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Short communication

Analysis of C₂–C₄ peroxyacyl nitrates and C₁–C₅ alkyl nitrates with a non-polar capillary column

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Abstract

Analysis of peroxyacetyl nitrate (PAN), peroxypropionyl nitrate, peroxy-*n*-butyryl nitrate, and peroxyisobutyryl nitrate (PiBN) with a non-polar capillary column indicated PAN *not* to coelute with PiBN. Isopropyl nitrate coeluted with PAN, *n*-butyl nitrate with PiBN and ethyl nitrate with chloroform, at oven temperature 30°C. In addition methyl nitrate, *n*-propyl nitrate, 2-butyl nitrate, 2-methyl-2-butyl nitrate, 3-pentyl nitrate and 2-pentyl nitrate were studied. Their response factors in the electron-capture detector were also determined. Tetrachloroethylene, carbon tetrachloride and chloroform whose vapors occur in the atmosphere were also examined. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ambient air measurements of peroxyacyl nitrates (PANs) exist mainly for PAN and less for peroxypropionyl nitrate (PPN). Peroxy-*n*-butyryl nitrate (PnBN) was measured in ambient air only in California, USA [1,2], while only one laboratory study exists on peroxyisobutyryl nitrate (PiBN) which reported coelution of PiBN and PAN on a polar stationary phase [3]. The implications of this coelution on the reported ambient air PAN data were stressed by Roberts et al. who disputed the coelution [4].

Ambient air alkyl nitrates studies are very limited. One reason being their coelution with other electron-capturing compounds, so that other detection meth-

ods, than the traditional and high-sensitivity GC–electron-capture detector (ECD) have also been used [5]. Simultaneous measurements of PANs and alkyl nitrates are very limited [6]

Since coelution of PAN with PiBN, as well coelution of PANs with alkyl nitrates and other electron-capturing compounds would mean an error in their measured ambient air concentrations, in the present work I have extended the range of the studied compounds reported in our past work [7] from PAN and PPN to C₂–C₄ PANs and from methyl, ethyl and 2-butyl nitrate to the full range of C₁–C₅ alkyl nitrates. Three common solvents whose vapors occur in the atmosphere were also studied.

2. Experimental

PAN, PPN, PnBN and PiBN were synthesized by

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nitration of the respective peroxy acids, prepared from the respective anhydrides. Methyl nitrate (MN) and ethyl nitrate (EN) were synthesized by nitration of absolute methanol and ethanol, respectively. 2-Butyl nitrate (2BN), *n*-butyl nitrate (nBN), 2-methyl-2-butyl nitrate (2M2BN), 3-pentyl nitrate (3PN) and 2-pentyl nitrate (2PN) were prepared by nitration of the respective alkyl bromides with AgNO₃ acetonitrile solution. Isopropyl nitrate (iPN) and *n*-propyl nitrate (nPN) were commercially available. Tetrachloroethylene, carbon tetrachloride and chloroform were also examined.

All studied compounds were introduced into a ~150 l PTFE chamber, filled with NO_x-free purified air, and thermostatted at 14±1°C in order to reduce the destruction of the thermally unstable PANs. Samples were drawn through the 0.5-ml sample loop of a six-port gas sampling valve, with a membrane pump.

The six-port valve was situated inside a Hewlett-Packard 5890A GC-ECD system. A non-polar HP-1 100% methyl silicone, 25 m×0.32 mm I.D., film thickness 1.0 μm capillary column was used. The oven was at 30°C for 35 min and then raised at 70°C/min to 100°C for 10 min. This last step assured the reconditioning of the column. The detector was held at 45°C. Sporadically the detector's temperature was raised to 150°C for reconditioning.

The identification of all compounds was made through comparison of their retention times with those of available pure compounds. Relative retention was also applied as an assurance step. Calibration of the ECD was performed as reported elsewhere [8].

3. Results and discussion

The elution order was PAN, PPN, PiBN and PnBN. To assure that the observed peaks were due to peroxyacyl nitrates, the detector's temperature was raised to 150°C. The observed peaks were decreased by 89–93%. At the chamber's temperature of 14±1°C the life of all peroxyacyl nitrates extends to many hours. The present results of the elution sequence of PANs, are in support of the comments of Roberts et al. [4] who disputed the coelution of PAN and PiBN reported by Grosjean et al. [3]. In non-

polar columns volatility controls the retention. Thus PiBN is less volatile than PAN and even PPN. The same elution order would also be expected in polar stationary phases because adding one or two carbon atoms will not significantly change the polarity of the PANs. The response factors of all studied peroxyacyl nitrates vs. PAN were the same, within ±10%, in agreement with our previous findings for PAN and PPN [8].

A typical chromatogram of the four peroxyacyl and the nine studied alkyl nitrates and the three halogenated compounds is shown in Fig. 1. Instead of the expected sixteen peaks only thirteen were observed. The relative to PPN retention, defined as $\alpha = (t_R - t_M)/(t_{RPPN} - t_M)$, where t_M is the retention time of air is given in Table 1. α -Values indicate coelution of EN and chloroform at $t_R = 4.068$ min, coelution of PAN with iPN at $t_R = 6.401$ min and coelution of PiBN with nBN at $t_R = 21.306$ min. EN was resolved from chloroform at oven temperature 0°C, PAN from iPN at -10°C, while PiBN was not resolved from nBN at -10°C.

The elution sequence observed here can be compared with that reported in the literature. The reported elution orders with the Carbowax 600 stationary phase were: MN, EN, iPN, nPN, 2BN, PAN, 3PN, 2PN, nBN [9] and MN, EN, iPN, nPN, 2BN, PAN, PPN, 2PN and nBN [6]. These elution orders are similar to that reported in the present work, except for the nBN, which I observed to elute before pentyl nitrates. Since in a non-polar column, as used here, retention will be controlled by volatility, the elution order observed here is the expected one since nBN has a b.p. of 135.5°C, and 2PN has a b.p. of 144°C (b.p. obtained from Roberts [10]). This is actually the reason for the observed linearity of log t_R vs. b.p. of each examined alkyl nitrate, (b.p. from Ref. [10]). The obtained straight line yields the b.p. at ambient pressure for 2M2BN (142°C) and for 3PN (144°C), values not available in the literature. The polarities would not be expected to change much by adding one or two carbon atoms in order to change the elution sequence within a homologous series with a polar column. With the polar capillary column DB-210, the elution order is iPN, PAN, nPN, PPN, 2BN [11] and with the OV-1701 MN, EN, iPN, nPN, 2BN [5]. The other higher alkyl nitrates studied here were not examined in these past studies.

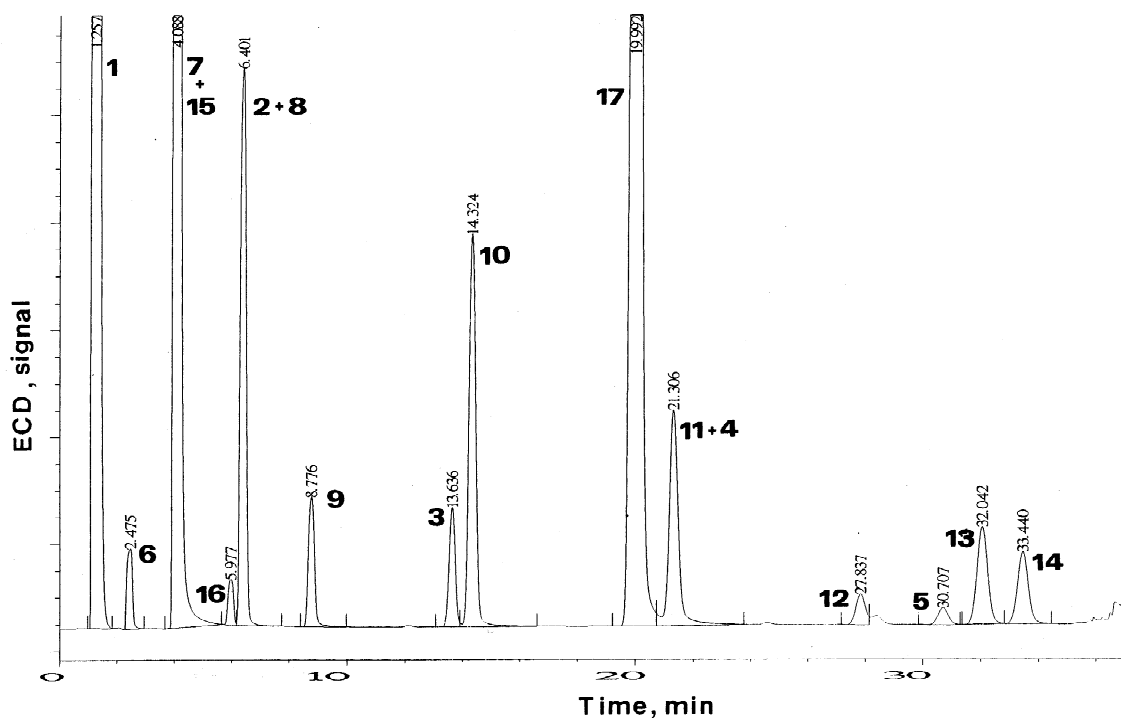


Fig. 1. Typical chromatogram of the four studied peroxyacyl nitrates, the nine alkyl nitrates, chloroform, carbon tetrachloride and tetrachloroethylene at oven temperature 30°C. **1** is the air peak. For other numbers see Table 1. For coelutions see text.

Table 1
Relative to PPN retention of all studied compounds

PANs			Alkyl nitrates			Halogenated compounds		
Peak no. (Fig. 1)	Compound	Relative retention	Peak no. (Fig. 1)	Compound	Relative retention	Peak no. (Fig. 1)	Compound	Relative retention
2	PAN	0.416	6	MN	0.098	15	CHCl ₃	0.229
3	PPN	1	7	EN	0.229	16	CCl ₄	0.381
4	PiBN	1.620	8	iPN	0.416	17	C ₂ Cl ₄	1.513
5	PhBN	2.379	9	nPN	0.607			
			10	2BN	1.055			
			11	nBN	1.620			
			12	2M2BN	2.147			
			13	3PN	2.488			
			14	2PN	2.604			

From run to run α changed less than 3%.

The response factors of each of these nitrogenous compounds were determined using the NO_x analyzer. The relative (to PAN) response was for MN, 0.83; EN, 0.93; iPN, 1.12; nPN, 1.12; 2BN, 0.93; nBN, 1.18; 2M2BN, 1.05; 3PN, 1.25; 2PN, 1.24.

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