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Simple cryoconcentration technique for the determination of peroxyacyl and alkyl nitrates in the atmosphere

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Abstract

A gaseous mixture of methyl nitrate, *n*-propyl nitrate, peroxyacetyl nitrate and peroxypropionyl nitrate was successfully cryoconcentrated using a gas sampling valve with its loop filled with glass beads placed inside the GC oven which was cooled at −50°C. The technique offered linearity over a ten fold concentration variation and sample volume range of 1–280 ml. The detection limit for 150 ml sample varied from 0.02–10 pptv depending on the compound. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Peroxyacyl and alkyl nitrates are important constituents of the atmosphere. Being end products in the termination reactions of NO_x they influence the formation of ozone and affect the oxidizing capacity of the atmosphere.

These nitrogenous compounds are usually separated in a GC followed by electron capture detection, ECD. This is particularly the case with peroxy acetyl nitrate, PAN, which has the largest concentrations in the atmosphere of all peroxyacyl nitrates. The alkyl nitrates have much smaller concentrations and the reported studies are very limited. When these compounds are determined in rural or remote regions a concentration step is necessary for all compounds. Atlas [1] and Flocke et al. [2,3] reported concentration procedures for the determination of alkyl nitrates. Walega et al. [4] and Bertman et al. [5] also reported cryoconcentration techniques for PAN, peroxy propionyl nitrate, PPN, and some alkyl nitrates. Alternatively for PAN, "cut" and "back-flush" techniques are reported [6].

We previously reported our observation that the PAN signal increased significantly when the sample flowed through a loop cooled at −50°C [7]. In the present work we report on the development of our earlier observation into a simple cryoconcentration technique, without additional complicated plumbing and additional than the chromatograph's cryogenic capabilities. The method is capable of determining peroxyacyl and alkyl nitrates in the atmosphere with detection limits from 0.02 to 10 pptv (parts per trillion volume) for 150 ml sample volume.

2. Experimental

Laboratory prepared samples, as presented later, of

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PAN, PPN, methyl nitrate, MN, and commercially available *n*-propyl nitrate, NPN, were introduced in a Teflon FEP (Dupont fluorocarbon film) chamber of volume ~150 l. The chamber was thermostated at $11° \pm 1°C$ in order to increase the life of the thermally sensitive PAN and PPN. Indeed direct injections of PAN and PPN, without the sampling loop, at the beginning and at the end of the experiment, showed no thermal decomposition. The cryoconcentration step consists of drawing from the Teflon bag a certain volume and passing it through a six port gas sampling valve situated inside the chromatograph's oven, which was cooled at $-50°C$. The $0.1 \ cm^3$ volume, I.D. 1 mm length 13 cm, stainless steel sample loop was filled with glass beads, 60/80 mesh, DMCS treated, obtained from Alltech (Deerfield, IL). Subsequently the oven temperature was quickly raised to 10–30°C. The same procedure was applied to ambient air sampling.

A Hewlett-Packard 5890A gas chromatograph equipped with an ECD, operated in the constant current mode, was used in these experiments. The analytical column was a HP-1 100% methyl silicone non polar, length 10 m, 0.53 mm I.D. and film thickness 2.65 μm. The initially used chromatographic program was: initial temperature $-50°C$ rate 70°C/min up to 30°C where it remained for 12 min followed by rate 70°C/min up to 100°C where it remained five min. However, because PAN in ambient air samples [7] and MN in all matrices are better resolved at 10°C, the finally used program was: initial temperature $-50°C$ rate 70°C/min up to 10°C where it remained for 25 min and subsequently at rate 70°C/min up to 100°C, where it remained for five min. The last ramp was added in order to clean the column from non eluting compounds as well as moisture contained in the sample. Every 12 h and for a period of 2–3 h, the oven was placed at 100°C and the detector at 150°C to recondition the whole system. In 24 h sampling during which the relative humidity varied from ~30% at midday to over 60% at sun rise, no operation difficulty was observed. When 24 h monitoring was not necessary reconditioning at above conditions occurred overnight. The oven temperatures below room temperature were achieved with liquid nitrogen cryogenic cooling. The detector was set at 45° and the packed injection port at 35°C. Helium of purity 99.999% was the carrier

gas at flow-rate of 4 ml/min and 10% CH_4 in Argon the make-up gas (both from Linde Hellas) at a flow-rate of 37 ml/min. Both gases were further purified with an oxisorb trap obtained from Messer Griesheim (Duesseldorf, Germany).

A home made timer started the chromatogram and switched on/off a membrane pump (Charles Austen Pumps, Surrey, UK) which pulled the sample through the $0.1 \ cm^3$ 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 all samples. When small volume samples were desired, the injection port situated upstream of the gas valve, with gas tight syringes (Precision Sampling Corp., Baton Rouge, LA) was used. When the oven was placed at higher than $-50°C$ temperatures during manual injections, it was necessary to bypass the glass beads sample loop, in order to reduce the PAN and PPN decomposition. The chromatographic data were acquired and evaluated by the HP-3365 Chemstation software. The great disadvantage observed in our previous effort to use the increased signal of the detector, when the sample passed through the loop at $-50°C$, was the lack of linearity of the ECD signal with the increase of the sampling time [7]. We attributed this phenomenon to sample breakthrough, particularly since cryotemperatures in other systems, used for the cryoconcentration of PAN and PPN were lower than $-100°C$ (with empty loops) [4,8,9]. Thus, in the present work, since our goal was to use only the cryogenic capabilities of the chromatograph and avoid external cooling devices, we filled the sample loop with glass beads which are known to increase the collection efficiency.

The identification of PAN and PPN, was made through comparison of the retention times of the assumed PAN and PPN peak with the retention time of pure PAN and PPN prepared in the laboratory by nitration of the respective peroxy acids according to the method of Gaffney et al. [10]. The peroxy acids were prepared according to the method of Nielsen et al. [11]. Additional checks of the PAN and PPN peaks involved: (1) the heating of the detector to 150°C. At this detector temperature the pure PAN and PPN peaks disappear to more than 80%; (2)

replacement of part of the PTFE Teflon sample line with a glass tube length 1 meter and inside diameter 4 mm and heating it with a resistance to about 160°C. At this temperature the thermally unstable PAN and PPN decompose; and (3) the PAN, PPN sample passed through an impinger containing a 25 mM solution of NaOH. When these compounds pass through the alkaline solution they hydrolyze. When these tests were carried out to pure synthesized in the laboratory PAN and PPN samples, of concentration 0.1–10 ppb, in pure air, all PAN and PPN peaks disappear.

The alkyl nitrates examined in this work were methyl nitrate and *n*-propyl nitrate. Methyl nitrate was synthesized in the laboratory by nitration of methyl alcohol and NPN was obtained from Janssen Chimica (Geel, Belgium). MN is the most volatile alkyl nitrate with the lowest boiling point (64.6°C) and if the here described method can cryoconcentrate it, then it would also retain its higher homologues.

Calibration of the ECD and determination of the response factors of the studied compounds, was carried out by sequential or separate introduction to the teflon chamber of a certain volume of each of the liquid solutions of PAN, PPN, MN and NPN to make a low ppb concentration while filling the chamber with Aadco purified air (Aadco Instruments, FL). The concentrations of the compounds were measured after their sequential or separate introduction into the chamber using a Thermo Environmental (TE Instruments, MA) model 42S high sensitivity (nominal detection limit 50 ppt) ambient air NO$_x$ analyzer, in the NO$_x$ mode using a Molebdenum catalytic converter operated at 360°C. The NO$_x$ analyzer was calibrated by a NIST traced nitric oxide primary standard obtained from Messer Griesheim Austria, using the gas phase titration mode of a Thermo Environmental model 146C dynamic calibrator. PAN and PPN were introduced into the chamber through a prewashed Nylon wool, which is reported [12] to retain traces of nitric acid, left over, from their synthesis, despite the washings.

In order to check the PAN/PPN to nitric oxide conversion efficiency of the Mo converter in separate experiments PAN/PPN was drawn from the chamber through an impinger containing 25 mM NaOH solution. The alkaline hydrolysis of PAN/PPN yielded nitrite anions, which were determined with a

Dionex 4500i ion chromatograph (Dionex Corp., CA). More details on the use of the alkaline hydrolysis for the determination of PAN can be found elsewhere [13]. The PAN/PPN concentrations derived from the nitrite anion concentrations agreed to within ±7% with their concentrations determined with the NO$_x$ analyzer.

Possible interference of halocarbons was also checked for Freons 12, 22 and 134a as well for perchloroethylene. Freons 12, 22 and 134a were introduced into the large volume teflon chamber and were cryoconcentrated with the procedure described above. Under our experimental conditions all elute well before the methyl nitrate peak. The relative to PAN retention was 0.19 ($\sigma = 0$) for Freon 12 and 0.14 ($\sigma = 0$) for Freon 22 and Freon 134a. Perchloroethylene eluted well beyond the last eluting studied compound PPN, at relative to PAN retention of 3.18 ($\sigma = 0$). Thus for the here reported compounds these halocarbons had no interference.

The relative to PAN retention of the studied nitrogenous compounds was: 0.32 ($\sigma = 0.014$) for methyl nitrate, 1.46 ($\sigma = 0.009$), for *n*-propyl nitrate and 2.44 ($\sigma = 0.015$) for PPN.

3. Results and discussion

A typical chromatogram of a laboratory made mixture, shown in Fig. 1, indicates baseline resolution, despite the large baseline widths. Similar baseline widths are reported in other concentration studies [5,12].

Two sets of experiments were carried out in order to check the linearity of the method. In the first set the linearity of the amount of the cryoconcentrated compounds was examined at various concentrations, each determined by the NO$_x$ analyzer. In these experiments 150 ml (at flow-rate 30 ml/min for five min) of the chamber mixture was cryoconcentrated. The average and the obtained standard deviations of 4–5 repetitions are shown in Fig. 2a–d for PAN, PPN, MN and NPN respectively. Good straight lines were obtained, with the worst being methyl nitrate. The slopes of the lines of Fig. 2a–d yield the response factors of each compound in the ECD and therefore their relative response factors. Thus the relative responses versus PAN were: for PPN is 1.08,
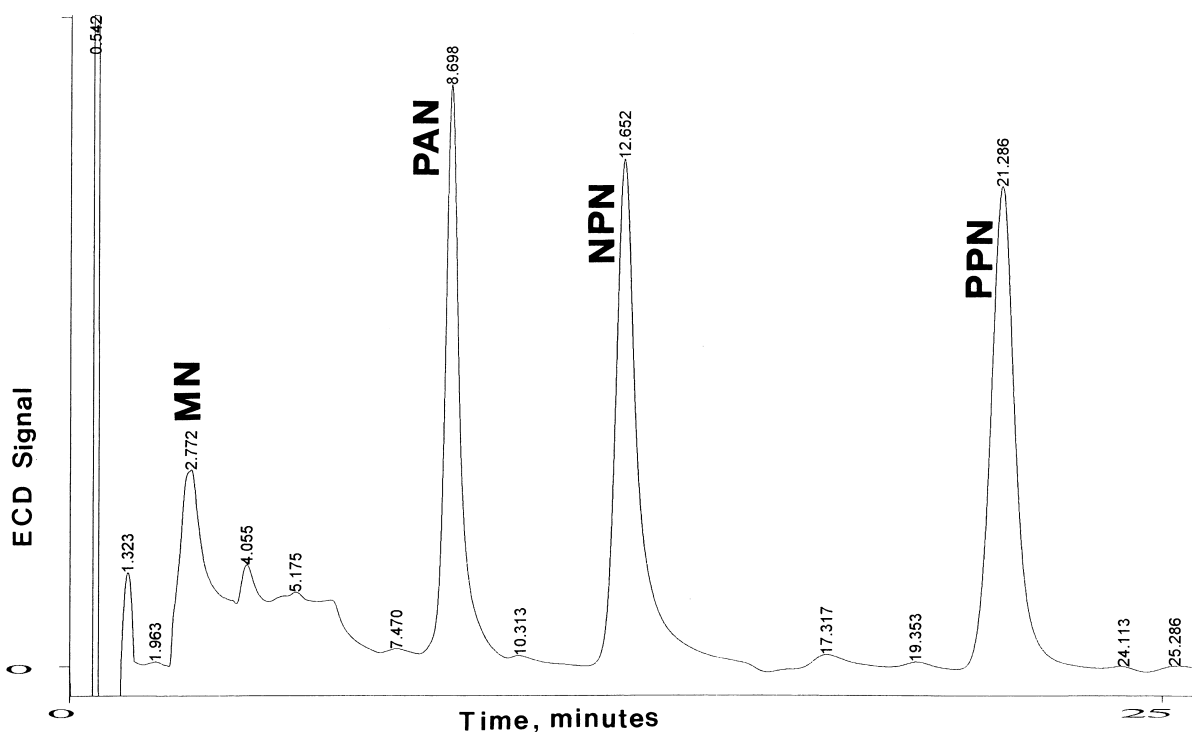
Fig. 1. A typical chromatogram after cryoconcentration of 150 ml sample from the Teflon FEP chamber containing: 1.19 ppb methyl nitrate, 1.18 ppb PAN, 0.93 ppb *n*-propyl nitrate and 1.29 ppb PPN.

for MN 0.70 and for NPN 1.00. These response factors are comparable to those determined by direct injection, either manually or with the six-port valve, but with the sampling loop empty, without the glass beads filling. The response factors versus PAN from direct injections were: PPN 1.0 (standard deviation 0.05), MN 0.82 (standard deviation 0.09) and NPN 1.15 (standard deviation 0.02). Similar response of MN vs. PAN of 82–90% is reported by Ridley et al. [12] and 85% by Walega et al. [4], who also report equal responses for PAN and PPN.

From these experiments the precision, reported as % relative standard deviation to the mean, of the method for each compound was obtained. For PAN the average, in all concentrations of Fig. 2a, % relative standard deviation to the mean was 3.9 for PPN 6.0, for MN 4.8 and PPN 5.7.

In the second set of experiments the linearity between the cryoconcentrated amount with the duration of the sampling times was examined. At 28 ml/min flow-rate the sampling times varied from 2 to 10 min. The detector's signal plotted against the sample volume, is shown in Fig. 3a–d for PAN, PPN, MN and NPN respectively. The signal of 1 ml sample directly injected is also shown in all figures. Excellent linearity is observed for PAN and NPN, followed by good linearity for methyl nitrate and somewhat less for PPN. To avoid non linearities due to pump's variations due to stop/start, especially in the small sampling times, the pump was always kept running and was connected to the sampling line only during the desired time periods.

In additional experiments it was examined if the cryocollection temperature could be raised, in order to reduce the consumption of liquid nitrogen. Temperatures in the range −60 to −20°C were examined. The results, reported as percent of the collection efficiency at −60°C, are shown in Table 1. Compared with the other higher tried temperatures, the one at −50°C is the best temperature for the cryocollection of all examined compounds, even though some question may arise as to the collection
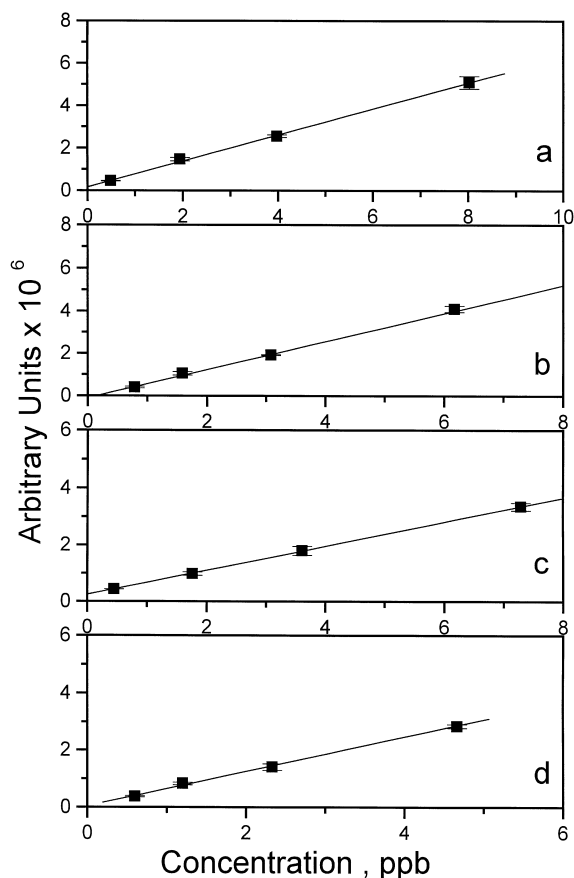
Fig. 2. (a) Linearity graph, ECD signal in arbitrary units, of cryoconcentration 150 ml sample of PAN, at different concentrations, (b) for PPN, (c) for MN and (d) for NPN.
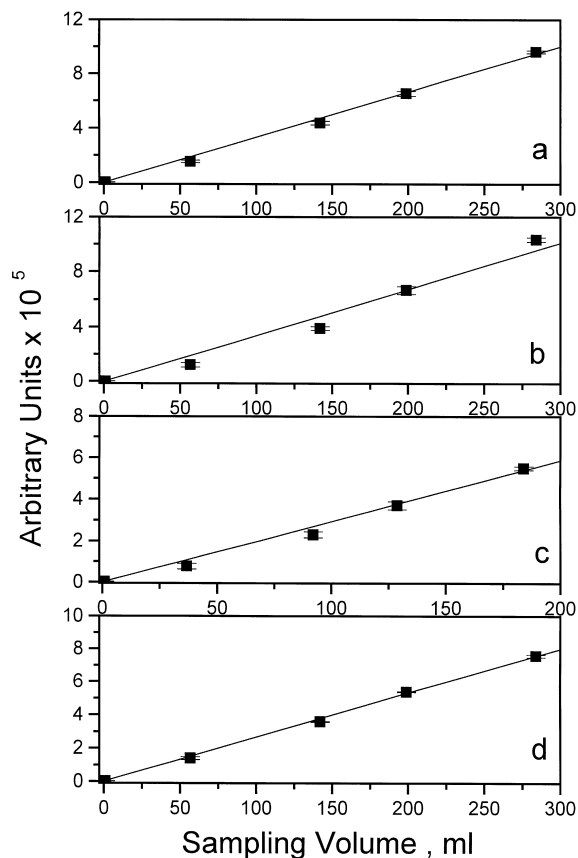

Fig. 3. (a) Linearity graph, ECD signal in arbitrary units, of cryoconcentration of PAN of concentration 0.49 ppb, as function of collected volume, (b) for 0.79 ppb PPN, (c) for 0.45 ppb methyl nitrate and (d) for 0.60 ppb *n*-propyl nitrate.

efficiency of methyl nitrate, whose collection at $-50°C$ is 88% of that at $-60°C$.

The described method was also applied to ambient air sampling. An ambient air chromatogram is shown in Fig. 4. As many more peaks appeared, the examined compounds were identified from the match of retention times with the laboratory made sample, shown in Fig. 1, and in particularly PAN and PPN by raising, in some runs, the detector's temperature to 150°C. At this detector's temperature PAN and PPN peaks practically disappear, depending on the nitrogen monoxide concentration in the air. At the shown chromatogram MN is 40 ppt, PAN 170 ppt and PPN 20 ppt. At the time where NPN is expected to elute, appeared a large peak, indicating concentrations not

explainable from the chemistry of the atmosphere. Thus this peak is not likely to be NPN. Efforts to identify this peak were not fruitful. The repeatability of the method in ambient air analysis can be

Table 1
Effect of cryocollection temperature on collection efficiency[a]

Temperature, °C	% Recovery compared to $-60°C$			
	Methyl nitrate	PAN	NPN	PPN
-50	88	102	104	113
-40	26	78	69	115
-30	32	62	53	112
-20	6	14	14	30

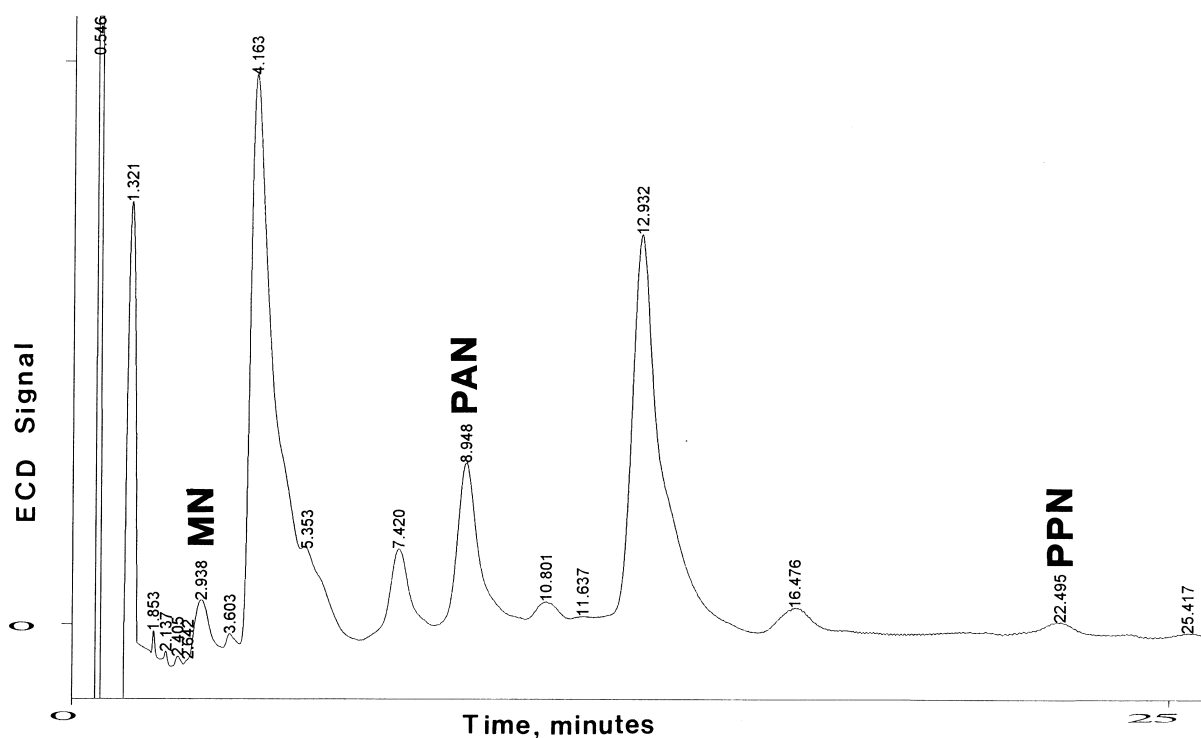[a] The numbers above are averages of at least three repetitions.

Fig. 4. An ambient air chromatogram obtained from the cryoconcentration of 92 ml sample. Concentration of MN is 40 ppt, PAN 170 ppt and PPN 20 ppt.

qualitatively inferred from three repeated measurements carried out one right after the other, in order to decrease the diurnal variations of the atmosphere. The repeatability reported, as percent of standard deviation to the mean of three repeated ambient air analysis carried out within 1.5 h, was 15% for MN, 12% for PAN and 16% for PPN.

The detection limits reported as 3s of the obtained cryoconcentration of purified air were: for PAN 4 ppt, PPN 0.04 ppt, MN 0.02 ppt and NPN 10 ppt, for a sample volume 150 ml. These detection limits were calculated using the response factors obtained from the cryoconcentration of the lowest concentrations of Fig. 2a–d. The high detection limits for PAN and NPN are due to the presence in the ambient air of coeluting compounds, which were only partly removed by our air purification system.

The great advantage of the here described method, is the use of simple inexpensive every day use chromatographic accessories, a gas sampling valve and a cryogenic valve, without additional compli-

cated plumbing or additional cryogenic apparatus, used in other methods.

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