Journal of Chromatography, 541 (1991) 99–108
Elsevier Science Publishers B.V., Amsterdam

CHROM. 22 958

Determination of peroxyacetyl nitrate, peroxypropionyl nitrate and alkyl nitrates of atmospheric importance using capillary columns

GERASSIMOS MINESHOS, NIKOLAOS ROUMELIS and SOTIRIOS GLAVAS*
Department of Chemistry, University of Patras, GR-261 10 Patras (Greece)
(First received August 3rd, 1990; revised manuscript received October 29th, 1990)

ABSTRACT

Three capillary columns were studied for the determination of peroxyacetyl nitrate, peroxypropionyl nitrate and some alkyl nitrates of atmospheric importance. Two non-polar HP-1 100% dimethyl polysiloxane columns, of 0.53 and 0.32 mm I.D., yielded the best resolution of all compounds studied. The intermediate polarity HP-17 50% methyl–50% phenyl polysiloxane wide-bore column could not resolve peroxypropionyl nitrate from 2-butyl nitrate. Compared with capillary columns with polar Carbowax stationary phases, the columns studied gave a better resolution of peroxyacetyl nitrate and peroxypropionyl nitrate, and there was no interfering water peak. Alkyl nitrates could be determined simultaneously. Detection limits were in the low ppb range.

INTRODUCTION

Peroxyacetyl nitrate (PAN) is a significant component of photochemical smog in urban centres [1,2]. In addition, PAN is ubiquitous in clean atmospheres, where it constitutes a major part of odd nitrogen [3]. Peroxypropionyl nitrate (PPN), the next higher PAN homologue, occurs in the atmosphere at concentrations that are a small fraction of those of PAN. Because of these extremely low concentrations of PPN, few ambient measurements of this compound have been reported [4]. Similarly, very few recent studies of atmospheric determinations of organic nitrates have been published [5,6].

The determination of PAN, PPN and organic nitrates is usually carried out by gas chromatography with electron-capture detection (GC–ECD). The columns used for the separation of PAN and PPN are usually packed columns with the stationary phases Carbowax 400 or Carbowax 600 and 4.8% QF-1 + 0.18% diglycerol on deactivated Chromosorb [4,7,8]. Recently capillarly columns have been employed for the determination of PAN and PPN [9–11]. ECD of PAN, PPN and organic nitrates is the preferred method of detection because of its high sensitivity. Calibrating the detector for PAN remains a very different task, however despite the numerous calibration procedures reported in the literature [12,13]. For the calibration of the detector for organic nitrates and PPN there are virtually no data. It is usually assumed

0021-9673/91/$03.50

that PPN and alkyl nitrates have the same response factors as PAN [1].

As we have recently shown, destruction of PAN and PPN on the column owing to their residence in the chromatographic column during analysis is much more extensive on a packed column than on a wide-bore capillary column [11], probably owing to the greater inertness of the capillary columns. In addition, capillary columns give better resolution and shorter analysis times. In this work we evaluated three capillary columns, differing in inside diameter, length and polarity of stationary phase, for the determination of PAN and PPN and examined their use for the simultaneous determination of some alkyl nitrates of atmospheric importance.

EXPERIMENTAL

All mixtures were prepared at room temperature in a 4.5-l glass flask, equipped with two ports with septa and a Teflon stopcock and connected to a vacuum line provided with Teflon stopcocks. Pure PAN and PPN solutions in tridecane were synthesized by nitration of the corresponding peroxy acids following the procedure of Gaffney *et al.* [14]. The peroxyacids were prepared from the anhydrides of acetic and propionic acids as specified by Nielsen *et al.* [15]. Methyl and ethyl nitrate were prepared by nitration of methanol and ethanol according to standard methods [16]. 2-Butyl nitrate was prepared by stirring 2-bromobutane dissolved in tetrahydrofuran (THF) with silver nitrate dissolved in water at room temperature for 4 h in the dark. After filtration of silver bromide, the THF layer containing 2-butyl nitrate was separated in a separating funnel. A pale yellow product remained after vacuum vaporization of THF at room temperature.

GC–ECD of the vapour of this reaction product diluted in air yielded only one peak. All the compounds studied were identified by their retention times. In addition, PAN and PPN were identified by observing that their chromatographic peaks disappeared when an air stream containing separately pure PAN and pure PPN was passed through an alkaline solution. Similarly, methyl and ethyl nitrate, which are major thermal decomposition products of PAN and PPN, respectively, were identified by observing that their peak areas increased when pure PAN or pure PPN was left to decompose in a glass flask at 50°C.

Gas chromatography

Three capillary columns were evaluated for the determination of PAN, PPN and methyl, ethyl and 2-butyl nitrate: two wide-bore columns of different polarity, *viz.*, a non polar HP-1 5-m fused-silica cross-linked 100% dimethyl polysiloxane (gum) of 0.53 mm I.D. and 2.65 μm film thickness, and an intermediate polarity HP-17 10-m fused-silica cross-linked 50% phenyl–50% methyl polysiloxane of 0.53 mm I.D. and 2.0 μm film thickness, and a non-polar HP-1 cross-linked methylsilicone gum 15-m column of 0.32 mm I.D. and 1.05 μm film thickness.

A Hewlett-Packard 5890A gas chromatograph equipped with a ^{63}Ni electron-capture detector, operated in the constant-current, variable-frequency mode, was employed in all analyses. The injector and oven temperatures in all instances were maintained at 30°C and the detector at 45°C. These temperatures were found in a recent study to be optimum for the determination of PAN and PPN [11]. Helium was the carrier gas at a flow-rate of 5 ml/min for the HP-1, 7 ml/min for the HP-17

wide-bore columns and 3 ml/min for the HP-1 0.32 mm I.D. column. The make-up gas was 10% CH_4/Ar with flow-rates 30 ml/min for all columns used.

Two factors were taken into consideration when selecting the flow-rates of the carrier and make-up gases: first that an optimum separation of all five compounds in the shortest possible time, principally in order to limit the destruction of PAN and PPN on the column, should be attained and second that the response of the detector should be as high as possible. Direct injections of 0.5 ml of sample mixtures were made manually into the injection port using gas-tight syringes provided with Teflon plungers for the wide-bore columns. The variation in the manual injections was $\pm 5\%$, as established from five replicate injections. For the column of 0.32 mm I.D., 0.1 ml of sample was introduced in the splitless mode of a split/splitless injection port. The integrator used was an HP Model 3396A.

Calibration

As mentioned earlier, calibration of the detector for the tested compounds is a major task. With PAN and PPN, the difficulty lies primarily in obtaining pure PAN and PPN standards and in their thermal instability. The methods of preparing PAN and PPN solutions in hexane or tridecane have solved the problem of preparation of the standards [15,16]. However, as these standards are not 100% pure and because of the thermal destruction of PAN and PPN, a primary calibration procedure is still necessary.

The first method of calibration that we employed involved alkaline hydrolysis of PAN or PPN and determination of the resulting nitrite anion by ion chromatography. PAN or PPN gaseous mixtures in synthetic air were prepared by injecting appropriate amounts of liquid PAN–tridecane into a FEP Teflon bag of *ca.* 100-l volume to make a PAN or PPN air mixture of approximate concentration 200 ppb. The PAN or PPN air mixture was pumped for 120 min through an impinger containing 10 ml of 25 m*M* sodium hydroxide solution at a flow-rate of 100 ml/min, such that gaseous samples taken after the impinger gave no ECD signal for PAN or PPN. Aliquots of the hydrolysis mixture were diluted 1:5 with eluent in order to reduce the system peak and injected into the ion chromatograph employing a 100-μl sample loop. From the total concentration of NO_2^- to which nitrate anion was added, as NO_3^- is probably an oxidation product of NO_2^-, and the volume of air passed through the impinger, we calculated the PAN concentration in the FEP bag. Simultaneous injection of a PAN or PPN air mixture into the gas chromatograph allowed the calibration of the detector for the given compound.

Attempts to employ the same calibration procedure for the alkyl nitrates failed because the alkyl nitrates were less than 10% retained in the hydrolysis solution and in an irregular manner. We also attempted to use the determination of acetate anions as the basis of calibration. This yielded 3 mol of acetate ions per mole of nitrite ions, however. This great deviation from the expected 1:1 mole ratio could be attributed to the presence of peracetic acid, which GC–ECD showed to be present, left over from the PAN synthesis.

A Dionex 4500i ion chromatograph with a conductivity detector was used for the determination of nitrite and nitrate anions. The columns used were Dionex AS4A with a Dionex AG4A precolumn and a micro-membrane suppressor column. With 1.8 m*M* $NaHCO_3$–1.7 m*M* Na_2CO_3 as the eluent at a flow-rate of 2 ml/min, the nitrite anions

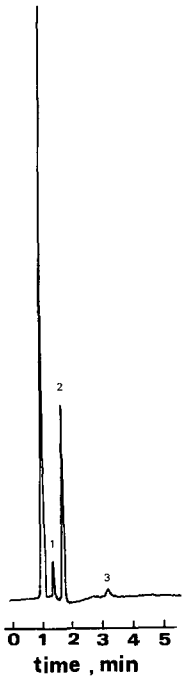

Fig. 1. Typical ion chromatogram from calibration procedure for PAN. Peaks: 1 = Cl^-; 2 = NO_2^-; 3 = NO_3^-.

eluted in 1.8 min, well resolved from the previous Cl^- peak, as shown in Fig. 1.

Before ion chromatography became available in our laboratory, we carried out calibration of the electron-capture detector for PAN, PPN and organic nitrates by first converting them to NO followed by chemiluminescence detection of NO. The main components of this system are a Pye Unicam Model 104 gas chromatograph, a molybdenum converter (a 20-cm long quartz tube of O.D. 1/4 in., packed with molybdenum cut wire heated to the desired temperature) and a chemiluminescence reaction cell situated in front of an EMI 9658R cooled photomultiplier.

In contrast to the commercially available NO_x instruments, our laboratory-made NO_x detector is operated at flow-rates typical of GC, *ca.* 30 ml/min, and has a detection limit of 10 ppb of NO. In the past this system was operated with a chromatographic column packed with the same material as the analytical packed column employed in GC–ECD. The idea was to separate the nitrogen-containing compounds on the column, convert them to NO as they elute from the column and detect them with the NO_x detector. As the NO_x detector can easily be calibrated with a primary NO standard, simultaneous injection of the nitrogen-containing compounds into the GC–ECD system would allow its calibration as well. Now, however, we operate our GC–NO_x system without this column because of destruction of PAN and PPN on the column and also because the NO primary standard does not yield reproducible results when passed through a column. Care must be exercised to introduce nitrogen-containing compounds that are as pure as possible, or at least without nitrogeneous impurities.

The first step in using the GC–NO_x system is to make an NO_x signal *vs.* molybdenum converter temperature plot, such as shown in Fig. 2, in order to find the converter temperature necessary for the complete conversion of nitrogen-containing compounds to NO. At the plateau of the diagram for each compound we assume a 100% conversion to NO.

Intercomparison of our two ECD calibration methods for PAN and PPN showed that the NO_x method yields only 77 ± 5% of the concentration obtained by ion chromatography for both PAN and PPN. This difference could presumably be attributed to a less than 100% efficiency of their conversion to NO.

RESULTS AND DISCUSSION

Response factors

Using the GC–NO_x chemiluminescence detection system we were able to determine the ECD response factors of all the compounds studied. The response factors of PAN and PPN obtained by GC–NO_x detection were corrected by 23% according to the calibration results based on the ion chromatographic method. As shown in Table I, contrary to the assumptions reported in the literature [1], the alkyl nitrates have different response factors to PAN. PAN and PPN have the highest response factors equal within experimental uncertainty. Although there was a slight column to column variation, the ECD response of methyl nitrate is on average 50 ± 5%, of ethyl nitrate 68 ± 2% and of 2-butyl nitrate 46 ± 2% of that of PAN. The PPN response, within the experimental uncertainty, is identical with that of PAN.

Chromatographic analyses

The primary aim of this work was to find a chromatographic column for the better determination of PAN and PPN, *i.e.*, with better resolution, shorter retention times and hence minimal on-column destruction. Recent interest in alkyl nitrates in the atmosphere, however, prompted us to examine whether the same column could also be used for the simultaneous determination of peroxyacyl nitrates and alkyl nitrates. For

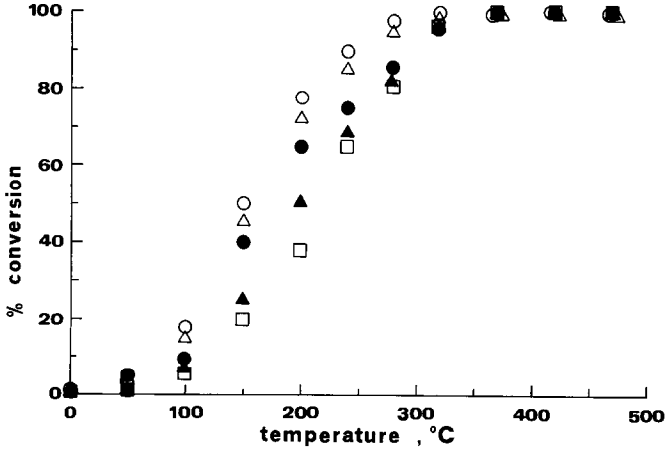

Fig. 2. Effect of temperature on conversion of nitrogen-containing compounds to NO on the molybdenum converter. ○, PAN; △, PPN; ●, methyl nitrate; ▲, ethyl nitrate; □, 2-butyl nitrate.

TABLE I

RESPONSE FACTORS (%) COMPARED WITH PAN BASED ON THE GC–NO_x DETECTION SYSTEM

Column	Methyl nitrate	Ethyl nitrate	2-Butyl nitrate	PAN	PPN
HP-1 wide-bore	45	70	48	100	93
HP-1 0.32 mm I.D.	59	69	44	100	89
HP-17 wide-bore	45	66	–	100	105

the alkyl nitrates we selected methyl and ethyl nitrate, which are the major organo-nitrogen thermal decomposition products of PAN and PPN, respectively, and 2-butyl nitrate, which was recently shown to occur in the atmosphere in the highest concentration of all $>C_3$ alkyl nitrates [5]. In addition to the resolution and retention times achieved, the three columns were also evaluated for the detection limits attained.

Figs. 3, 4 and 5 show typical chromatograms of a mixture of the above compounds with the 5-m wide-bore HP-1, the 15 m × 0.32 mm I.D. HP-1 and the 10-m wide-bore HP-17 columns, respectively. With all the columns the carrier gas flow-rate was adjusted so that the retention times of PAN and PPN would be ca. 2–3 and 4.5–6.5 min, respectively, in order to minimize as much as possible their destruction on the column, provided of course that the resolution was satisfactory. The make-up gas was adjusted so as to obtain the maximum ECD response without impairing the resolution of the least resolved peaks, air–methyl nitrate and PPN–2-butyl nitrate.

PAN and PPN on the non-polar HP-1 wide-bore column are eluted in 2.00 and 4.60 min, respectively. A typical chromatogram is shown in Fig. 3. PAN and ethyl nitrate are baseline resolved from the other peaks. The resolution between PPN and 2-butyl nitrate is 0.6, as shown in Table II. This column gives a poorer separation of methyl nitrate from the air peak. One can, however, still use this column to determine methyl nitrate down to the low ppb range for direct injection. Although the resolutions achieved with this short column are inferior to those with the HP-1 0.32 mm I.D. column, consistent with its small number of theoretical plates, as shown in Table II, its great advantage is its large sample capacity. Sample volumes up to 1 ml could be used with this column, thus improving the detection limits for the determination of PAN, at the expense of the resolution of methyl nitrate from the air peak and thus its poor detection. With this column the detection limit of PAN could be lowered to 50 ppt for direct injection of a 1-ml sample. PPN, which has the same ECD response factor as PAN, would have the same detection limit as PAN when measured alone. When PPN

TABLE II

CHROMATOGRAPHIC CHARACTERISTICS OF THE THREE COLUMNS

Column	I.D. (mm)	Length (m)	N_{sys} (maximum)	Resolution, PPN–2-butyl nitrate
HP-1	0.53	5	1200	0.6
HP-1	0.32	15	7600	1.4
HP-17	0.53	10	520	–

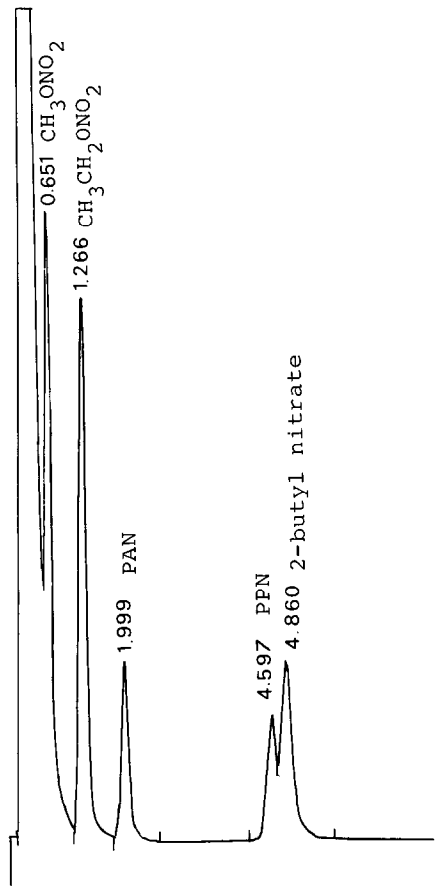

Fig. 3. Typical chromatogram of studied mixture with HP-1 wide-bore column. Numbers at peaks indicate retention times in min.

is present in the mixture studied, however, it has a higher detection limit because of its slight overlapping with 2-butyl nitrate and therefore increased uncertainty in the integration. It is estimated that in samples with approximately equal area counts of PPN and 2-butyl nitrate, the PPN detection limit for direct injection of a 0.5-ml sample would be 0.2 ppb.

The detection limits of methyl, ethyl and 2-butyl nitrate are 7, 1 and 5 ppbv, respectively. As with PPN, the detection limits, in addition to the varied response factors, depended on the resolution achieved. This explains the lower detection limit for ethyl nitrate compared with the other alkyl nitrates.

The HP-1 0.32 mm I.D. capillary column yielded a much better resolution of methyl nitrate from the air peak and of PPN from 2-butyl nitrate, as shown in Fig. 4. The optimum retention times of PAN and PPN with this column increased by almost 25% compared with the HP-1 wide-bore column. These increased retention times would result in increased destruction of PAN and PPN during their passage through the column [11]. For this reason, and as the resolution achieved was satisfactory, it was

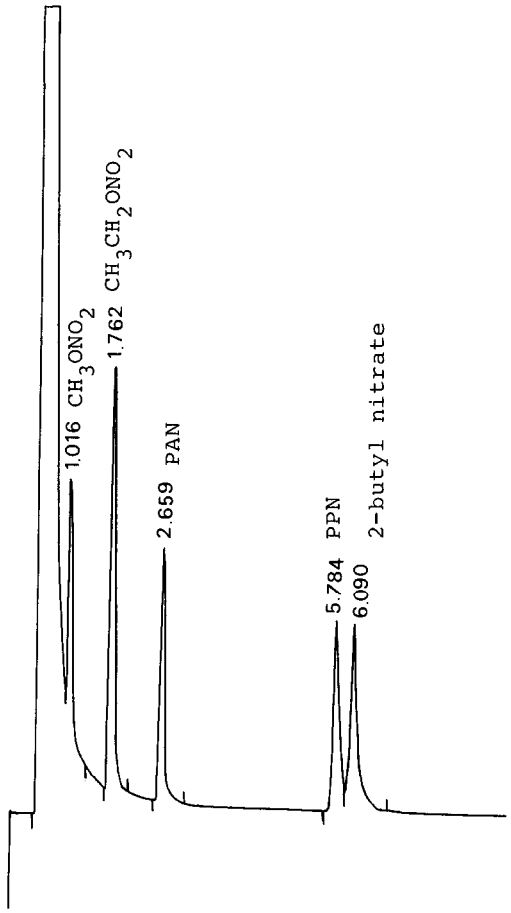

Fig. 4. Typical chromatogram of studied mixture with HP-1 0.32 mm I.D. column.

not necessary to employ a full 25- or 30-m capillary column. The resolution of 1.4 between PPN and 2-butyl nitrate achieved with this column was the best of all columns when the sample injected was 0.1 ml. The low sample capacity of this column, however, did not allow injection volumes larger than 0.2 ml without significant deterioration of the resolution of methyl nitrate from the air peak, at a methyl nitrate concentration of 8 ppb. This sample limitation was only applicable to methyl nitrate. Sample volumes of 0.5 ml can easily be injected in the splitless mode and thus lower the detection limits mainly of PAN and ethyl nitrate, but also of PPN and 2-butyl nitrate. The detection limits obtained were 0.3, 0.6, 7 and 3 ppbv for PAN, ethyl nitrate, 2-butyl nitrate and PPN, respectively.

The intermediate polarity HP-17 column also gives very good separations of PAN. As shown in Fig. 5 however, PPN is not resolved from 2-butyl nitrate. On the other hand, it is obvious that on this column methyl nitrate is better resolved from the air peak than with the HP-1 columns. The number of theoretical plates of this column calculated from the PAN peak, which is eluted in 3.07 min when the carrier gas

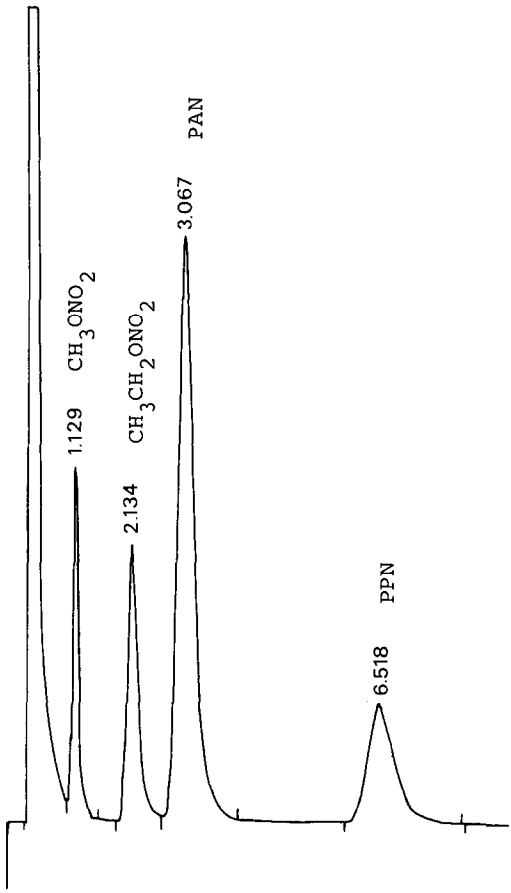

Fig. 5. Typical chromatogram of studied mixture with HP-17 wide-bore column.

flow-rate is 7 ml/min, is significantly less than those for the other two columns, as shown in Table II. The numbers of theoretical plates were calculated taking into account the slight peak asymmetry using the equation

$$N_{sys} = 41.7(t_R/W_{0.1})^2/(B/A + 1.25)$$

where t_R is the retention time, $W_{0.1}$ is the peak width at 0.1 of the peak height and B/A accounts for the peak asymmetry [17]. The detection limits for PAN and methyl and ethyl nitrate, which are almost baseline resolved, were 0.1, 1 and 0.7 ppbv, respectively, for a direct 0.5-ml sample injection.

CONCLUSIONS

The non-polar 100% dimethyl polysiloxane gum column is superior to the more polar 50% dimethyl–50% phenyl polysiloxane column for the separation of PAN,

PPN and alkyl nitrates. When these columns are compared with a capillary column with a polar Carbowax stationary phase, as recently reported by Helmig *et al.* [10], they present clear advantages. First, PAN and PPN are better resolved with all the columns examined in this work and second, and very important, there is no water peak, so that no precolumn and backflushing are required. An additional advantage, of course, is that our tested columns can be used for the simultaneous determination of alkyl nitrates. The elution of chlorofluorocarbons with these columns does not seem to be a disadvantage because preliminary tests with some chlorofluorocarbons have shown them to elute in the "windows" of the chromatogram of PAN, PPN and alkyl nitrates. Finally, the columns used in this work have been in continuous operation for almost 2 years with an average number of 30 injections per day, which could explain their small number of theoretical plates. Comparison with the capillary Carbowax column, which has a short lifetime, again favours the less polar stationary phases presented here. As the HP-1 wide bore column seems to be comparable to, if not better than, the HP-1 0.32 mm I.D. column, and given the facility with which wide-bore columns can be installed in a gas chromatograph equipped with packed-type injection ports, we propose this type of column for the determination of nitrogen compounds of atmospheric importance.

ACKNOWLEDGEMENTS

This work was financially supported by the Commission of the European Communities under Contract EV4V-0070-D(B). N.R. thanks the Hellenic Refineries of Aspropyrgos for a fellowship.

REFERENCES

1 J. M. Roberts, *Atmos. Environ.*, 24A (1990) 243.
2 P. J. Temple and O. C. Taylor, *Atmos. Environ.*, 17 (1983) 1583.
3 H. B. Singh, *Environ. Sci. Technol.*, 21 (1987) 320.
4 H. B. Singh and L. J. Salas, *Atmos. Environ.*, 23 (1989) 231.
5 E. Atlas, *Nature (London)*, 331 (1988) 426.
6 F. Juttner, *J. Chromatogr.*, 442 (1988) 157.
7 J. Rudolph, B. Vierkorn-Rudolph and F. Z. Meixner, *J. Geophys. Res.*, 92 (1987) 6653.
8 E. Tsani-Bazaca, S. Glavas and H. Gusten, *Atmos. Environ.*, 22 (1988) 2283.
9 J. M. Roberts, R. W. Fajer and S. R. Springston, *Anal. Chem.*, 61 (1989) 771.
10 D. Helmig, J. Muller and W. Klein, *Atmos. Environ.*, 23 (1989) 2187.
11 N. Roumelis and S. Glavas, *Anal. Chem.*, 61 (1989) 2731.
12 H. Meyrahn, G. Helas and P. Warneck, *J. Atmos. Chem.*, 5 (1987) 405.
13 D. Grosjean and J. Harrison, *Environ. Sci. Technol.*, 19 (1985) 749.
14 J. S. Gaffney, R. Fajer and G. I. Senum, *Atmos. Environ.*, 18 (1984) 215.
15 T. Nielsen, A. M. Hansen and E. L. Thomsen, *Atmos. Environ.*, 16 (1984) 2447.
16 A. P. Black and F. H. Babers, in A. H. Blatt (Editor), *Organic Syntheses*, Collective Vol. 2, Wiley, New York, 1967, p. 412.
17 J. P. Foley and J. G. Dorsey, *Anal. Chem.*, 55 (1983) 730.