

Photoionization assessment of C₃ - C₅ alkadienes and alkenes in urban air

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Open access reviewed manuscript version of
Journal of Chromatography 591 (1992) 358-361

ABSTRACT

Hydrocarbons from samples of traffic-polluted urban air were separated by gas chromatography on an Al_2O_3 column and assessed simultaneously with photoionization (PID) and flame ionization (FID) detectors after effluent splitting. The 10.2 eV photoionization detector selectively detects alkadienes and alkenes but not alkanes and alkynes in the C_3 - C_5 region. The maximum PID / FID response ratio for alkadienes and alkenes is also obtained in this region. The analytical system as a whole is particularly favourable for the C_3 - C_5 alkenes. Analytical data are given for propadiene, 1,3-butadiene, propene, butenes and pentenes.

INTRODUCTION

In the complex hydrocarbon mixture of urban air, volatile arenes and alkenes are of particular interest with respect to impact on health as well as the environment. It was early recognized that the photoionization detector offers a high selectivity for these hydrocarbons as compared with alkanes [1], because of the lower ionization potential of unsaturated hydrocarbons. Techniques based on the simultaneous use of photoionization and flame ionization detectors in parallel [2] or in series [3] have been developed with applications to urban air in mind. These techniques were also described in a review of multiple detection in gas chromatography [4].

The purpose of the present study is to demonstrate the advantages of the dual detector technique for assessing $C_3 - C_5$ hydrocarbons in urban air. Applications are based on a recently described system for adsorption sampling and gas chromatographic separation [5]. This system is particularly advantageous for the $C_3 - C_5$ alkenes, permitting the full capability of the selective detection to be utilized.

EXPERIMENTAL

Samples of urban air (0.2 - 2 l) were passed through triple-layer adsorbent cartridges with Tenax TA in the front end followed by Carbotrap and Carbosieve S-III. In the laboratory, the hydrocarbons were thermally desorbed and analyzed using temperature-programmed gas chromatography. The column (Chrompack) was a 50 m x 0.32 mm i.d. PLOT capillary with Al_2O_3 treated with 5 % KCl as the stationary phase. The temperature sequence was 0-110 °C (10 °C min⁻¹), 110 °C (14 min), and 110-200 °C (4 °C min⁻¹). Further analytical data are given in a recent methodological report focussed on alkenes recorded by FID [5].

The column effluent (He, 2 ml/min) was split with ~55% to the flame ionization detector and ~45% to an optional 10.2 eV photoionization detector (HNU, model PI-52) which was kept at ~200 °C. The splitting device and detector arrangement were similar to those reported in a basic study of the use of parallel FID and PID [2]. Makeup gas (He, ~10 ml/min) was used for the PID.

RESULTS AND DISCUSSION

The chromatograms in Fig. 1 illustrate the excellent selectivity of the photoionization detector for the environmentally critical C₃-C₅ alkadienes and alkenes. The alkynes and the predominant alkanes recorded by flame ionization are virtually absent in the PID chromatogram. Relevant data for the alkadienes and alkenes are given in Table I.

Response ratios

From Fig.1, the high PID/FID response ratio for alkadienes and alkenes is evident. This ratio depends strongly on a number of instrumental parameters, and few data have been given [2]. Normalized PID/FID response ratios are more widely valid and therefore preferred. Among the C₃ - C₅ alkenes and alkadienes, propene was chosen as the reference hydrocarbon because it is frequently determined and reported. In Table I, PID/FID ratios normalized to propene are given for the sample corresponding to Fig. 1 and for a duplicate sample. These two high-concentration samples offer a more complete and reliable set of data than samples corresponding to normal urban air pollution levels. The PID selectivity is highest for the conjugated alkadiene 1,3-butadiene. For alkenes, the ratio tends to be lower for 1-alkenes than for 2-alkenes, to increase with branching, and to decrease with molecular weight.

The propene-normalized PID/FID ratios for benzene and toluene were found to be 1.5 and 1.4, permitting comparisons with data normalized to these hydrocarbons which are favourably recorded by PID. For a 10.0 eV PID, toluene-normalized PID/FID ratios have been reported for many hydrocarbons including alkenes and alkadienes [2]. The PID/FID ratios given in Table I agree closely for the hydrocarbons included in both sets of data.

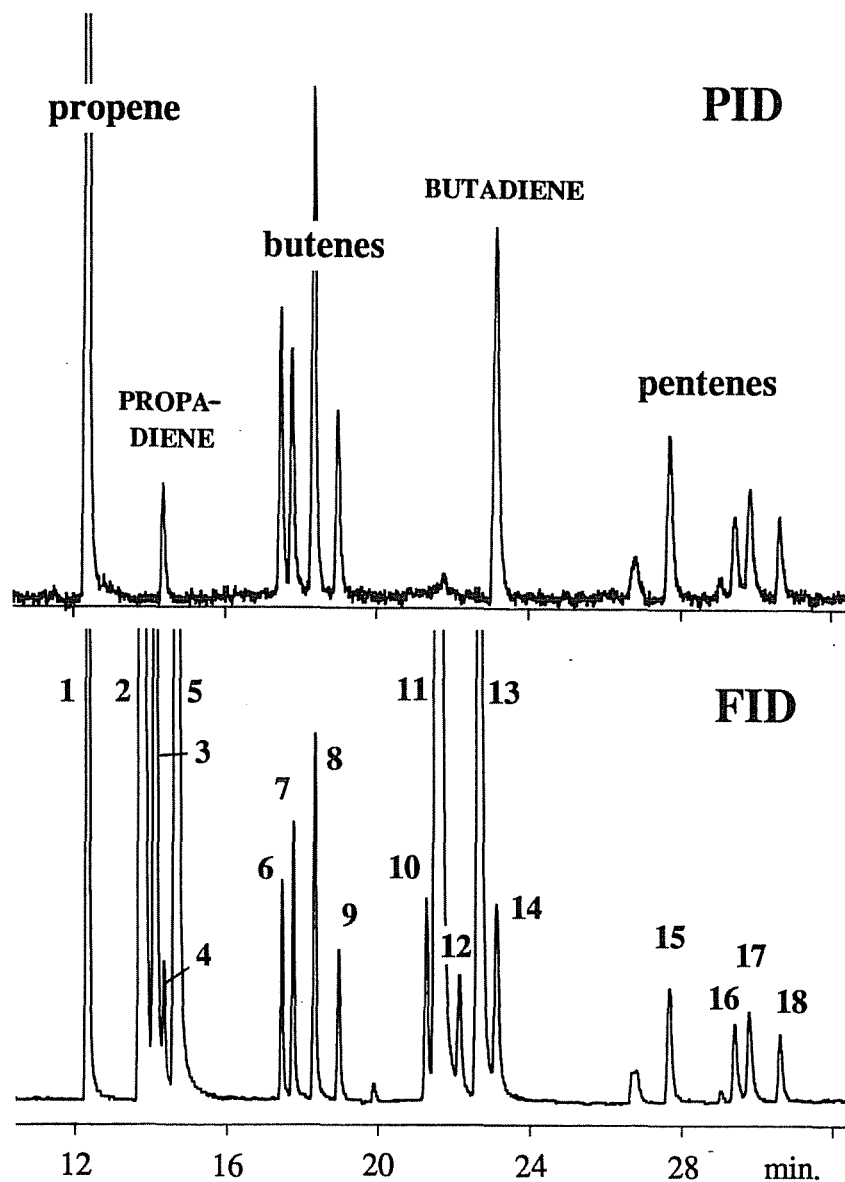


Fig. 1 Simultaneous photoionization and flame ionization recording of chromatograms of hydrocarbons from traffic-polluted urban air. (1 propene, 2 ethyne, 3 methylpropane, 4 propadiene, 5 butane, 6 *trans*-2-butene, 7 1-butene, 8 methylpropene, 9 *cis*-2-butene, 10 cyclopentane, 11 methylbutane, 12 propyne, 13 pentane, 14 1,3-butadiene, 15 *trans*-2-pentene, 16 1-pentene, 17 2-methyl-1-butene, 18 *cis*-2-pentene).

TABLE I.

NORMALIZED PID/FID RESPONSE, URBAN CONCENTRATIONS AND PHYSICAL DATA OF VOLATILE ALKADIENES AND ALKENES.

The concentrations given reflect a high exposure level of pedestrians to vehicle-polluted urban air (Göteborg, 11/30 -89, street intersection, 0°C, winter inversion). The proportions of the hydrocarbons are expressed as % of total hydrocarbons except methane, and retention data are given relative to *n*-alkanes in methylene units (MU). Columns 1,3,4 and 5 give data for the sample corresponding to Fig. 1.

	PID/FID (propene:1.00) duplicate samples		Conc. $\mu\text{g}/\text{m}^3$	CH_x Fraction %	Rel. retention MU	Boiling point $^{\circ}\text{C}$
Alkadienes						
propadiene	1.03	1.06	2.0	0.2	3.95	-35
1,3-butadiene	1.56	1.51	6.1	0.5	5.03	-4
Alkenes						
propene	1.00	1.00	26	2.0	3.57	-47
<i>trans</i> -2-butene	1.28	1.30	3.7	0.3	4.35	1
1-butene	0.81	0.83	5.2	0.4	4.39	-6
methylpropene	1.24	1.28	7.7	0.6	4.46	-7
<i>cis</i> -2-butene	1.13	1.15	3.2	0.3	4.54	4
<i>trans</i> -2-pentene	1.19	1.18	3.6	0.3	5.36	36
1-pentene	0.81	0.78	2.4	0.2	5.48	30
2-methyl-1-butene	0.92	0.93	2.9	0.2	5.51	31
<i>cis</i> -2-pentene	0.98	1.03	1.9	0.2	5.57	37

For C₇-C₂₂ hydrocarbons, the PID selectivity at 10.2 eV for alkenes compared to alkanes decreases rapidly with molecular weight [6]. Consequently, PID detection offers by far the best selectivity in the C₃-C₅ region.

Alkadienes

Propadiene and 1,3-butadiene were the two prominent alkadienes assessed. They are seldom reported in studies of urban air because they elute close to, and are masked by, alkanes on nonpolar columns. As illustrated by Fig. 1, they may be well enough separated on the Al₂O₃ column for FID assessment, but PID offers superior selectivity and response. It should be noted that propadiene and 1,3-butadiene were not separated from adjacent alkanes when certain different temperature programs were used. Actually, the two C₄ alkanes (methylpropane and *n*-butane) have been reported to elute both before propadiene [7] and after propadiene [8] on Al₂O₃/KCl columns.

The results of a number of urban air samples from different vehicle-polluted locations indicated almost the same proportions between the two alkadienes. The concentration of 1,3-butadiene was about three times higher than that of propadiene. It is concluded that propadiene as well as propene and 1,3-butadiene are combustion products. The concentration of the carcinogenic 1,3-butadiene is typically 20-25% of the concentration of propene [9] which is frequently reported.

Evidently, the presence of anthropogenic alkadienes in outdoor urban air, as reported in Table I, is predominantly due to vehicle exhaust. For smokers and passive smokers, tobacco smoke is a major source of 1,3-butadiene [10].

Alkenes

The $\text{Al}_2\text{O}_3/\text{KCl}$ column is well suited to the assessment of alkenes in urban air with FID detection [5], but PID detection offers increased selectivity and confirmation of alkene identity. Because of its high ionization potential, ethene is not detected by PID. In addition to ethene and propene, the major portion of the butenes originates from engine combustion in traffic-polluted urban air [9]. The pentenes and part of the butenes originate from tailpipe emissions of unburnt petrol and from petrol vapour [5]. In Table I, the alkenes are characterized with respect to abundance in urban air, relative retentions and boiling points.

The pentenes, particularly 2-methyl-2-butene, are the most reactive of the C_3 - C_5 alkenes and alkadienes and may be partially lost during adsorbent sampling by reaction with ozone and other agents in urban air. In Fig.1, the pentenes are recorded in the expected proportions [5] except for the deviating small peak of 2-methyl-2-butene in front of 1-pentene. The loss of 2-methyl-2-butene illustrates the danger of relying on good chromatographic results without controlling the quality of sampling. It was found that sampling losses could be avoided by treating the front end of the adsorbent layer with antioxidative thiosulphate before sampling. This technique was recently described in more detail for the sampling of easily oxidized monoterpenes on Tenax cartridges [11].

Conclusions

The results demonstrate that dual PID/FID assessment is particularly favourable for C_3 - C_5 alkadienes and alkenes with respect to sensitivity as well as selectivity. The greatest advantages are obtained for the majority of samples containing much larger amounts of volatile alkanes. The applied

methods for sampling from air and for gas chromatographic separation [5] are also especially favourable for C₃ - C₅ alkenes in contrast to several conventional methods. It is concluded that the reported analytical approach is a powerful aid for meeting the increasing interest in these genotoxic and efficiently photooxidantforming hydrocarbons.

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