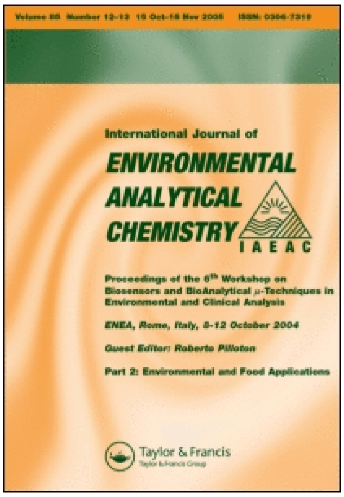

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Multisorbent tubes sampling used in thermal desorption cold trap injection with gas chromatography-mass spectrometry for C_2-C_6 hydrocarbon measurements in an urban atmosphere

Olatz Baroja[a]; M. Aranzazu Goicolea[a]; M. Carmen Sampedro[a]; Esther Rodríguez[b]; Zuriñe Gómez De Balugera[b]; Andrés Alonso[c]; Ramón J. Barrio[a]
[a] Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain [b] Department of Chemical and Environmental Engineering (EUITIT), University of the Basque Country, Nieves Cano 12, Vitoria-Gasteiz, Spain [c] Environment Department, City Council, 01005 Vitoria-Gasteiz, Spain

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MULTISORBENT TUBES SAMPLING USED IN THERMAL DESORPTION COLD TRAP INJECTION WITH GAS CHROMATOGRAPHY-MASS SPECTROMETRY FOR C_2–C_6 HYDROCARBON MEASUREMENTS IN AN URBAN ATMOSPHERE

OLATZ BAROJA[a], M. ARANZAZU GOICOLEA[a], M. CARMEN SAMPEDRO[a],
ESTHER RODRÍGUEZ[b], ZURIÑE GÓMEZ DE BALUGERA[b],
ANDRÉS ALONSO[c] and RAMÓN J. BARRIO[a,]*

[a]*Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain;* [b]*Department of Chemical and Environmental Engineering (EUITIT), University of the Basque Country, Nieves Cano 12, Vitoria-Gasteiz, Spain;* [c]*Environment Department, San Prudencio 30, City Council, 01005 Vitoria-Gasteiz, Spain*

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Three solid adsorbents (Carbotrap, Carbotrap C, and Carbosieve III) were evaluated for sampling trace non-methane hydrocarbons in urban atmospheres. The sampled atmosphere was pumped through a multisorbent tube containing the three sorbents separated by a small amount of silanized glass wool. The trapped compounds were recovered by thermal desorption and analysed by combining cryogenic enrichment with gas chromatography and mass spectrometry. Adsorption/thermal desorption and breakthrough experiments were performed to test their ability to quantitatively trap the light hydrocarbons. The technique was suitable for determination of low ppbv concentrations of these compounds. Ambient atmospheric sampling was conducted in Vitoria-Gasteiz (Basque Country, Spain), and the measurements cover a period of one year (2001–2002). Fifteen C_2–C_6 hydrocarbons are identified and quantified, and seasonal trends are discussed.

Keywords: NMHCs; Multisorbent tubes sampling; Thermal desorption; GC-MS

INTRODUCTION

Non-methane hydrocarbons (NMHCs) have been recognized as one of the principal trace constituents in the atmosphere. NMHCs play an essential role in the formation of photochemical air pollution. They are precursors for ozone production at ground level when sunlight and nitrogen oxides are present. This ozone is usually characterized

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*Corresponding author. Fax: +34-945-013014. E-mail: qapbadir@vc.ehu.es

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as 'bad ozone', which can endanger both our environment and human health. Motor vehicle exhaust has been considered as a major NMHC source in urban areas [1,2]. Different techniques are available for sampling NMHCs in air: stainless steel canisters [3,4], diffusive samplers [5], semi-continuous on-line air stream sampling [6], and pumped sorbent tubes [7]. Most of the methods that have been developed for volatile organic compounds (VOCs) in air have been either canister-based or sorbent-based. The respective advantages and limitations of canister and sorbent methods have been discussed in the literature [8–10].

Solid adsorbents are used extensively to identify and measure VOCs in air, mainly C_6 higher hydrocarbons [11–13]. The sampled atmosphere is pumped through an adsorbent bed comprising one or more adsorbent materials, which trap VOCs. The adsorbent is a macroreticular polymeric or carbon-based material (Tenax, Carbotrap, Carbosieve, Porapack, etc.). The trapped compounds may be recovered by various techniques, but thermal desorption is the most recommended technique because of its reliability and cost-effectiveness [14]. Tenax is the most widely used of these adsorbents, but highly volatile compounds such as NMHCs are not trapped efficiently, and some of these compounds break through the Tenax, giving erroneous results. A stronger sorbent was needed to trap the highly volatile compounds, and even multisorbent traps had to be used for this purpose. Before a multisorbent trap can be used for collecting compounds in air, data on the breakthrough volumes are needed.

The equilibrium trapping capacity of the adsorbent is proportional to the analyte concentration at low concentrations and under constant conditions of temperature and relative humidity. The trapped mass is not only a function of the analyte concentration and the nature of the adsorbent; it is also affected by the nature and concentrations of the other volatile organic compounds present in the sample population [15]. This effect of competition between VOCs at the adsorbent surface on the breakthrough volume is shown in Eq. (1):

$$m_{\mathrm{T}} = \frac{K_i c_i}{K_i c_i + \sum_{j=1}^{j=n} K_j c_j}, \tag{1}$$

where m_{T} is the mass of analyte trapped, K_i is the partition constant of the analyte on the adsorbent trap, c_i is the concentration of analyte, K_j is the partition constant of the n other trapped species, and c_j is the concentration of the n trapped species.

Modelling and experimental observation have suggested that the combination of competition and concentration can have a significant effect on breakthrough volumes with reported reductions of as much as 73% [16,17]. This loss of sampling efficiency compels us to adopt procedures to validate active sampling, adsorbent-based hydrocarbon analysis.

The main objective of this study was therefore to develop a sampling and analysis method, using thermal desorption-gas chromatography-mass spectrometry, to enable compilation of a comprehensive inventory of the occurrence and concentrations of hydrocarbons in urban air. With the method described here, a total of 16 hydrocarbons were monitored simultaneously.

Experimental

Sampling Site Description

Ambient air samples were collected from July 2001 to July 2002 at Vitoria-Gasteiz (in northern Spain, 42° 51′ N latitude, 2° 41′ W longitude and an altitude of 528.6 m above sea level), a city with about 250 000 inhabitants. The location of the sampling point was carried out following European Community guidelines [18], using a metropolitan sampling cabin sited in a traffic-orientated urban street. It is located in the district of Zaramaga, which is a residential zone. The station is located 3 m from a two-way one lane road, and 25 m from a two-way three-lane road. Sampling protocols were broadly based on methods and approaches described in current methodology for sampling and analysis of VOCs by diffusive sampling [19,20].

Sampling Conditions

All samples were collected between 14.00 and 14.13 am once a week. Airflow through the adsorbent bed was generated by a low-flow SKC pump, Mod. 224–44 Ex (SKC, PA). The pump was attached to an adsorbent tube using clear inert Tygon tubing. An EL-FLOW F-201C (Bronkhorst HighTech., Netherlands) thermal mass flow meter and controller with a control module, Mod. E-7000, was used to correct for pressure and temperature and obtain units of volume at the reference conditions (293 K and 101.3 kPa). Each sample was collected with a flow rate of 30 mL/min. During trapping, the pump was connected to the mains electricity supply. Fluctuations in the trapping flow velocity were registered by the mass-flow detector which was connected on-line.

MATERIAL AND METHODS

Gas Standards

Four different cylinder gas standards were used to prepare calibration curves: (1) Scotty IV (Scott Speciality Gases, Inc.) Cat. No. 2-3470-U: methane, ethane, ethylene, acetylene, propane, propylene, propyne, and *n*-butane each at 15 ppm in nitrogen; (2) Scotty IV Cat. No. 2-3471: *n*-butane, iso-butane, *cis*-2-butene, *trans*-2-butene, 1-butene, iso-butylene, 1,3-butadiene, and ethyl acetylene each at 15 ppm in nitrogen; (3) Scotty II Cat. No. 2-3445: iso-butane, 2-methylbutane, 2,2-dimethylpropane, 2-methylpentane, 3-methylpentane, and 2-2-dimethylbutane, each at 15 ppm in nitrogen; (4) Scotty IV Cat. No. 501786: methane, ethane, propane, butane, and hexane each at 15 ppm in nitrogen. The cylinders were equipped with a pressure regulator and a syringe adaptor. The gas standards were directly injected in the adsorbent tube placed in the TCT system using a 50- and 1000-µL SampleLock gas-tight microsyringe Hamilton (Reno, NV). A linear calibration curve was constructed for each analyte by injecting selected volumes of target compounds. A calibration curve was built for each of the compounds using at least five points. Correlation coefficients ranged from 0.9900 (ethane) to 0.9999 (iso-pentane).

Adsorbents

Solid adsorbent sampling has proven useful in air sampling and has become an alternative technique for analysis at atmospheric NMHCs. In particular, the advent of multistage adsorbent cartridges has led to major advances in solid-adsorbent techniques. The use of such techniques allows compounds of interest to be selectivity sampled [21,22]. Multibed sampling cartridges allow a wider range of compounds to be sampled.

Three different adsorbents were used in a multiplilayer-bed tube (Varian Anal. Instrum., The Netherlands) to trap the NMHCs: Carbotrap/CarbotrapC/CarbosieveIII, as adsorbent of increasing strength. Carbotrap and Carbotrap C graphitized carbon blacks are ideal adsorbents for trapping C_4–C_6 hydrocarbons. Carbosieve III is a carbon molecular sieve that has the greatest ability to trap low-molecular-weight organic compounds (C_2–C_3) owing to its large surface area. The length and diameter of the glass tubes were 16 and 0.4 cm, respectively. Sorbents were separated from each other with small plugs made of glass wool. A number of trials have been carried out on a total of 350 mg of adsorbent, varying the quantities of each of the components of the multiplier bed. The best results, for volumes of air sampled at 400 mL, were obtained with tubes containing 100 mg of Carbotrap, 100 mg of Carbotrap C, and 150 mg of CarbosieveIII. In this way, all the study target compounds were captured, with no losses due to elution and with sufficient detectability guarantees. Before use, the sampling tubes were conditioned by heating at 300°C for 2 h and purged with helium at a flow rate of 100 mL/min. After each use or storage, they were reconditioned at 300°C for 30 min while being purged with helium at 100 mL/min. Each tube was used for a maximum of 10 samplings.

Protection and Storage of the Samples

As soon the pump was turned off, the tubes were removed from the sampling train and sealed with Swagelock end caps to avoid any desorption. Sample tubes were put into special plastic bags that were tightly closed and frozen at −45°C until analysis. Blank multisorbent open tubes were placed into the bags together with the used bags to detect any possible cross-contamination during storage. There were no cases of NMHC residues appearing in blank tubes.

Instrumental Analysis

All samples were thermally desorbed on a Chrompack thermal desorption cold trap injector (TCT, Mod. CP-4010). The technique is well established and has been described previously [23]. Briefly, a sample tube, with the multisorbent material containing target compounds, is placed inside the desorption oven and connected to a fused silica capillary cold trap. At the same time, the capillary cold trap is cryogenically cooled. In the next step, the desorption oven is heated, and thermally desorbed components are transported to the cold trap by a carrier gas stream. The components are refocused on the cold trap. Then, the capillary cold trap is flash-heated, and the components are injected onto the analytical column where they are separated.

The usual cold trap employed in VOCs analysis is a fused silica capillary (i.d. 0.53 mm). Nevertheless, when working with especially volatile compounds, a special fused silica material for cold trap must be used. In this case, a CP-Sil 8 CB (i.d. = 0.53 mm, DF = 5 µm) partially filled (15 mm) with Tenax TA (Chrompack, Cat. No. 16425) was used to retain all compounds in the head column.

The basic operating conditions were: rod temperature 250°C, trap temperature (using liquid nitrogen) −175°C, desorption temperature 300°C, desorption time 8 min, desorption flow 40 mL/min, desorption trap temperature 200°C, injection time 1 min in splitless mode.

Later, the trap was flash-heated up to 200°C, and compounds were subsequently injected into a gas chromatograph Hewlett-Packard (Palo Alto, CA) model 5890 Series II, equipped with a mass spectrometry detector model 5972. The NMHCs were separated using a Plot Al_2O_3/KCl column (50 m × 0.32 mm i.d.; Hewlett-Packard) using helium as the carrier gas at a flow rate of 0.95 mL/min and the following temperature programme: 50°C (3 min) at 3°C/min up to 80°C, 80°C for 1 min, at 5°C/min up to 170°C, 170°C for 10 min. The MS detector was run in scan mode to confirm the identity of all analytes, at a transfer line interface temperature of 200°C. The determination of compound identity was determined using a Wiley mass-spectral library.

RESULTS AND DISCUSSION

Determination of Ethane Breakthrough Volume

The term 'breakthrough volume' is defined as the calculated volume of carrier gas per gram of adsorbent resin which causes the analyte molecules to migrate from the front of the adsorbent bed to the back of the adsorbent bed [24]. No reports have been found concerning the breakthrough volumes for NMHCs on the multisorbent tubes employed in this project at normal sample temperatures. These data are required to determine the maximum sampling volume established to prevent losses of the most volatile hydrocarbon from the triple-layer adsorbent cartridges during sampling. In this study, ethane is the compound with the smaller breakthrough volume, and this will determine the total volume for sampling.

In order to accurately determine the breakthrough volume as a function of temperature, a modified system based on other previously mentioned papers [24–26] was used. The multisorbent tube under test (Carbotrap/Carbotrap C/Carbosieve III) was connected to an injection port inside a GC oven, using 530 µm uncoated fused silica capillary tubing, and the other end of the sample tube was connected to a FID detector. The capillary column was connected to both ends of the adsorbent resin bed using a septum and swagelok union. Helium was used as the carrier gas, and carrier gas flows were adjusted from 35 to 50 mL/min with a flow calibrator (Chrompack FP-meter). Similarly, the temperature was controlled using the GC oven temperature controller. A correction was made for dead time of the packed adsorbent material and connecting lines. This dead time was determined by injecting a non-retained analyte (methane). For most temperatures, this dead time was about 0.148 min. All samples were run in triplicate at each temperature. Breakthrough volumes can be obtained from the expression:

$$B_v = \frac{(R_t - D_t) \times F}{W_a \times 1000}, \tag{2}$$

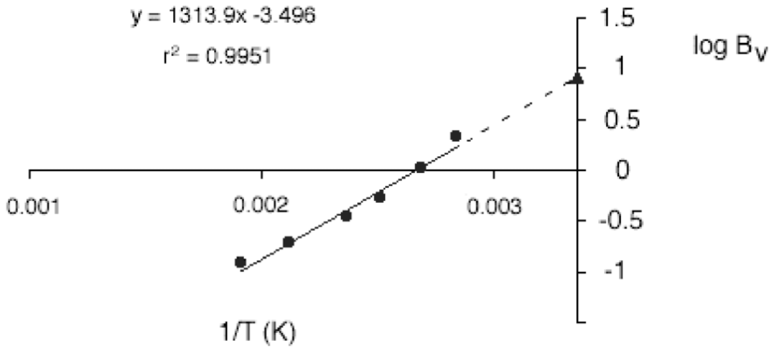

FIGURE 1 Breakthrough volume at different temperatures for ethane in the multisorbent tube. A graph of $\log_{10} B_v$ *vs.* $1/T$ (K). A line plot can be extrapolated to ambient temperature (σ). At 298 K the B_v for the ethane is 8.2 L/g.

where B_v is breakthrough volume (litres per gram of adsorbent), R_t is retention time (min), D_t is dead time (min), W_a is adsorbent weight (g), and F is carrier gas flow (mL/min). When collecting samples onto the adsorbent material bed, the safe sample volume ($B_s = B_v \times 0.5$) should not be exceeded so that all the analyte can be trapped on the adsorbent material bed.

After calculating retention volumes at at least five different temperatures, usually higher than the trapping temperature, the specific retention volume at 25°C was obtained by linear extrapolation [11] of the graph $\log B_v$ *vs.* $1/T$ (Fig. 1). A value of 820 ± 97 mL was obtained once the uncertainty in the intercept was estimated.

For the breakthrough experiments made using the experimental model described above, no breakthrough was observed for any of the compounds for an air volume of 800 mL. Thus, to guarantee effective sampling, the volume used in all ambient sampling in the metropolitan cabin was $B_s = 400$ mL.

To confirm the maximum sampling volume during the air sampling, two adsorbent tubes were connected in series, and 400-mL air samples were collected. If more than 5% of one or more of the analytes is observed with the second tube, breakthrough is shown to have occurred at that sample volume [19,27]. Figure 2 shows as an example the two chromatograms obtained on a certain day. No NMHCs were observed with the second backup tube.

Analytical Method Validation

Table I shows the retention times of the compounds, the coefficients of variation, and the detection limits of the method. The regression coefficients are higher than 0.990 in all cases, and the detection limits range from 0.07 to 1.68 ng, which proves the accuracy and sensitivity of this TCT-GC-MS analytical methodology in quantifying these NMHCs in air.

In order to check the precision of the method, several standards containing the analytes at two different levels of concentration were analysed on the same day ($n = 5$), and the relative standard deviation (RSD) of the results was determined. The RSD of the tests at the lower of the two concentrations studied was less than 12.6%, thus proving the high repetitivity of the analytical method even at low concentrations.

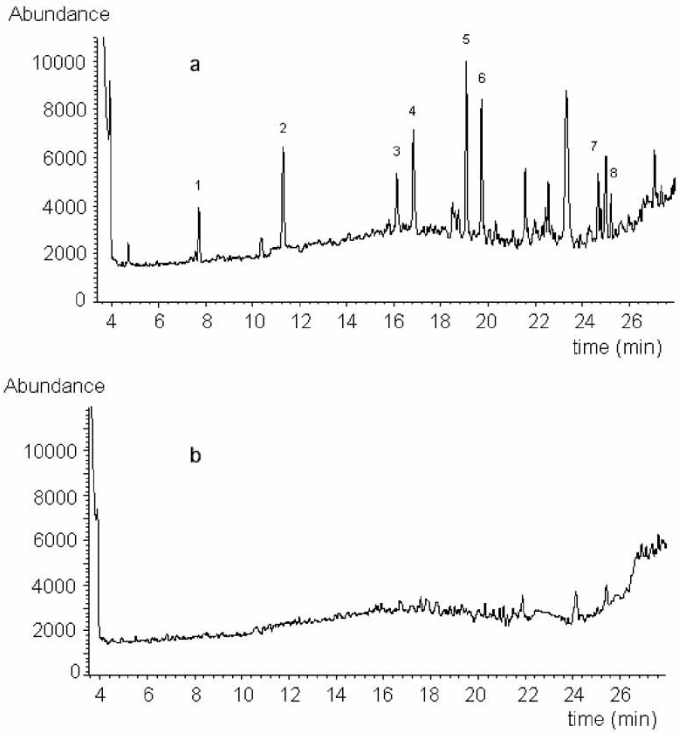

FIGURE 2 Total ion chromatograms obtained on March 1, 2002, using two sorbent tubes in series. (a) Tube 1 (first), and (b) tube 2 (following). Numbered compounds are (1) 1-propene, (2) *n*-butane, (3) 1-butene, (4) isobutene, (5) isopentane, (6) *n*-pentane, (7) 2-methylpentane, (8) hexane. Experimental conditions in the text.

TABLE I Retention times, linear regression analysis, correlation coefficients, standards deviations at two different levels 50 and 250 μL (the concentrations of the different gas cylinders is 15 ppm in nitrogen), and detection limits of TCT-GC-MS determination of NMHCs

Compound	*Retention time* (min)	*Slope* (Abundance/ng) × 10^5	*Intercept* (Abundance/ng) × 10^5	*Correlation coefficient*	*DL* (ng)	*CV (5) n = 5*	
						50 μL *level*	250 μL *level*
Ethane	2.96	1.5	0.03	0.990	0.21	8.11	10.51
Propane	5.18	3.9	0.3	0.997	0.10	8.10	11.35
Propene	8.49	3.5	3.0	0.997	0.14	7.79	10.24
Isobutane	11.21	13.4	2.1	0.998	0.03	6.88	9.07
Butane	12.23	3.0	3.2	0.996	0.13	7.34	9.12
Trans-2-butene	16.76	7.8	1.1	0.998	0.05	10.57	6.42
1-Butene	17.06	7.0	1.0	0.998	0.08	9.56	11.63
Isobutene	17.74	6.3	0.9	0.998	0.11	7.13	11.69
Cis-2-butene	18.34	6.3	0.9	0.998	0.11	7.77	6.98
Isopentane	19.88	9.0	0.4	0.999	0.08	5.80	8.08
Pentane	21.04	1.6	1.1	0.995	0.03	6.48	12.57
1,3-Butadiene	21.18	0.8	0.1	0.998	0.81	9.01	7.05
2-Methylpentane	25.36	3.8	−0.8	0.999	0.11	7.04	10.19
3-Methylpentane	25.48	4.5	−0.04	0.999	0.11	8.14	9.25
Hexane	26.52	0.4	−0.00	0.997	1.52	4.49	7.43

TABLE II Distributed air volume sampling (DAV) data tests (concentrations in ppbv)

	Tube 1 399 mL 28.5 mL/min	*Tube 2* 350 mL 25 mL/min	*Tube 3* 229 mL 18.5 mL/min	*Mean ± SD*	*%CV*
Propane	0.43	0.46	0.52	0.47 ± 0.04	8.7
Propene	0.65	0.58	0.75	0.66 ± 0.08	12.8
n-Butane	0.52	0.45	0.53	0.50 ± 0.04	7.7
Isobutene	0.62	0.67	0.68	0.65 ± 0.03	5.3
Isopentane	0.13	0.12	0.11	0.12 ± 0.01	7.3
n-Pentane	1.12	0.87	1.08	1.03 ± 0.13	12.9

Distributed air volume sampling (DAV) tests were carried out to check the absence of systematic sampling errors, such as the occurrence of chemical reactions between NMHCs and Carbotrap–Carbotrap C-Carbosieve III adsorbent [28,29]. This routine control requires the simultaneous collection of several samples, each at a different flow rate; if there are no sampling errors, the concentration of each compound has to be equal in all samples. The test was carried out both on real samples taken in the municipal cabin. Table II shows, as an example, the results obtained in a monthly routine DAV test in July 2002. As can be observed, the RSD values of the NMHC concentrations, recorded the sampling day in the urban atmosphere of Vitoria-Gasteiz and determined from the analysis of the different samples, were lower than 12.9% in all cases, which can be considered satisfactory. The results of this test proved the absence of systematic sampling errors throughout the two years over which the study was carried out.

The quality assurance and quality control programme also included the routine sampling of urban air and background air samples in duplicate and the daily calibration of the TCT-GC-MS analytical method.

The sampling statistical validity was checked by analysis of variance of the results obtained in the analyses of air samples. To this end, two pumps were sampling simultaneously, each connected to a flow tube holder with multiple port manifolds, attached to the multilayer-bed tubes. This enabled each of the samples to be collected in duplicate for the study. This sampling was repeated over a period of 10 days. The values of the F factor obtained for the NMHCs recorded that sampling day were lower than the critical value of this parameter for this distribution, $F(1,2,95\%) = 18.513$. These results proved that NMHC concentrations can be represented by the mean value of the results obtained by analysing these samples, and so the samples can be considered statistically representative of the urban air in the zone.

Field Study

The effectiveness of the method was tested by means of a field study: about 49 air samples were collected and analysed during the period 2001–2002. The sampling frequency was approximately one sample every 8 days throughout the four seasons of the year. In this study, spring is defined as lasting from March to May (12 samples), summer from June to August (12 samples), autumn from September to November (15 samples), and winter from December to February (10 samples).

The C_2–C_6 hydrocarbons detected in the ambient air in Vitoria-Gasteiz were ethane, propane, 1-propene, isobutane, *n*-butane, *trans*-2-butene, 1-butene, iso-butene, *cis*-2-

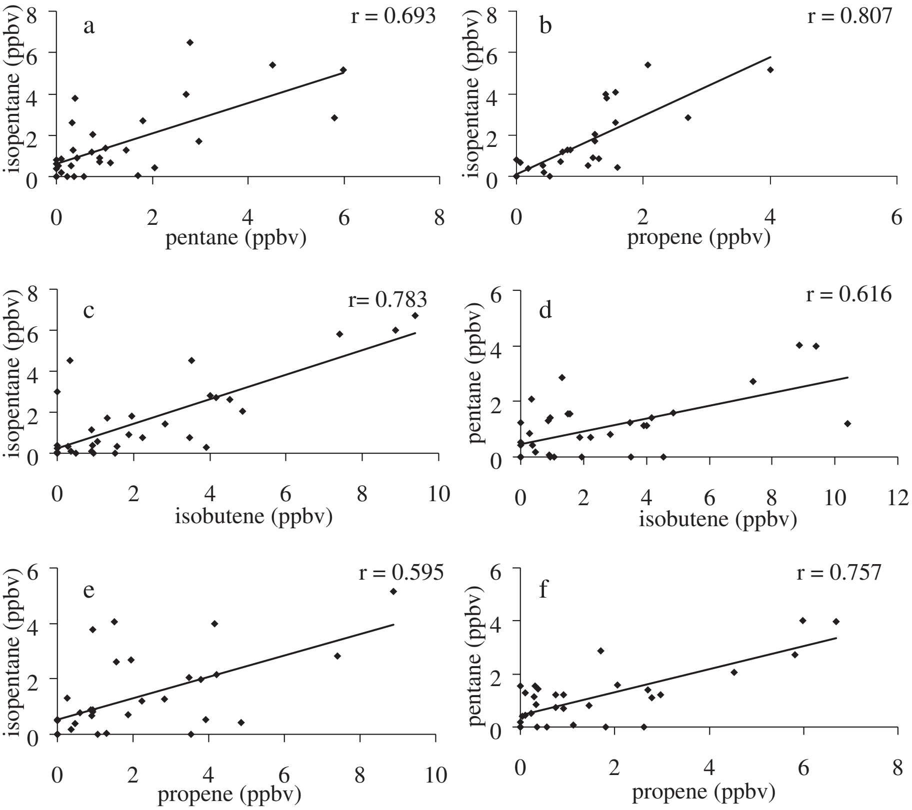

FIGURE 3 Correlation plot of (a) isopentane *vs.* pentane, (b) isobutene *vs.* propene, (c) isopentane *vs.* isobutene, (d) pentane *vs.* isobutene, (e) isopentane *vs.* propene, and (f) pentane *vs.* propene.

butene, isopentane, *n*-pentane, 1,3-butadiene, 2-methylpentane, 3-methylpentane, and hexane. The total NMHC daily levels run between 0.0 (thereby indicating that no compounds were detected) and 218.18 mg/m^3.

The alkanes family provides the largest contributions to the total hydrocarbons, each accounting for 57% on an average ppbv basis. The alkenes account for much a smaller average contribution, supposedly 43%.

The predominant hydrocarbons were isopentane and propene. The presence of isopentane and *n*-pentane indicates a dominance of an anthropogenic component [30]. In the urban atmosphere, C_4–C_5 alkanes are the unburned product of vehicular emission [31] and are also emitted from gasoline evaporation and from liquefied petroleum gas [32]. There is an evident correlation ($r = 0.807$) between pentane and isopentane (Fig. 3a). This reveals that both are primarily emitted from common anthropogenic sources, such as vehicle emission. *n*-Butane shows a reasonable correlation with C_5 alkanes (isopentane and pentane; $r = 0.462$ and $r = 0.584$). This suggests that a substantial part of *n*-butane must have been emitted from vehicular emission.

Another marked correlation (Fig. 3b) has been found between 1-propene and isobutene ($r = 0.783$); these compounds must be emitted from the same source. The correlation between the isobutene and the C_5 alkanes was studied to determine whether isobutene could be emitted from the same source as isopentane and pentane (Fig. 3c

TABLE III Mean concentration (±SD) for selected hydrocarbons measured in the Vitoria-Gasteiz urban area and in other cities (ppbv)

Compound	*Vitoria-Gasteiz* (*Spain*)	*Great Lille* (*France*) [33]	*London* (*UK*) [34]	*Dublin* (*Ireland*) [35]	*Kathmandu* (*Nepal*) [32]	*Mexico DF* (*Mexico*) [36]	*Chicago* (*USA*) [37]
Ethane	0.31 ± 1.24	3.22	4.18	4.51	7.71	14.0	6.4
Propane	0.60 ± 1.39	1.37	2.04	2.18	5.97	158.0	3.2
1-Propene	2.48 ± 2.86	0.45	1.36	1.66	12.75	5.0	1.4
Isobutane	0.07 ± 0.21	0.61	1.38	1.72	16.41	33.1	1.2
n-Butane	0.83 ± 1.68	1.20	3.23	4.16	42.19	70.4	6.0
Trans-2-butene	0.31 ± 0.85	0.34	0.21	0.23	0.63	–	–
1-Butene	0.93 ± 1.53	0.14	0.20	0.07	2.46	2.1	–
Isobutene	1.69 ± 1.96	–	–	–	–	1.8	–
Cis-2-Butene	0.30 ± 0.82	0.13	0.12	0.20	0.44	–	–
Isopentane	3.03 ± 6.27	1.06	2.57	2.86	25.91	19.4	4.1
n-Pentane	1.03 ± 1.08	0.39	0.56	0.97	24.81	14.4	3.8
1,3-Butadiene	0.61 ± 1.61	0.07	0.21	0.40	3.39	–	–
2-Methylpentane	0.75 ± 1.17	0.18	0.95	0.45	16.12	8.1	2.4
3-Methylpentane	0.22 ± 0.65	0.12		0.42	13.42	5.3	2.4
Hexane	1.56 ± 2.84	0.15	0.24	0.53	13.79	12.2	2.0

and d). These correlations are appreciable ($r = 0.693$, $r = 0.757$) and indicate an important anthropogenic influence. However, most interesting are the observed covariations of NMHC of different chemical groups, for instance alkanes and alkenes. In the case of propene, which correlates with iso- and *n*-pentane ($r = 0.595$ and $r = 0.616$) indicating a dominance of an anthropogenic component (Fig. 3e and f).

Comparison with NMHCs mixing ratios from other cities indicates that Vitoria-Gasteiz has NMHC levels similar to other European cities (Table III). In developing countries, the concentrations of NMHC in the atmosphere are considerably higher. The comparison of the composition pattern of hydrocarbon components observed in Vitoria with different cities is useful for identifying characteristics of the city.

The univariate analysis, focused on the NMHC temporal characteristics, represents the NMHC mean concentration profiles on a seasonal scale. This analysis provides a first identification of some important NMHC associations with similar temporal structures related to their dominating sources. The seasonal variation of NMHCs in the troposphere is known to be influenced by various factors such as seasonal variability of OH radicals, anthropogenic source strength variations, and meteorological conditions [38].

Almost all NMHC values determined show maximum values during autumn and winter. This behaviour is often related to a more efficient removal mechanism and better dispersion conditions in summer [34]. Studies in European urban areas seen to indicate that existing seasonal variations are minor, with weaker concentrations during warm and sunny periods in general associated with better dispersive dilution and mixing, and more active photochemistry [39].

The seasonal mean levels of the NMHC measured are reported in Fig. 4. It can be seen that the concentrations of NMHC in ambient air are maximal in winter and minimal in summer. This behaviour has been frequently observed with hydrocarbons with longer atmospheric lifetimes (e.g. ethane and propane) [40,41]. The seasonal contributions of the different hydrocarbon families suppose a maximum contribution of alkanes in winter (the 32% of the total hydrocarbons measurement in this year). Also, the lowest contributions are from alkenes in the summer (about 3%).

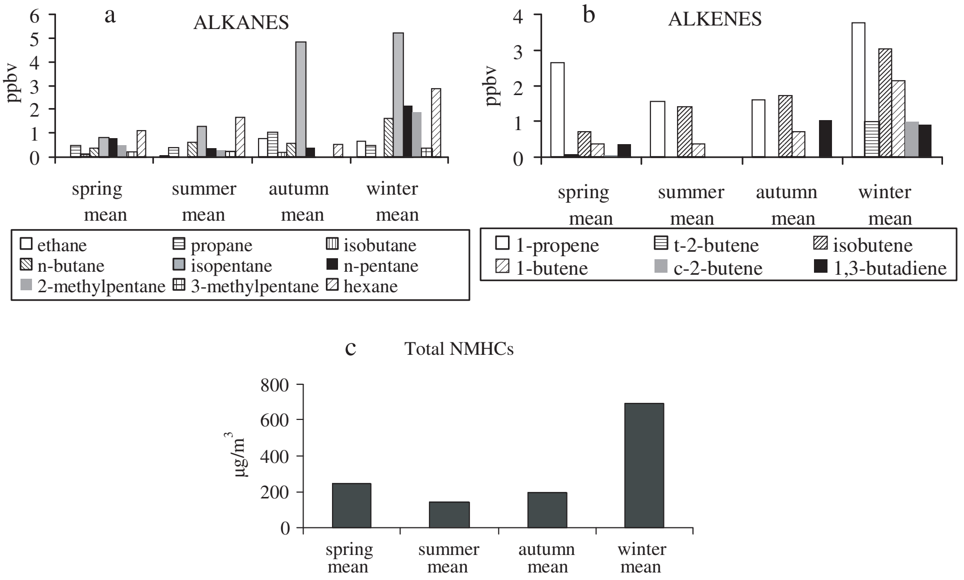

FIGURE 4 Seasonal variation of NMHCs in Vitoria-Gasteiz. (a) Alkanes, (b) alkenes and (c) total NMHCs.

Field [42] and Lacoge [43], have observed in their studies that while the minimum concentrations are mostly observed in August for the majority of compounds, the typical fuel components (e.g. butane, isopentane and *n*-pentane) tend to have higher levels in the summer. However, in our study, this does not happen. This could be due to the fall in the flow of traffic in this city in the summer (15–20% less), thereby resulting in a smaller emission rate.

Finally, it is worth mentioning the high concentrations of hexane recorded during the autumn and winter months. The source of this compound has been traced to the industrial areas surrounding the city, specifically to the surface-treatment industries, of which there are a significant number in this municipality. The pollutants in these kinds of industries arise from the evaporation of solvents, paint, grease removers, and the so-called non-confined emissions. This concurs with the abnormally high average levels of toluene (26.7 $\mu g/m^3$ in 2001 and 11.5 $\mu g/m^3$ in 2002) [44], recorded particularly during the months of intense activity in these industries. According to the survey carried out by the Town Hall of Vitoria-Gasteiz, the annual non-confined quantities applied are 2442.5 and 152.4 t/year for solvents and paints, respectively [44]. This would cause the evaporative emissions of these industries to contribute considerably to the levels of these pollutants (hexane and toluene) in Vitoria-Gasteiz.

CONCLUSIONS

Sample collection using multisorbent tubes coupled with TCT-GC-MS has been used to identify and quantify the C_2–C_6 saturated and unsaturated NHMCs in the urban atmosphere of Vitoria-Gasteiz. A protocol using 400 mL of air sampled in 13 min has been presented. The method enables studies to be carried out on the composition and the seasonal variations of these compounds in the period between June 2001 and July 2002. The results show similarities with other European cities.

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