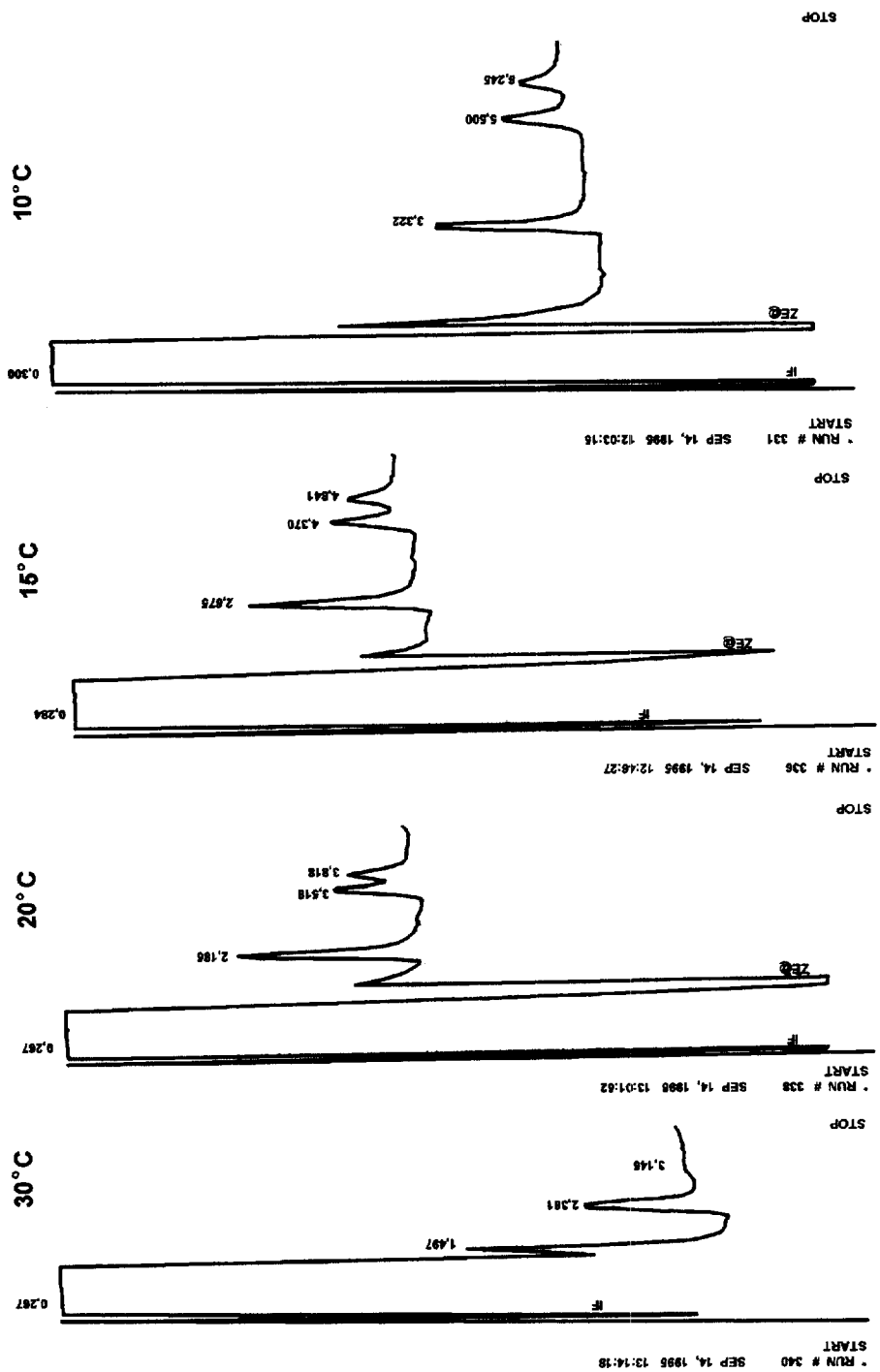

Fig. 1. Variation of the resolution of PAN and a coeluting peak with oven temperature. PAN is the third eluting peak at 3.818, 4.841 and 6.245 min at oven temperatures of 20, 15 and 10°C, respectively.

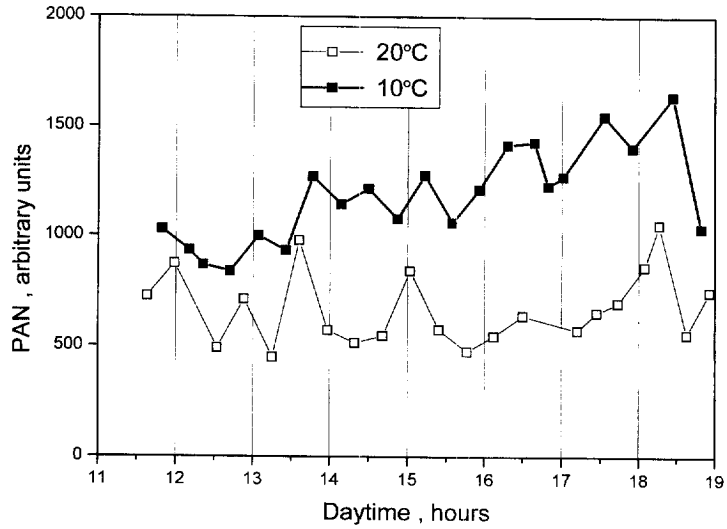

Fig. 2. Ambient PAN air sampling at 10 and 20°C oven temperatures.

temperatures of 20 and 10°C, shown in Fig. 2, indicated on average a larger than 55% PAN response at 10°C compared to 20°C. An injection at one oven temperature was followed by an injection at the second temperature, as soon as the setting up of the GC at the new condition allowed. This finding that the lower the oven temperature the higher the PAN signal, complements rather than contradicts our past finding that the longer the retention time of PAN (and PPN), the greater its destruction on the column

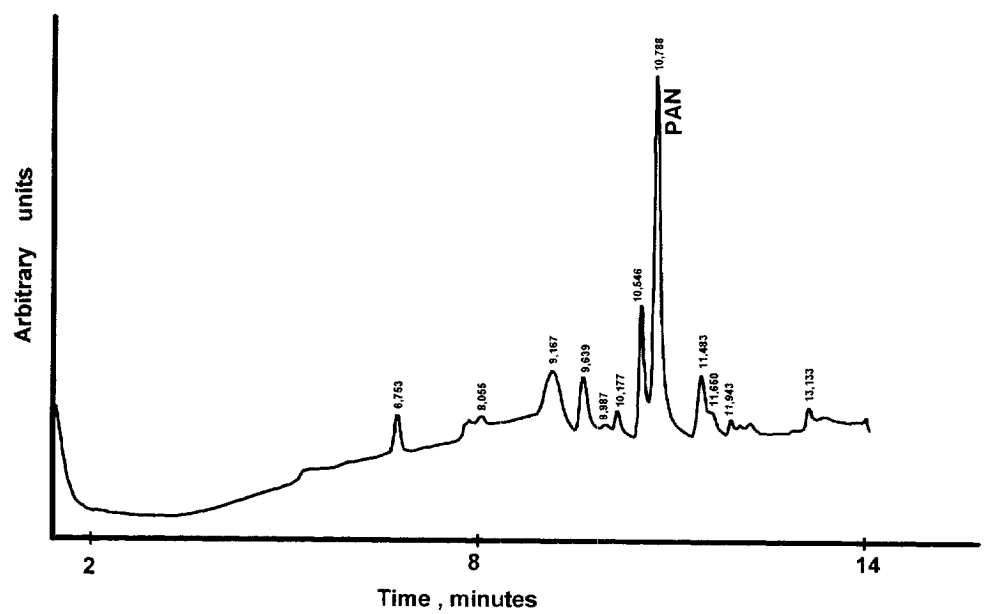

Fig. 3. Increased response for PAN along with other trace air constituents, as a result of sample loading at oven temperature −50°C. Chromatographic conditions: Program: −50°C for 2 min, 7°C/min to 85°C. Injection through gas sampling valve situated inside the oven. Detector at 45°C.

[7]. A more appropriate statement would be: the lower the oven temperature and the shorter the retention time, the higher the resulting sensitivity.

Although the oven temperature of 10°C yielded satisfactory results for the determination of PAN, experiments performed with still lower temperatures proved very promising. When the oven temperature was cooled to −50°C, a temperature a little higher than the minimum allowed temperature of the column, during sample loading and initial chromatographic program temperature, very large PAN peaks appeared along with numerous other peaks most probably due to chlorofluorocarbons and possibly alkyl nitrates. A typical chromatogram is shown in Fig. 3. The disadvantage of this procedure is the lack of linearity between the sample size and the PAN signal. Most probably PAN was breaking through and was not quantitatively collected in the sample loop.

A great disadvantage of the proposed oven cooling to below room temperature is the requirement for a cryogen, which in our case was liquid nitrogen. At oven set at 10°C with two samples per hour, the rate of consumption of liquid nitrogen was 30 l per 24 h operation.

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